

SYNTHESIS OF A NEW THIOPHENE DERIVATIVE AND ITS USES AS AN
ELECTROCHROMIC DEVICE COMPONENT

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

BY

BAŞAK YİĞİTŞOY

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

JUNE 2006

Approval of the Graduate School of Natural and Applied Sciences

Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Hüseyin İşçi
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis and for the degree of Master of Science.

Prof. Dr. Levent Toppare
Supervisor

Examining Committee Members

Prof. Dr. İdris M. Akhmedov
(METU, CHEM)

Prof. Dr. Levent Toppare
(METU, CHEM)

Prof. Dr. Cihangir Tanyeli
(METU, CHEM)

Prof. Dr. Teoman Tinçer
(METU, CHEM)

Dr. Elif Şahin
(Dicle Univ., CHEM)

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name:

Signature :

ABSTRACT

SYNTHESIS OF A NEW THIOPHENE DERIVATIVE AND ITS USES AS AN ELECTROCHROMIC DEVICE COMPONENT

Yiğitsoy, Başak

M.S., Department of Chemistry

Supervisor: Prof. Dr. Levent Toppare

June, 2006, 72 pages

2,5-Di(thiophen-2-yl)-1-*p*-tolyl-1H-pyrrole (DTTP) was synthesized via reaction of 1,4-di(2-thienyl)-1,4-butanedione with *p*-toluidine in the presence of catalytical amount of *p*-toluenesulfonic acid (PTSA). Homopolymer P(DTTP) was achieved both by chemical and electrochemical techniques. Chemical polymerization of the monomer yielded a soluble polymer. The average molecular weight was determined by gel permeation chromatography (GPC) as M_n : 2.5×10^3 g/mol. The monomer was electrochemically polymerized in the presence of LiClO₄, NaClO₄ (1:1) as the supporting electrolyte in acetonitrile. Copolymer of DTTP in the presence of EDOT was synthesized via potentiodynamic method in ACN/ NaClO₄/LiClO₄ (0.1 M) solvent-electrolyte couple. Structural characterizations of samples were carried out via ¹H, ¹³C Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared Spectroscopy (FTIR). Electrochemical behaviors of monomer and polymers were determined by Cyclic Voltammetry (CV). The morphologies of the polymer films were examined by Scanning Electron Microscopy (SEM). Conductivities of the films

were measured by four probe technique. Electrochromic and spectroelectrochemical behavior of the polymers coated on ITO glass electrode were investigated, and their ability of employment in device construction was examined. Spectroelectrochemistry analysis of P(DTTP) revealed an electronic transition at 428 nm corresponding to $\pi - \pi^*$ transition with a band gap of 2.1 eV whereas P(DTTP-co-EDOT) revealed an electronic transition at 448 nm corresponding to $\pi - \pi^*$ transition with a band gap of 1.8 eV. Electrochromic investigations showed that P(DTTP) switches between greenish yellow and blue while P(DTTP-co-EDOT) was found to be multichromic, switching between red, yellow and blue. Switching time of the polymers was evaluated by a kinetic study upon measuring the percent transmittance (%T) at the maximum contrast point. Dual type polymer electrochromic devices (ECDs) based on P(DTTP) and P(DTTP-co-EDOT) with poly(3,4-ethylenedioxythiophene) (PEDOT) were constructed. Spectroelectrochemistry, electrochromic switching and open circuit stability of the devices were studied. They were found to have good switching times, reasonable contrasts and optical memories.

Keywords: Electrochemical polymerization; soluble conducting polymers; electrochemical copolymerization, electrochromic properties

ÖZ

YENİ BİR TİYOFEN TÜREVİ SENTEZİ VE ELEKTROKROMİK CİHAZ BİLEŞENİ OLARAK KULLANIMI

Yiğitsoy, Başak

Yüksek Lisans, Kimya Bölümü

Tez Yöneticisi: Prof. Dr. Levent Toppare

Haziran 2006, 72 sayfa

2,5-Di(tiyofen-2-il)-1-p-tolil-1H-pirol (DTTP); *p*-toluidin ve 1,4-di(2-tiyenil)-1,4-butandiyon'un az miktarda *p*-toluensulfonik asit (PTSA) varlığındaki reaksiyonu ile sentezlenmiştir. Homopolimer P(DTTP) hem kimyasal hem de elektrokimyasal yolla sentezlenmiştir. Monomerin kimyasal polimerleşmesi sonucunda çözünür polimer elde edilmiştir. Çözünen polimerin ortalama molekül ağırlığı Jel Geçirgenlik Kromatografisi (GPC) ile 2.5×10^3 gr/mol olarak belirlenmiştir. Monomer elektrokimyasal olarak LiClO₄, NaClO₄ (1:1) destek elektrolitleri varlığında asetonitrilde polimerleştirilmiştir. DTTP'nin EDOT varlığında kopolimeri ACN/NaClO₄/LiClO₄ (1:1) çözücü-elektrolit ikilisinde potensiyodinamik metotla sentezlenmiştir. Polimerlerin kimyasal yapıları ¹H, ¹³C Nükleer Manyetik Rezonans (NMR) and Fourier Transform Infrared Spektroskopisi (FTIR) ile karakterize edildi. Monomerin ve polimerlerin elektrokimyasal davranışları Dönüşümlü Voltametri (CV) ile belirlendi. Polimer filmlerinin morfolojisi Taramalı Elektron Mikroskobu ile incelendi. Polimer filmlerinin iletkenlikleri dört nokta tekniği ile ölçüldü. ITO

üzerine kaplanmış polimerlerin elektrokromik ve spektroeletrokimyasal davranışları ve elektrokromik cihaz yapımında kullanılabilme yetisi incelendi. Spektroeletrokimyasal analizler P(DTTP)'nin spektroeletrokimyasal analizi sonucu $\pi-\pi^*$ geçişi 428 nm'de gözlenmiş ve bant aralığı 2.1 eV olarak hesaplanmıştır, öte yandan P(DTTP-co-EDOT)'nin λ_{max} ve E_g değerleri sırasıyla 448 nm ve 1.8 eV bulunmuştur. Elektrokromik çalışmalar sonucunda P(DTTP)'nin yeşilimsi sarı ve mavi renk arasında değiştiğini, P(DTTP-co-EDOT)'nin multikromik bir malzeme olduğu; kırmızı, yeşil ve mavi renkleri arasında değiştiği gözlemlenmiştir. Renklerin değişim hızları kinetik çalışma ile yüzde transmitansın en yüksek kontrast farkında ölçülmüştür. (%T) P(DTTP) ve P(DTTP-co-EDOT) in poly(3,4-etilendioksitiyofen) (PEDOT) ile dual tip elektrokromik cihazı yapılmıştır. Cihazların spektroeletrokimyasal özellikleri, elektrokromik çevirmeleri ve açık devre hafızaları araştırılmıştır. Cihazların iyi çevirme zamanları, uygun optik kontrastları ve optik hafızaları olduğu bulundu.

Anahtar sözcükler: Elektrokimyasal polimerleşme, çözünen iletken polimerler, elektrokimyasal kopolimerizasyon, elektrokromik cihazlar

TO MY FAMILY

ACKNOWLEDGMENTS

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

I would like to thank, Prof. Dr. İdris Mecidođlu Akhmedov, Prof. Dr. Cihangir Tanyeli and Prof. Dr. Mustafa Güllü for their valuable discussions.

I would like to express my special thanks to Dr. Elif Şahin, Dr. Ertuđrul Şahmetliođlu, Dr. Senem Kıralp, Metin Ak and Pınar Çamurlu for their endless helps besides their kind friendships.

Special thanks go to my dear friends Serhat Varış, Görkem Günbaş, Simge Tarkuç, Özlem Türkarıslan and Yusuf Nur for their friendship; useful conversations and cooperation. I also would like to thank all my lab-mates in our research group for their kind friendship.

Words fail to express my eternal gratitude to my parents and my sister Gül Yiđitsoy, who have given me unending support and encouragement.

Finally, I wish to thank Fatih for his never-ending support and love even though he is kilometers away.

TABLE OF CONTENTS

| | |
|---|-------|
| ABSTRACT | iv |
| ÖZ..... | vi |
| DEDICATION | viii |
| ACKNOWLEDGMENTS | ix |
| TABLE OF CONTENTS | x |
| LIST OF FIGURES | xiv |
| LIST OF TABLES..... | xvii |
| ABBREVIATIONS..... | xviii |
| | |
| INTRODUCTION | 1 |
| 1.1 Conducting Polymers..... | 1 |
| 1.1.1 Historical Background | 2 |
| 1.2 Band Theory and Conduction Mechanism in Conducting Polymers | 3 |
| 1.2.1 Band Theory | 4 |
| 1.2.2. Conduction Mechanism | 5 |
| 1.2.2.1 Charge Carriers | 5 |
| 1.2.2.2 Doping | 7 |
| 1.2.2.3 Hopping | 10 |
| 1.3 Synthesis of Conducting Polymers: | 11 |
| 1.3.1 Chemical Polymerization: | 11 |
| 1.3.2 Electrochemical Polymerization:..... | 12 |
| 1.3.2.1 Electrolytic Medium..... | 13 |
| 1.3.2.2 Mechanism of Electrochemical Polymerization..... | 14 |
| 1.3.2.3 Monomer Structure: | 15 |

| | |
|---|----|
| 1.4 Conducting Copolymers and Composites | 17 |
| 1.5 Characterization of Conducting Polymers..... | 18 |
| 1.6 Applications of Conducting polymers | 19 |
| 1.7 Electrochromism: | 20 |
| 1.7.1 Types of Electrochromic Materials | 21 |
| 1.7.2. Spectroelectrochemistry | 22 |
| 1.8 Electrochromic Devices (ECD)..... | 22 |
| 1.9 Characteristics of Electrochromic Device..... | 24 |
| 1.9.1 Electrochromic Contrast and Switching Speed..... | 24 |
| 1.9.2 Open Circuit Memory and Stability: | 24 |
| 1.10 Colorimetry..... | 24 |
| 1.11 Aims of the Work..... | 26 |
| | |
| EXPERIMENTAL | 27 |
| 2.1 Materials..... | 27 |
| 2.2 Instrumentation | 27 |
| 2.2.1 Potentiostat..... | 27 |
| 2.2.2 Cyclic Voltammetry System..... | 28 |
| 2.2.3 Electrolysis Cell | 30 |
| 2.2.4 Nuclear Magnetic Resonance (NMR) | 30 |
| 2.2.5 Fourier Transform Infrared Spectrometer (FTIR)..... | 30 |
| 2.2.6 Scanning Electron Microscope (SEM)..... | 31 |
| 2.2.7 Four-Probe Conductivity Measurements | 31 |
| 2.2.8 Gel Permeation Chromatography (GPC)..... | 32 |
| 2.2.9 UV-VIS Spectrophotometer | 32 |
| 2.2.10 Colorimetry Measurements | 32 |
| 2.3 Procedure | 32 |
| 2.3.1 Synthesis of Monomer | 32 |
| 2.3.1.1 Synthesis of 1,4-Di(2-thienyl)-1,4-butanedione..... | 32 |

| | |
|---|----|
| 2.3.1.2 Synthesis of 2,5-Di(thiophen-2-yl)-1- <i>p</i> -tolyl-1H-pyrrole | 33 |
| 2.4 Chemical Polymerization of DTTP with Ferric Chloride..... | 34 |
| 2.5 Gel Permeation Chromatography (GPC) | 35 |
| 2.6 Potentiodynamic Studies of Polymers..... | 35 |
| 2.7 Electrochemical Synthesis of P(DTTP) and P(DTTP-co-EDOT)..... | 36 |
| 2.7.1 Synthesis of Homopolymer of DTTP..... | 36 |
| 2.7.2 Synthesis of Copolymer of DTTP with 3,4-Ethylenedioxythiophene (EDOT) P(DTTP-co-EDOT)..... | 36 |
| 2.8 Investigation of Electrochromic Properties of Polymers..... | 37 |
| 2.8.1 Spectroelectrochemical Studies | 37 |
| 2.8.2 Switching Properties of Polymers..... | 37 |
| 2.8.3 Colorimetry Studies of Polymers | 38 |
| 2.9 Electrochromic Device (ECD) Construction | 38 |
| 2.9.1 P(DTTP)/PEDOT Electrochromic Device | 38 |
| 2.9.2 P(DTTP-co-EDOT)/PEDOT Electrochromic Device | 39 |
| 2.9.3 Preparation of the Gel Electrolyte..... | 39 |
| 2.10 Characterization of Electrochromic Devices..... | 40 |
| 2.10.1. Spectroelectrochemistry Studies of Electrochromic Devices | 40 |
| 2.10.2 Switching Properties of Electrochromic Devices | 40 |
| 2.10.3 Open Circuit Memory..... | 40 |
| 2.10.4 Stability of the electrochromic Electrochromic Devices..... | 41 |
| 2.10.5 Colorimetry Studies of Electrochromic Devices | 41 |
| RESULTS AND DISCUSSION | 42 |
| 3.1. Characterization by ¹ H-NMR and ¹³ C- NMR Spectroscopy | 42 |
| 3.2. FTIR Spectra | 44 |
| 3.3. Cyclic Voltammograms | 46 |
| 3.4 Conductivities | 48 |
| 3.5 Morphologies of Films | 48 |

| | |
|--|----|
| 3.6 Gel Permeation Chromatography (GPC) | 49 |
| 3.7. Investigation of Electrochromic Properties of Polymers..... | 50 |
| 3.7.1 Spectroelectrochemistry | 50 |
| 3.7.2 Electrochromic Switching..... | 52 |
| 3.8 Characterization of Electrochromic Devices (ECDs) | 56 |
| 3.8.1 Spectroelectrochemistry of ECDs..... | 56 |
| 3.8.2 Switching of ECDs..... | 58 |
| 3.8.3 Colorimetry of ECDs..... | 59 |
| 3.8.4 Open Circuit Stability | 61 |
| 3.8.5 Stability of the electrochromic ECDs | 62 |
| CONCLUSION..... | 65 |
| REFERENCES | 67 |

LIST OF FIGURES

| | |
|--|----|
| Figure 1.1 Structures of some common conducting polymers | 2 |
| Figure 1.2 Conductivities and stabilities of some common conducting polymers..... | 3 |
| Figure 1.3 Band diagrams for (a) metals, (b) semiconductors and (c) insulators. | 5 |
| Figure 1.4 A schematic description of the formation of polaron, bipolaron, and soliton pair on a trans-polyacetylene chain on doping. | 6 |
| Figure 1.5 p-type doping of PTh..... | 7 |
| Figure 1.6 Charge carries in PPy and its corresponding energy bands in the mid gap | 9 |
| Figure 1.7 Conductivities of some metals, semiconductors and insulators | 10 |
| Figure 1.8 Chemical synthetic routes of polyheterocycles..... | 12 |
| Figure 1.9 Electrochemical synthetic routes to polyheterocycles..... | 12 |
| Figure 1.10 Resonance stabilization and electropolymerization mechanism of pyrrole. (a) Resonance stabilization of radical cation of pyrrole. (b) Proposed mechanism for the electrochemical polymerization of pyrrole..... | 15 |
| Figure 1.11 Potential coupling reactions for pyrrole during oxidative polymerization | 16 |
| Figure 1.12 Applications of conducting polymers | 19 |
| Figure 1.13 Schematic representation of ECDs..... | 23 |
| Figure 1.14 CIELAB color space..... | 25 |
| Figure 2.1 Triangular wave function..... | 28 |
| Figure 2.2 A cyclic voltammogram for a reversible redox reaction..... | 29 |
| Figure 2.3 Cyclic voltammetry cell..... | 30 |
| Figure 2.4 Four-probe conductivity measurement | 31 |
| Figure 2.5 Square wave voltammetry | 38 |

| | |
|--|----|
| Figure 3.1 ¹ H-NMR spectrum of the monomer | 43 |
| Figure 3.2 ¹³ C-NMR spectrum of the monomer | 43 |
| Figure 3.3 ¹ H-NMR spectrum of the chemically synthesized P(DTTP). | 44 |
| Figure 3.4 FTIR spectra of (a) DTTP, (b) electrochemically synthesized P(DTTP), and (c) chemically synthesized P(DTTP)..... | 45 |
| Figure 3.5 FTIR spectrum of P(DTTP-co-EDOT)..... | 46 |
| Figure 3.6 Cyclic voltammogram of P(DTTP) | 47 |
| Figure 3.7 Cyclic voltammograms of (a) pure PEDOT, (b) DTTP in the presence of EDOT, P(DTTP-co-EDOT) | 48 |
| Figure 3.8 SEM micrographs of (a) solution side of P(DTTP), (b) solution side of PEDOT (c) solution side of P(DTTP-co-EDOT). | 49 |
| Figure 3.9 (a) 2D Spectroelectrochemical spectrum of P(DTTP) with applied potentials between 0.0 and +0.6 V in ACN/NaClO ₄ /LiClO ₄ (0.1 M). ; (a) 0.0 V, (b) +0.2 V, (c) +0.3V, (d) 0.4 V, (e) 0.5 V, (f) 0.6 V. (b) 3D Spectroelectrochemical spectrum of P(DTTP) with applied potentials between 0.0 and +0.6 V in ACN/NaClO ₄ /LiClO ₄ (0.1 M)..... | 51 |
| Figure 3.10 (a) 2D Spectroelectrochemical spectrum of P(DTTP-co-EDOT) with applied potentials between -0.6 V and +0.8 V in ACN/NaClO ₄ /LiClO ₄ (0.1 M)., a) -0.6 V, (b) 0.0 V, (c) +0.4 V, (d) 0.6 V, (e) 0.8 V. (b) 3D Spectroelectrochemical spectrum of P(DTTP-co-EDOT) with applied potentials between -0.6 and +0.8 V in ACN/NaClO ₄ /LiClO ₄ (0.1 M)..... | 52 |
| Figure 3.11 Electrochromic switching, optical absorbance change monitored at 428 nm for P(DTTP) between 0.0 V and 0.6 V..... | 53 |
| Figure 3.12 Electrochromic switching, optical absorbance change monitored at 448 nm for P(DTTP-co-EDOT) between -0.6V and +0.8 V..... | 54 |
| Figure 3.13. (a) 2D Spectroelectrochemical spectrum of the device with applied potentials between -0.6 and +1.6 V (a) -0.6 V, (b) -0.4 V, (c) -0.2 V, (d) 0.0 V, (e) .2 V, (f) 0.4 V, (g) 0.6 V, (h) 0.8 V, (i) 1.0 V, (j) 1.2 V, (k) 1.4 V, (l) 1.6 (b) 3D | |

| | |
|--|----|
| Spectroelectrochemical spectrum of the device with applied potentials between -0.6 and +1.6 V..... | 56 |
| Figure 3.14 (a) 2D Spectroelectrochemical spectrum of the device with applied potentials between -0.6 and +1.6 V (a) -0.6 V, (b) -0.4 V, (c) -0.2 V, (d) 0.0 V, (e) .2 V, (f) 0.4 V, (g) 0.6 V, (h) 0.8 V, (i) 1.0 V, (j) 1.2 V, (k) 1.4 V, (l) 1.6 | |
| (b) 3D Spectroelectrochemical spectrum of the device with applied potentials between -0.6 and +1.6 V..... | 57 |
| Figure 3.15 Electrochromic switching, optical absorbance change monitored at 617 nm for device between -0.6 V and 1.6 V. | 58 |
| Figure 3.16 Electrochromic switching, optical absorbance change monitored at 448 and 615 nm for device between -0.6 V and 2.0 V..... | 59 |
| Figure 3.17 Open circuit memory of P(DTTP)/PEDOT ECD monitored at 0.0 V and +1.6 V potentials applied for one second for every 200 seconds time interval..... | 61 |
| Figure 3.18 Open circuit memory of P(DTTP-co-EDOT)/PEDOT ECD monitored at 0.6 V and +2.0 V potentials at a) 448 nm and b) 615 nm. | 62 |
| Figure 3.19. Cyclic voltammogram of the P(DTTP)/PEDOT device as a function of repeated scans 500 mV/s: after 1st cycle (plain), after 1000 cycles (dash). | 63 |
| Figure 3.20 Cyclic voltammogram of P(DTTP-co-EDOT)/PEDOT device as a function of repeated scans 500 mV/s: after 1st cycle (plain), after 1000 cycles (dash). | 64 |

LIST OF TABLES

| | |
|--|----|
| Table 3.1 Conductivities of P(DTTP) and P(DTTP-co-EDOT) | 48 |
| Table 3.2. GPC Results | 50 |
| Table 3.3 Electrochromic properties of P(DTTP) | 55 |
| Table 3.4 Electrochromic properties of P(DTTP-co-EDOT)..... | 55 |
| Table 3.5 Electrochromic properties of P(DTTP)/PEDOT ECD | 60 |
| Table 3.6 Electrochromic properties of P(DTTP-co-EDOT)/PEDOT ECD..... | 60 |

ABBREVIATIONS

| | |
|-----------------|---|
| DTTP | 2,5-Di(thiophen-2-yl)-1- <i>p</i> -tolyl-1H-pyrrole |
| P(DTTP) | Poly(2,5-di(thiophen-2-yl)-1- <i>p</i> -tolyl-1H-pyrrole) |
| EDOT | 3,4-Ethylenedioxythiophene |
| P(DTTP-co-EDOT) | Poly(2,5-di(thiophen-2-yl)-1- <i>p</i> -tolyl-1H-pyrrole-co-ethylenedioxythiophene) |
| Th | Thiophene |
| Py | Pyrrole |
| PEDOT | Poly(3,4-ethylenedioxythiophene) |
| ACN | Acetonitrile |
| PMMA | Poly(methylmethacrylate) |
| PC | Propylene carbonate |
| NMR | Nuclear Magnetic Resonance |
| FTIR | Fourier Transform Infrared Spectrometer |
| CV | Cyclic Voltammetry |
| SEM | Scanning Electron Microscopy |
| GPC | Gel Permeation Chromatography |
| ECD | Electrochromic Device |
| HOMO | Highest Occupied Molecular Orbital |
| LUMO | Lowest Unoccupied Molecular Orbital |
| E_g | Band Gap Energy |
| CIE | La Commission Internationale de l'Éclairage |
| L a b | Luminance, hue, saturation |

CHAPTER I

INTRODUCTION

1.1 Conducting Polymers

The discovery of increase in conductivity of doped polyacetylene (PA) by many orders of magnitude [1,2] was a major breakthrough in the area of conducting polymers. Honoring Hideki Shirakawa, Alan MacDiarmid 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.

1.1.1 Historical Background

Although the polymers were regarded as insulators about 30 years ago, the report on discovery of conducting polymers and electroactive polymers changed this narrow perspective.

The research on the utilization of electrically conducting properties of polymers began early in the 1960s [3]. At the beginning of 1970s, it was found that

the intrinsic conductivity of an inorganic explosive polymer, polysulfur nitride $(\text{SN})_x$ (10^3 S/cm) is comparable with the conductivity of a copper metal ($1 \times 10^6 \text{ S/cm}$) [4]. In 1977, Heeger, MacDiarmid and Shirakawa discovered that the conductivity of a conjugated polymer increases 12 orders of magnitude when the polymer is doped with strong electron acceptor; iodine.

Despite high conductivity of polyacetylene film in doped form, the material was unprocessable since it was unstable in air and insoluble in solvents. Synthetic work focused on increasing the processibility of PA by means of increasing its stability and solubility [5]. Unfortunately, the electrical conductivities of the PA derivatives were much lower than the conductivity of PA. Naturally, much work has been devoted to develop stable and processable conducting polymer structures. In 1979, syntheses of highly conducting (100 S/cm) and homogeneous free standing films of polypyrrole were reported [6].

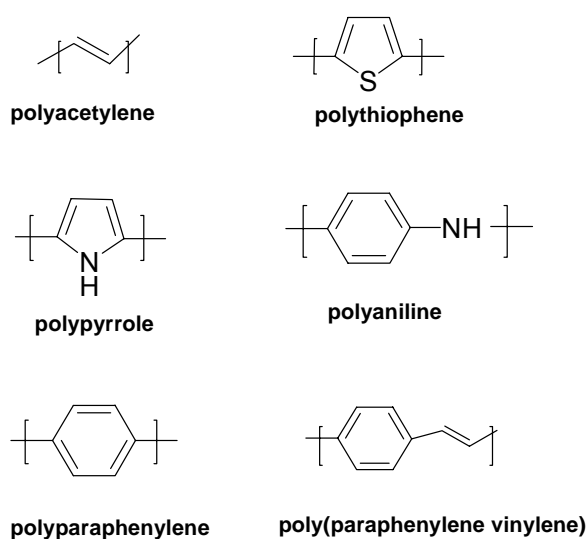


Figure 1.1 Structures of some common conducting polymers.

New class of conducting polymers (Fig. 1.1) such as polypyrrole [6], polythiophene [7], polyaniline [8], poly (*p*-phenylene) [9] and poly (*p*-phenylene vinylene) [10] and their derivatives e.g. poly(3,4-ethylenedioxythiophene) (PEDOT) [11] have been studied extensively for several decades since they can be easily modified than PA allowing for more diversity of structures. The processing possibilities and stability of some common conducting polymers were given in Fig. 1.2.

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

Figure 1.2 Conductivities and stabilities of some common conducting polymers.

1.2 Band Theory and Conduction Mechanism in Conducting Polymers

Conducting polymers have high conductivity almost as metals due to the free movement of electrons through their structure. For polymeric systems to be conductive, they must possess not only charge carriers, but also an orbital system in which the charge carriers can move. Conjugated polymers can meet the second requirement through overlapping π orbitals, which provide reasonable carrier mobility along the polymer backbone. Since most organic polymers do not have intrinsic charge carriers, the charge carriers must be provided by an external process called doping.

The basic ideas or concepts of band theory are useful frameworks for establishing the origins of electronic conduction and charge carriers.

1.2.1 Band Theory

According to band theory, extended delocalized energy bands are formed by the combination of atomic orbitals and the conductivity then depends on the relative population of each band and the energy difference between bands.

The electrical properties of direct-gap inorganic semiconductors are determined by their electronic structures, and the electrons move within discrete energy states called bands. By analogy, the bonding and antibonding π orbitals of the sp^2 hybridized π -electron materials (e.g., polyenes) generate energy bands that are fully occupied (π band) and empty (π^* band) [12].

Neutral conjugated polymers are usually treated as semiconductors and band theory can be used to describe their electronic energy levels. Conjugated polymers generates two discrete energy bands, the highest occupied electronic levels constitute the valence band (VB) and the lowest unoccupied levels, the conduction band (CB). The width of the forbidden band, or band gap (E_g) between the VB and CB determines the intrinsic electrical properties of the material [13]. The HOMO–LUMO gap of a linear π -conjugated system depends on various structural factors such as chain length, bond length alternation, planarity, the presence of electron-acceptor or electron donor substituents and the resonance stabilization energy of the aromatic cycles [14]. Band gap refers to onset energy of the π - π^* transition in neutral conjugated polymers. The band gap of a polymer can be approximated from the onset of absorption of the π to π^* transition in the UV-VIS spectrum.

Electrons must have certain energy to occupy a given band and need extra energy to move from the valence band to the conduction band. Moreover, the bands should be partially filled in order to be electrically conducting since neither empty

bands nor full ones can carry electricity. Owing to the presence of partially filled energy bands, metals have high conductivities. (Fig 1.3a).

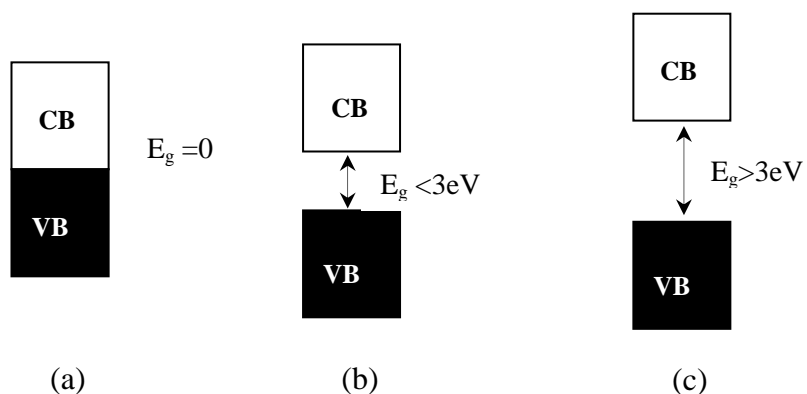


Figure 1.3 Band diagrams for (a) metals, (b) semiconductors and (c) insulators.

The energy bands of insulators (Fig 1.3c) and semiconductors (Fig 1.3b), however, are either completely full or completely empty. For instance, most conventional polymers have full valence bands and empty conduction bands, which are separated from each other by a wide energy gap. In contrast, conjugated polymers have narrower band gaps, and doping can change their band structures by either taking electrons from the valence band (*p* doping) or adding electrons to the conduction band (*n* doping) [12].

1.2.2. Conduction Mechanism

1.2.2.1 Charge Carriers:

When an electron is added (removed) to the conduction band (from the top of the valence band) of a conjugated polymer (Fig. 1.4a), the conduction (valence) band ends up being partially filled, and a radical anion (cation),

commonly termed a polaron is created (Fig. 1.4b). The formation of polarons causes the injection of states from the bottom of the conduction band and the top of the valence band into the band gap. A polaron carries both spin ($1/2$) and charge ($\pm 1 e$). Addition (removal) of a second electron on a chain already having a negative (positive) polaron results in the formation of a bipolaron (spinless) through dimerization of two polarons, which can lower the total energy (Fig. 1.4c).

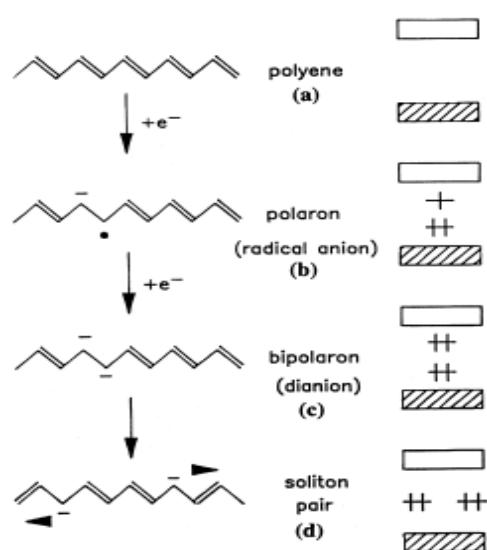


Figure 1.4 A schematic description of the formation of polaron, bipolaron, and soliton pair on a *trans*-polyacetylene chain on doping.

In conjugated polymers with a degenerate ground state (i.e., two equivalent resonance forms) like *trans*-polyacetylene, the bipolarons can further lower their energy by dissociating into two spinless solitons at one-half of the gap energy (Fig. 1.4d). Solitons do not form in conjugated polymers with nondegenerate ground states, such as polypyrrole, polythiophene, and polyaniline [12].

1.2.2.2 Doping

It is possible to control the electrical conductivity of a polymer over the range from insulating to highly conducting (metallic) state. This process is referred as doping. The insulating neutral polymer is converted into an ionic complex consisting of a polymer cation (or anion) and a counter which is the reduced form of the oxidizing agent (or the oxidized form of the reducing agent). In the solid state physics terminology, the use of an oxidizing agent corresponds to p-type (Fig. 1.5) doping and that of reducing agent to n-type doping [15].

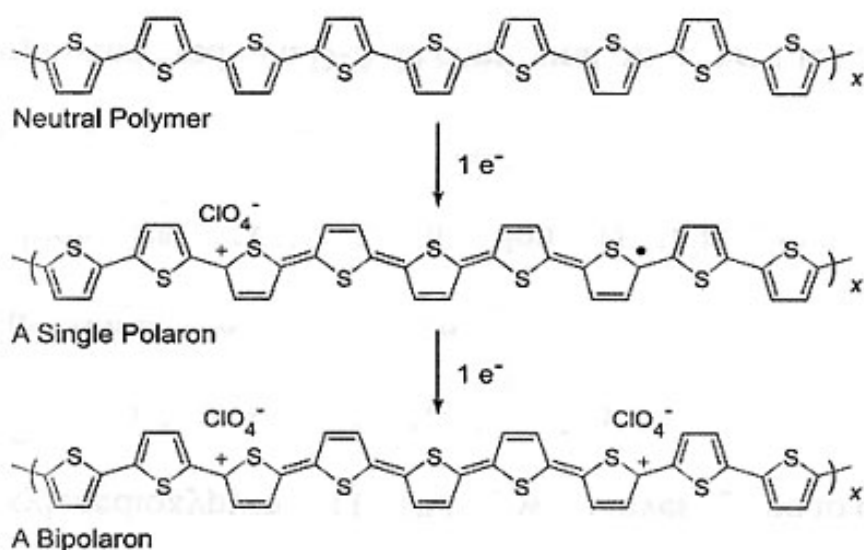
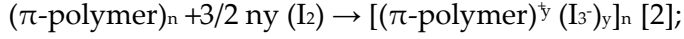


Figure 1.5 p-type doping of PTh.

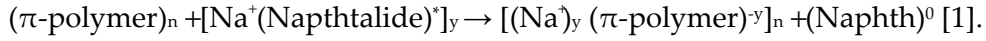
Both doping and undoping processes, involving dopant counter ions which stabilize the doped state, may be carried out chemically and electrochemically [16].

Chemical doping involves charge-transfer redox chemistry:

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



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

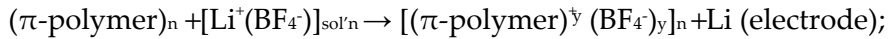


Although chemical doping is an efficient and straightforward process, it is typically difficult to control. Attempts to obtain intermediate doping levels often result in inhomogeneous doping. Electrochemical doping was invented to solve this problem [17].

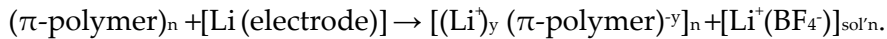
The oxidation or reduction of the polymer can be achieved electrochemically by subjecting the neutral polymer to appropriate oxidizing and reducing voltage in an electrochemical cell. The charge on the polymer chain is then neutralized by the counter ion from the electrolyte solution [15].

Electrochemical doping is illustrated by the following examples:

(a) *p* type



(b) *n* type



The doping level is determined by the voltage between the conducting polymer and the counter electrode; at electrochemical equilibrium the doping level is precisely defined by that voltage. Thus doping at any level can be achieved by setting the electrochemical cell at a fixed applied voltage and simply waiting for the system to come to electrochemical equilibrium [18].

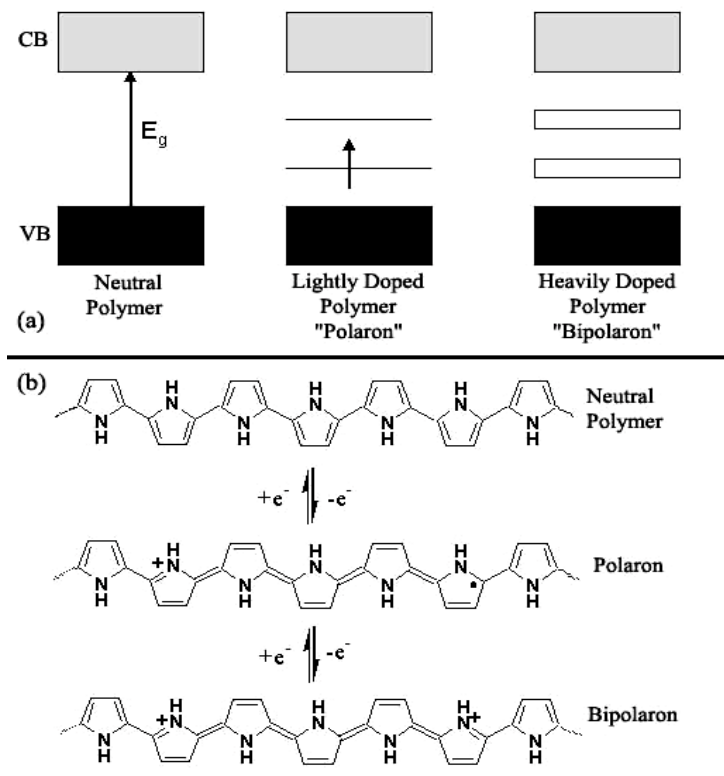


Figure 1.6 Charge carries in PPy and its corresponding energy bands in the mid gap.

An advantage of conducting polymers is that their conductivity can be tuned over eight or more orders of magnitude in the same material. The doping level of conducting polymers affects range of conductivity from insulator to metal. Figure 1.7 shows the typical conductivity ranges of the three most common conducting polymers (PA, PPy, PTh).

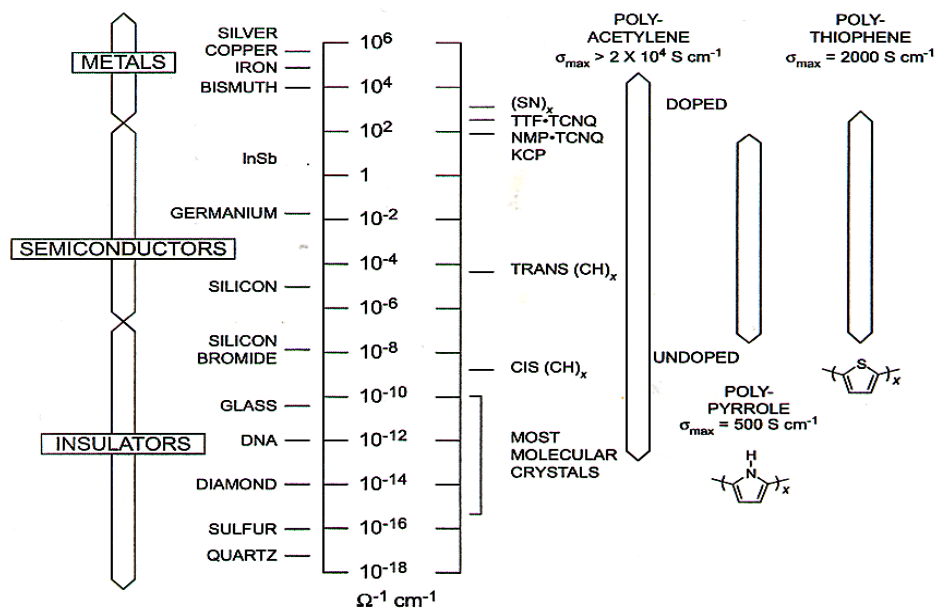


Figure 1.7 Conductivities of some metals, semiconductors and insulators.

1.2.2.3 Hopping

Variable range of hopping process in which electrons are delocalized on monomer rings is a well described conductivity mechanism. This mechanism, which is known as hopping conduction, is observed in two well-known varieties, nearest neighbor hopping and variable range hopping. The latter conduction mechanism is distinguishable from other conduction mechanisms by its different temperature dependence:

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

γ depends on the dimensionality of the hopping process [19].

Single chain or intramolecular transport, interchain transport and interparticle transport are the three main types of transport for the carrier

mobility. The intrachain movement depends on the effective conjugation of the polymer, while the inter chain jumping is determined by the stacking of the polymer molecules. Both a macroscopic (interparticle) and microscopic (intra and interchain) level gives information about conductivity.

1.3 Synthesis of Conducting Polymers:

Conductive polymers are widely synthesized by chemical or electrochemical polymerization techniques. Other type of techniques used to synthesize conducting polymers includes photochemical polymerization, metathesis polymerization, plasma, pyrolysis and solid state polymerizations [20].

1.3.1 Chemical Polymerization:

Of the chemical polymerization techniques, oxidative methods represent the least expensive and most widely exploited means by which conjugated polymers can be prepared [21]. Conducting polymers can be produced by chemical polymerization following the routes of oxidative coupling and condensation of the monomeric precursors (Fig 1.8). Oxidative coupling is based on the oxidation of the monomer under Friedel-Crafts conditions [22]. In addition to anhydrous FeCl_3 [23] other Lewis acids [24] are used in oxidative chemical polymerization.

These oxidants are able to oxidize the monomers in appropriate solution, leading to chemically active cation radicals of the monomers used. The cation radicals formed thus react with monomer molecules, yielding oligomers or insoluble polymers. Chemical polymerization occurs in the bulk of the solution, and the resulting polymers precipitate as insoluble solids [25]. The properly substituted heterocyclic and other aromatic monomers form highly soluble

polymers. These polymers can be analyzed by traditional analytical techniques to determine their primary structure.

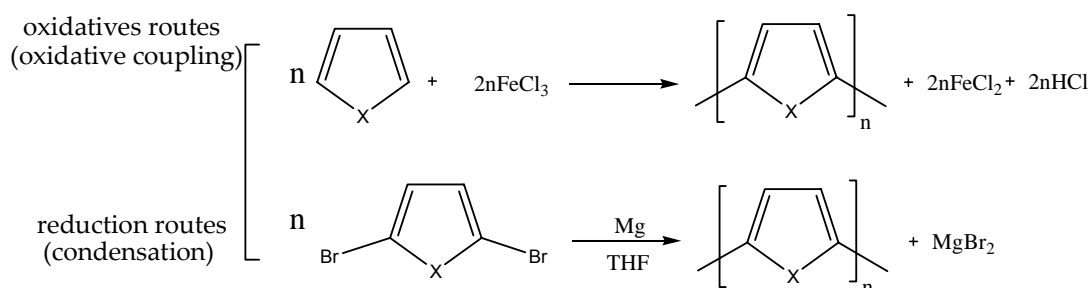


Figure 1.8 Chemical synthetic routes of polyheterocycles.

1.3.2 Electrochemical Polymerization:

Electropolymerization is a standard oxidative method for preparing electrically conducting conjugated polymers. The electrochemical routes for synthesis of polyheterocycles are anodic and cathodic couplings, which parallel the chemical oxidative coupling and condensation reactions (Fig. 1.9).

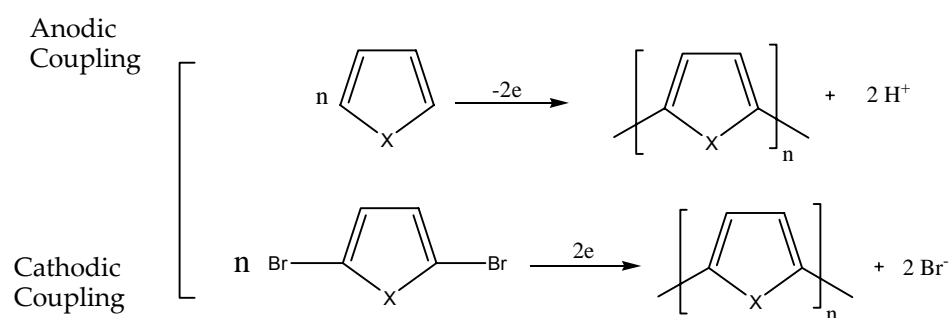


Figure 1.9 Electrochemical synthetic routes to polyheterocycles.

Electrochemical synthesis is simple, selective and a reproducible method. It has the advantage of producing the material on an electrode on which to perform analysis of the growing process and the further experimental by electrochemical or spectroscopic techniques. Furthermore, the method allows easy control of the film thickness by the deposition charge. Anodic coupling consists of oxidation of the monomer into a polymer accompanied with proton elimination. Anodic coupling is preferred because (1) it uses the unmodified monomer and (2) the resultant polymer, being more easily oxidized (doped), is produced in the conductive state and therefore, allows the continuous deposition of the material up to considerable thickness.

The type of solvent, electrolyte system, choice and concentration of monomer and electrodes strongly affect the properties of the final conducting polymer [22].

1.3.2.1 Electrolytic Medium

Since the electrochemical polymerization reaction proceeds via radical cation intermediates, nucleophilic character of the solvent and electrolyte impose certain restrictions on their choice. The solvent used in the electrochemical polymerization must be of sufficiently high dielectric constant in order to guarantee ionic conductivity of the medium. The solvent dissolves and dissociates the supporting electrolyte and posses a potential window open at the potentials required to oxidize or reduce polymer. Nitriles are preferred because they provide the widest range in both oxidation and reduction with a high dielectric constant ($\epsilon= 37$ for ACN) [22].

The choice of supporting electrolyte depends on the solubility and degree of dissociation and its nucleophilicity. Morphology of the resulting film is significantly affected by the nature of electrolyte used [26]. Supporting electrolyte used in electrochemical polymerization serves for two purposes;

- a) It makes electrolytic bath solution conducting and
- b) It dopes the polymer by allowing one of its ions to couple with monomer unit [15].

Salts of perchlorates, tetrafluoroborates and hexafluorophosphate are widely used ones for the synthesis of conducting polymers.

The competitive reactions of the radical cations or the oxidized polymer with nucleophiles in the medium can be avoided by high concentration of monomer (0.1 M or more). As the oxidation potential of the monomer decreases, the number of competitive reactions decreases so that even millimolar concentrations may be used for efficient polymerization [22].

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

1.3.2.2 Mechanism of Electrochemical Polymerization

The proposed mechanism for the electrochemical oxidative polymerization of a heterocycle is shown in Fig. 1.10.

In the first step, the heterocyclic monomer is oxidized to yield a radical cation. High concentrations of radical cations remain near the electrode surface due to faster transfer of electron with respect to diffusion of monomer to the bulk solution. The second step is controversy step because coupling may proceed by two different routes. The coupling proceeds either by the combination of two radical cations to yield a dimeric pyrrole dication or electrophilic addition of radical cation to heterocyclic monomer followed by oxidation to a dimeric pyrrole dication. Third step is a chemical step involving elimination of two protons to regain aromatic character. The dimer present in near the electrode surface is further oxidized to

yield radical cation to produce trimer. This mechanism of polymerization is called ECE mechanism where E and C are defined as electrochemical and chemical processes, respectively [27].

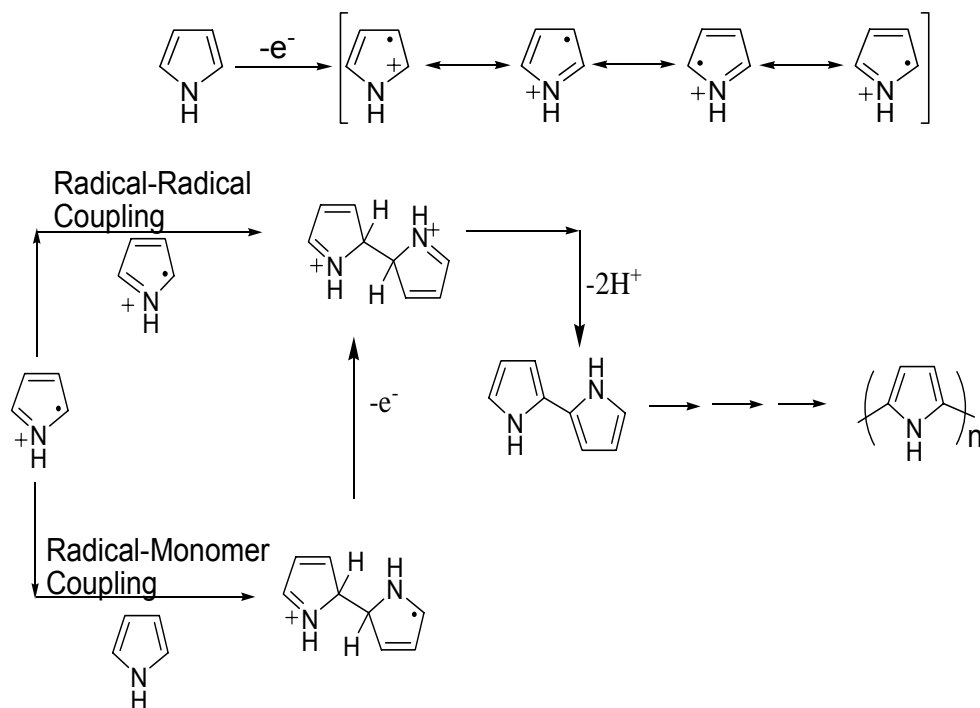


Figure 1.10 Resonance stabilization and electropolymerization mechanism of pyrrole. (a) Resonance stabilization of radical cation of pyrrole. (b) Proposed mechanism for the electrochemical polymerization of pyrrole.

1.3.2.3 Monomer Structure:

The goals in the synthesis of conducting polymers are to design new and novel structures, to increase the order of the polymer backbone and also the conductivity, processibility, solubility in certain solvents [28].

The synthetic effort is focused on the tailoring properties of conducting polymers by adding new substituents to structure. Thiophene (Th) and pyrrole

(Py) are two common monomers used to synthesize diversity of conducting polymer due to their low cost and availability. A common disadvantage for both pyrrole and thiophene is that they are available for coupling on the β positions. β coupling causes a problem during polymerization because it breaks the conjugation along the polymer backbone. The β coupling can take place by either β site or α site of another monomer (α - β and β - β). The break in conjugation leads to decrease in conductivity and increase in band gap (Fig 1.11). Substitution of these monomers in the 3 or 4 positions by the attachment of various alkyl and alkoxy groups protect the monomer against β coupling [29].

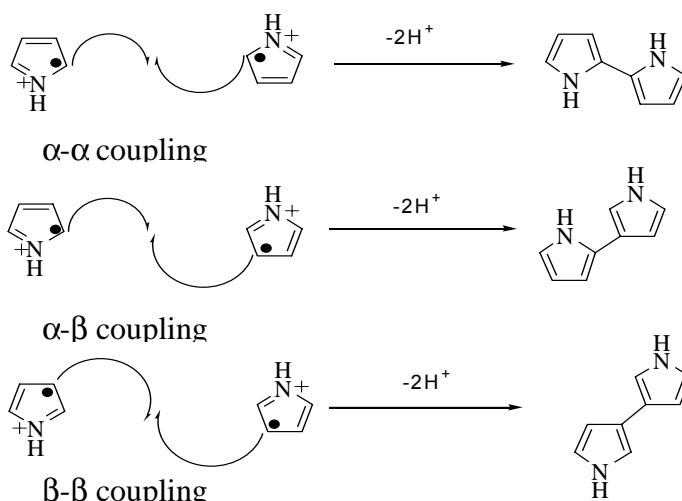


Figure 1.11 Potential coupling reactions for pyrrole during oxidative polymerization [29].

Oxidation potential, band gap and electrochromic properties of the resultant polymers can be adjusted by structural modification of Th and Py. Thiophenes substituted by electron withdrawing groups have higher oxidation potentials than Th and introduction of electron donating groups to Th decreases

the oxidation potential with respect to Th [30]. The solubility of polymers is possible by substitution with long alkyl chains [31].

The processibility of a conducting polymer can be improved by copolymerization through increase of chain flexibility via incorporation of flexible centers in the main chain side chain substitution [32].

1.4 Conducting Copolymers and Composites

Copolymerization, a process in which two or more monomers are incorporated as integral segments of a polymer, is used to produce copolymers with properties that are different from those of homopolymers. In general copolymers possess physical and mechanical properties intermediate between both homopolymers. The magnitude of the numerical values of these properties generally depends on the concentration of the monomer units incorporated into the copolymer. The primary advantage of copolymerization is that it leads to a homogeneous material, the properties of which can be regulated by adjusting the ratio of the concentration of monomer in the feed [33].

In comparison with the chemical copolymerization, one of the advantages for the electrochemical copolymerization is that the effect of the applied potential and the monomer concentration ratio on the copolymerization rate and on the copolymerization behavior is readily observable. This is much more favorable for determining the optimum copolymerization conditions. In addition, the copolymerization potential of two different monomers plays an important role in the properties of a copolymer [34].

Synthesis and characterization of conducting copolymers of pyrrole and thiophene with various other polymers were reported in the literature [35, 36]. The strong electron donor properties of EDOT represent an interesting tool for the molecular engineering of the band gap of π -conjugated systems. One of the simplest

ways to take advantage of these properties is to associate EDOT with electron withdrawing groups by synthesizing copolymers [37].

When an electrically conducting phase is dispersed with a sufficient quantity in a polymeric resin, a conductive composite is formed. The unique properties of such composites make them technologically superior to or more cost effective than alternative materials [38]. Structural and electrical properties can be improved by the preparation of composite materials containing a conducting polymer composed with a nonconducting polymer such as poly(vinyl chloride) (PVC) poly(vinyl alcohol) (PVA) and natural rubber [39-41].

1.5 Characterization of Conducting Polymers

A variety of techniques can be employed to characterize conducting polymers. Many examples exist in the literature, some of which include; cyclic voltammetry for understanding redox processes in conducting polymers, optical characterization of conducting polymers for non-linear optical materials, nuclear magnetic resonance for structure confirmation, chain orientation and molecular motion, gel permeation chromatography for molecular weight, Raman analysis for vibrational assignments, differential scanning calorimetry and thermogravimetric analysis for evidence of glass and melting transitions and decomposition temperatures, dependence of conductivity on temperature and electrical field and magnetic susceptibility to understand the conductivity mechanism; electroluminescence to screen for potential use light emitting diodes (LEDs) various types of X-ray analysis to understand the crystal structure [28].

1.6 Applications of Conducting Polymers

Conducting polymers are used for the replacement of metals and put into practice in the development of electronic/optoelectronic devices like electrochromic devices (ECDs) [42], solar cells [43], light emitting diodes (LEDs) [44] and field effective transistors (FETs) [45].

In thin film technologies, conducting polymers can be used as conducting layers. A field with a wide technical importance is the antistatic protection and the electromagnetic interference shielding by conducting polymers. The possibility of a reversible switching of conducting polymers between two redox states rose speculations for rechargeable batteries. Conducting polymers can be regarded as membranes due to their porosity. They could be used for separation of a gas or liquids. The use of conducting polymers in sensor technologies consists as an electrode modification to improve selectivity, to impart selectivity, to suppress interference and to support as a matrix for sensor molecules [46].

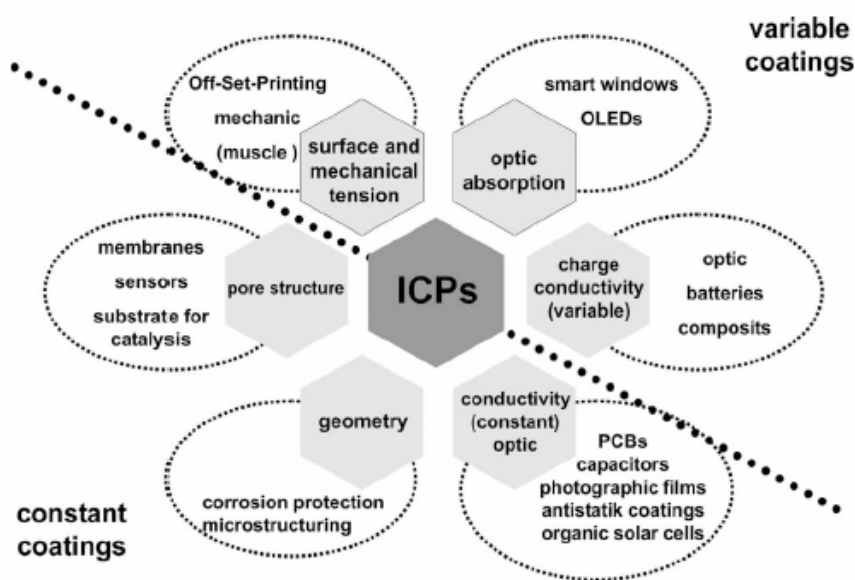


Figure 1.12 Applications of conducting polymers [47].

1.7 Electrochromism

Electrochromism refers to the ability of a material to change its optical properties within the whole electromagnetic spectrum under an applied voltage, such as in the visible region (400-800 nm) and in the near-infrared (NIR) region (e.g., 1000-2000 nm). [48]

Metal oxides such as WO_3 [49], metal complexes [50] and conjugated polymers [51] are presently known electrochromic materials.

Conducting polymers have received more attention than inorganic materials owing to their advantages over inorganic compounds, such as fast switching ability, high coloration efficiency, fine tuning of the band gap through chemical structure modification and multiple colors with the same material [52].

Electrochromic changes are induced by redox processes which are accompanied by ion insertion/expulsion and result in a modification of the polymer's electronic properties giving rise to changes in the color of the material. The color exhibited by the polymer is closely related to the band gap. Tuning of color states is possible by suitable choice of monomer. This represents a major advantage of using conducting polymers for electrochromic applications. Subtle modifications to the monomer can significantly alter spectral properties [53].

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

π - π^* transition and the polaron absorption are fully depleted, while a lower energy transition, peaked in the near-IR beyond the range of the spectrophotometer, increases. This absorption is assigned to the bipolaronic (dication) state of the conjugated polymer. Such optical and structural changes are reversible through repeated doping and dedoping over many redox cycles, making electrochromic polymers potentially useful in applications for modulating transmissivity and color [54].

1.7.1 Types of Electrochromic Materials

There are three main types of electrochromic materials in terms of their electronically accessible optical states. The first type includes materials with at least one colored and one bleached state. These materials are especially useful for absorption/transmission-type device applications such as smart windows and optical shutters. Typical examples of this area are metal oxides, viologens, and polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT). A second class of materials consists of electrochromes with two distinctive colored states. These electrochromic materials lack a transmissive state but are useful for display-type applications where different colors are desired in different redox states. Polythiophene is a good example of this type, where the thin films of this polymer switch from red to blue upon oxidation. A third class includes the growing interest in the electrochromic field, where more than two color states are accessible depending on the redox state of the material. This is the area where conjugated polymers have found the most interest due to their versatility for making blends, laminates, and copolymers [54].

One of the more prominent uses for electrochromic polymers is at window applications, where a device can be cycled between transparent and tinted states through the use of a polymer with transmissive and absorptive color states. Also, as the palette of available colors in electrochromic polymers grows, these

materials should become more useful for display technology [55] In addition to applications as smart windows, displays, and storage devices, electrochromic materials have attracted a great deal of interest for use in devices that operate in the infrared and microwave regions, as well in key components (i.e., variable optical attenuators) in telecommunications that operate in the NIR region (e.g., around 1310 and 1550 nm) [48].

1.7.2. Spectroelectrochemistry

Spectroelectrochemistry is a technique that examines electronic and optical changes of conducting polymers that occur upon doping. It provides information about electronic band gap intraband states formed upon doping (polaron and bipolaron).

1.8 Electrochromic Devices (ECD)

Electrochromic displays are typically assembled by combining an electrode covered with a thin layer of electrochromic materials, transparent solid polymer electrolytes and a complimentary electrochromic material as a counter electrode. If the back of the counter electrode is covered with a reflective material it will act as an electrochromic mirror [15].

The electrochromic devices are very similar to batteries. It consists of at least one transparent electrode in electromagnetic spectrum with electrochemically reversible cathode material (which colors upon being oxidized) and anode material (which colors upon being reduced) and ion-conducting electrolyte.

One of the electrodes is oxidized, while the other is being reduced upon external externally applied potential, leading to a device switching between

combination of the neutral color of one film and the oxidized color of the other film, and vice versa [56].

The ion-conducting electrolyte must not only provide physical separation between cathode and anode, a source of cations and anions to balance redox reactions, but must also be transparent in the given region of the spectrum. The ion conducting electrolyte (gel electrolyte) is usually an inorganic salt dissolved in a solvent such as propylene carbonate with a stiffener polymer poly(methyl-methacrylate) [28].

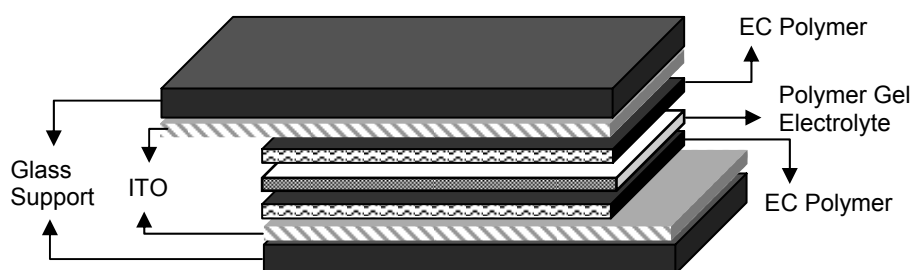


Figure 1.13 Schematic representation of ECDs.

The requirements for high performance electrochromic devices are: a) high electrochromic efficiency, expressed in $\text{cm}^2 \text{C}^{-1}$ and related to the injected charge in the material to change its color; b) short response time; c) good stability; d) optical memory, defined as the color stability under open circuit potential conditions; e) optical contrast, also called write-erase efficiency, and f) color uniformity [57].

1.9 Characteristics of Electrochromic Device

1.9.1 Electrochromic Contrast and Switching Speed

Electrochromic contrast is probably the most important factor in evaluating an electrochromic material. It is often reported as a percent transmittance change ($\% \Delta T$) at a specified wavelength where the electrochromic material has the highest optical contrast. Switching speed is often reported as the time required for the coloring/bleaching process of an electrochromic material. The switching speed of electrochromic materials is dependent on several factors such as the ionic conductivity of the electrolyte, accessibility of the ions to the electroactive sites (ion diffusion in thin films), magnitude of the applied potential, film thickness, and morphology of the thin film [54].

1.9.2 Open Circuit Memory and Stability:

Open Circuit Memory is defined as the time the material retains its absorption state after the electrical field is removed.

Electrochromic stability is usually associated with electrochemical stability since the degradation of the active redox couple results in the loss of electrochromic contrast and hence the performance of the electrochromic material. [54]

1.10 Colorimetry

The colors of the electrochromic materials were defined precisely by achieving colorimetry measurements. Colorimetry is defined as the measurement of color. The measurement of color allows colored objects to be described, ordered and compared. CIE system was employed as a quantitative scale to define colors.

1976 CIE $L^*a^*b^*$ system of colorimetry established by The Commission Internationale de l'Eclairage (International Commission on Illumination) is used for an objective description of the color of the ECDs, where L corresponds to brightness or luminance, a refers to hue, dominant wavelength, or chromatic color, and b known as the saturation, chroma, tone, or purity [56,58].

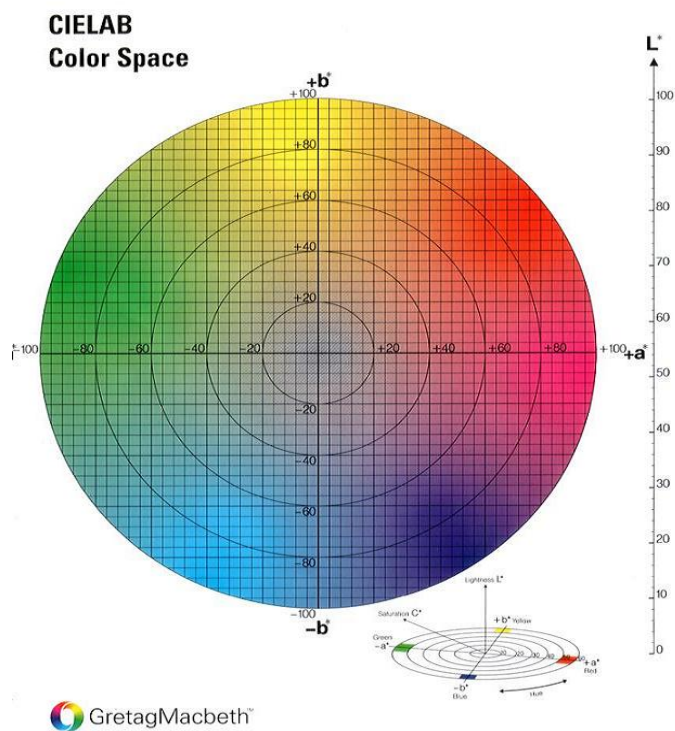


Figure 1.14 CIELAB color space.

1.11 Aims of the Work

Aims of the work are *i)* to synthesize fully conjugated thiophene functionalized monomer named as 2,5-di(thiophene-2-yl)-1-*p*-tolyl-1H-pyrrole (DTTP) and characterize monomer and polymer. *ii)* Electrochemically polymerize or copolymerize them with a comonomer (EDOT) in thin film forms. *iii)* Examine the electrochromic properties of the homopolymers and copolymers and construct electrochromic devices with PEDOT and finally *iv)* evaluate the electrochromic performances of these devices.

CHAPTER II

EXPERIMENTAL

2.1 Materials

AlCl_3 (Merck), succinyl chloride (Aldrich), *p*-toluidine (Merck), NaOH (Merck), dichloromethane (Sigma-Aldrich), toluene (Merck), acetonitrile (ACN) (Merck), methanol (Merck), LiClO_4 (Aldrich), NaClO_4 (Aldrich), poly(methylmethacrylate) (PMMA) (Aldrich), propylene carbonate (PC) (Aldrich) were used without further purification. Thiophene (Aldrich) was distilled before use. Ferric chloride (Aldrich), 3,4-Ethylenedioxythiophene (EDOT) (Aldrich), *p*-toluene sulfonic acid (PTSA) (Sigma) and nitromethane (Aldrich) were used as received.

2.2 Instrumentation

2.2.1 Potentiostat

A VoltaLab PST050 and a Solartron 1285 Potentiostats were used to provide a constant potential in the electrochemical polymerization. This device can attain to keep the voltage difference between the working and reference electrodes at a

constant desired value during the electrolysis and compensates for the voltage drop in the electrolysis solution.

2.2.2 Cyclic Voltammetry System

Cyclic voltammetry measurements were carried out by cycling the potential of an electrode, which is immersed in an unstirred solution, and measuring the resulting current at the working electrode.

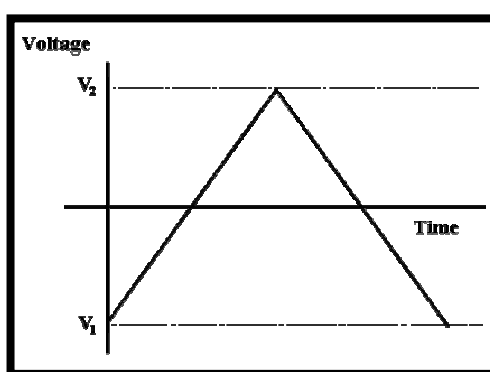


Figure 2.1 Triangular wave function

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

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

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

$$i_p = (2.69 \times 10^5)n^{3/2}AD^{1/2}CV^{1/2}$$

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

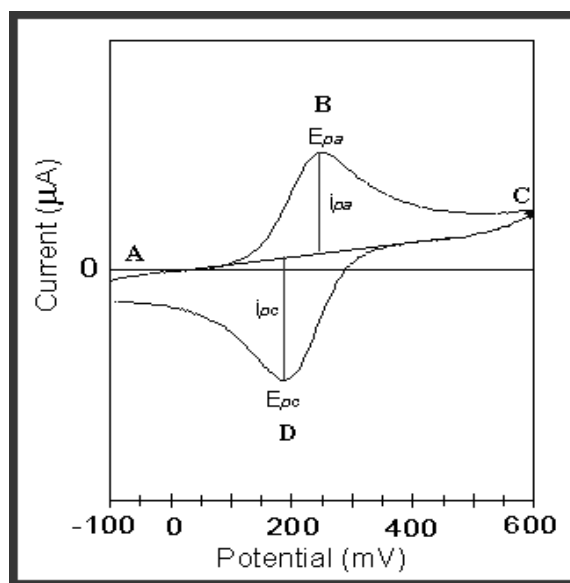


Figure 2.2 A cyclic voltammogram for a reversible redox reaction

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

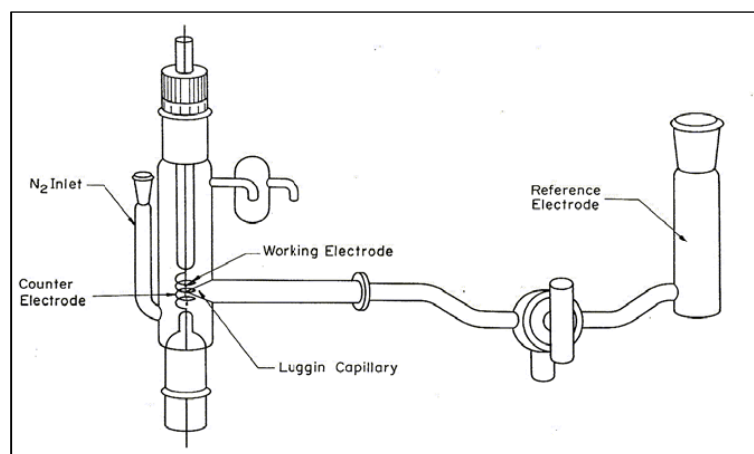


Figure 2.3 Cyclic voltammetry cell

2.2.3 Electrolysis Cell

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

2.2.4 Nuclear Magnetic Resonance (NMR)

^1H -NMR and ^{13}C -NMR spectra of samples were recorded on a Bruker Spectrospin Avance (DPX-400) Spectrometer using CDCl_3 as the solvent.

2.2.5 Fourier Transform Infrared Spectrometer (FTIR)

The FTIR spectra of monomer (DTTP), homopolymer P(DTTP) and copolymer P(DTTP-co-EDOT) was recorded on a Nicolet 510 FTIR spectrometer.

2.2.6 Scanning Electron Microscope (SEM)

JEOL JSM-6400 scanning electron microscope was used to analyze the surface morphologies of the polymer films.

2.2.7 Four-Probe Conductivity Measurements

Four probe method were used to measure electrical properties of conducting polymers due to its advantage over two probe technique. This is the elimination of errors caused by contact resistance. Figure 2.4 demonstrates a simple four-probe measurement setup. Four equally spaced osmium tips touch the surface of polymer film taped on an insulating substrate. A known steady current is passed through the electrodes 1 and 4 and measured while the potential drop ΔV between contacts 2 and 3 assessed.

Conductivity is calculated from the following equation,

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

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

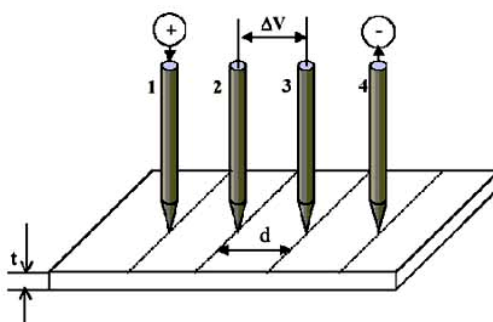


Figure 2.4 Four-probe conductivity measurement

2.2.8 Gel Permeation Chromatography (GPC)

GPC (PL220) was conducted for the determination of molecular weight of insulating precursor polymer.

2.2.9 UV-VIS Spectrophotometer

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

2.2.10 Colorimetry Measurements

Colorimetry measurements were done via Minolta CS-100 spectrophotometer.

2.3 Procedure

2.3.1 Synthesis of Monomer

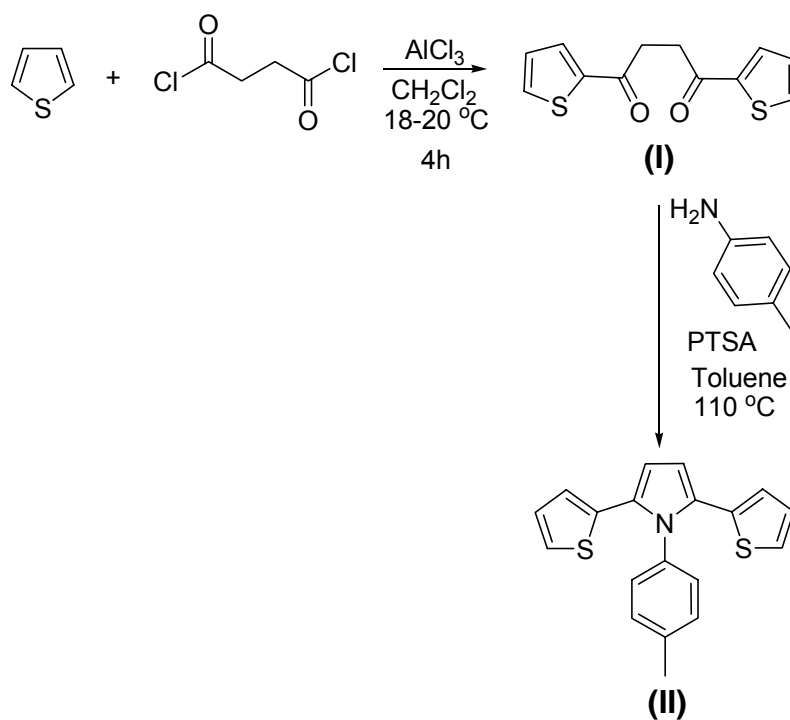
2.3.1.1 Synthesis of 1,4-Di(2-thienyl)-1,4-butanedione (I)

Among the various methods leading to 1,4-di(2-thienyl)-1,4-butanedione [59-66], the double Friedel-Crafts reaction, first proposed by Merz and Ellinger [65], was chosen. Thiophene and succinyl chloride were utilized as the reactants and aluminum chloride as the Lewis acid catalyst, since it is the most direct one-step procedure with good yields (78%). To a suspension of AlCl_3 (16 g, 0.12 mol) in CH_2Cl_2 (15 ml), a solution of thiophene (9.61 ml, 0.12 mol) and succinyl chloride (5.51 ml, 0.05 mol) in CH_2Cl_2 was added drop wise. The red mixture was stirred at room temperature for 4 h. This was then poured into ice and concentrated HCl (5

ml) mixture. After stirring, the dark green organic phase was separated. This phase was washed with concentrated NaHCO₃ solution and brine solution, and then dried over MgSO₄. After evaporation of the solvent, a blue green solid remained, which was suspended in ethanol. Filtration and washing with ethanol yielded the 1,4-bis(2-thienyl)butane-1,4-dione. The synthetic route of 1,4-di(2-thienyl)-1,4-butanedione is shown in Scheme 2.1.

2.3.1.2 Synthesis of 2,5-Di(thiophen-2-yl)-1-*p*-tolyl-1H-pyrrole (DTTP) (II)

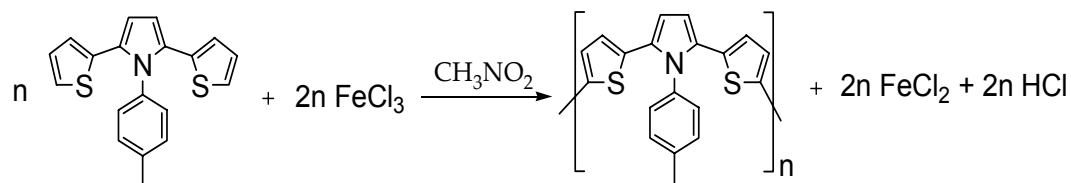
The monomer 2,5-di(thiophen-2-yl)-1-*p*-tolyl-1H-pyrrole was synthesized from 1,4-di(2-thienyl)-1,4-butanedione and *p*-toluidine in the presence of catalytical amount of *p*-toluene-sulfonic acid (PTSA). Refluxing 1,4-di(2-thienyl)-1,4-butanedione (1.25 g, 5 mmol), *p*-toluidine (0.75g, 7 mmol), *p*-toluenesulfonic acid (PTSA) (0.1 g, 0.58 mmol) and toluene (20 mL) in a round bottom flask equipped with an Argon inlet and mechanical stirrer for 24 hours yielded the target monomer. Afterwards, toluene was evaporated and 2,5-di(thiophene-2-yl)-1-*p*-tolyl-1H-pyrrole was obtained via column chromatography. Elution with dichloromethane: hexane (1:1) of SiO₂ flash column gave the desired compound at the solvent front. The synthetic route of the monomer is shown in Scheme 2.1.



Scheme 2.1 Synthetic route of 2,5-di(thiophen-2-yl)-1-*p*-tolyl-1H-pyrrole (DTTP)

2.4 Chemical Polymerization of DTTP with Ferric Chloride

Chemical polymerization of DTTP was fulfilled using ferric chloride as the oxidizing agent. DTTP (1×10^{-3} M) was dissolved in nitromethane (15 mL). A solution of iron(III) chloride (2×10^{-3} M) dissolved in nitromethane (5 mL) was dropwise added to the monomer solution. The reaction was carried out for 15 min. The dark colored polymer was first washed with methanol, filtered, compensated with 30% NaOH, and dried under vacuum for ^1H - NMR analyses.



Scheme 2.2 Oxidative chemical polymerization of DTTP where $n=1 \times 10^{-3}$ M in this synthesis

2.5 Gel Permeation Chromatography (GPC)

For determination of molecular weight, chemically synthesized P(DTTP) was dissolved in tetrahydrofuran and GPC studies were conducted. Molecular weights were determined on the basis of polystyrene standards.

2.6 Potentiodynamic Studies of Polymers

CV was employed in order to assay the electroactivity of the polymers and to accomplish the oxidation-reduction peak potentials of the polymer. The measurements were achieved at room temperature under nitrogen atmosphere by using NaClO_4 (0.1 M) and LiClO_4 (0.1 M) / ACN solvent-electrolyte couple. A background voltammogram was run to ensure that no impurity was present before the addition of substrate. Experiments were carried out sweeping the potential between 0.0 V and +1.0 V with 500 mV/sec scan rate. Solution contained 0.01 M DTTP.

For the investigation of oxidation and reduction potentials of P(DTTP-co-EDOT) copolymer, same conditions were employed and the solutions contained $2 \mu\text{L}$ EDOT in addition to 0.01 M DTTP. The potential was swept between -1.0 V and +1.5 V with 500 mV/sec scan rate.

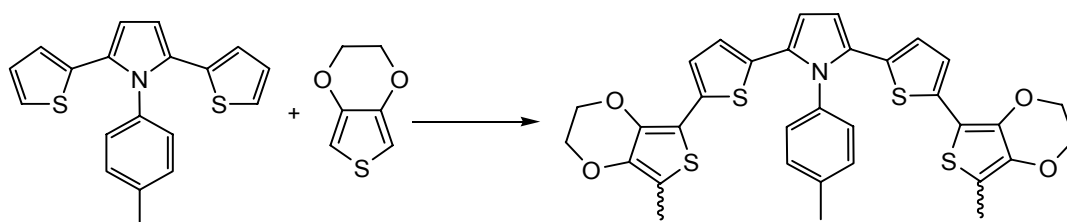
2.7 Electrochemical Synthesis of P(DTTP) and P(DTTP-co-EDOT)

2.7.1 Synthesis of Homopolymer of DTTP

Electrochemical polymerization of DTTP was carried out by sweeping the potential between 0.0 V and +1.0 V with 500 mV/sec scan rate, in the presence of 50 mg DTTP in NaClO₄ (0.1 M) and LiClO₄ (0.1 M)/ACN solvent-electrolyte couple. The working and counter electrodes were Pt wires and the reference electrode was Ag wire electrode. P(DTTP) was washed with ACN in order to eliminate excess NaClO₄/LiClO₄ and unreacted monomer after the potentiodynamic electrochemical polymerization.

2.7.2 Synthesis of Copolymer of DTTP with 3,4-Ethylenedioxythiophene (EDOT) P(DTTP-co-EDOT)

The potentiodynamic polymerization of DTTP with EDOT was carried out in a solution containing 0.01 M DTTP and 20 μL EDOT in NaClO₄ (0.1 M) and LiClO₄ (0.1 M)/ACN solvent-electrolyte couple by sweeping the potential between -0.5 V and +1.1 V with 500 mV/sec scan rate in a one compartment cell with two platinum foils as the working and counter electrodes and a pseudo reference electrode (Ag wire). P(DTTP-co-EDOT) was washed with ACN in order to remove excess NaClO₄/LiClO₄ and unreacted monomer after the potentiodynamic electrochemical polymerization.



Scheme 2.3 Copolymerization of DTTP with EDOT.

2.8 Investigation of Electrochromic Properties of Polymers

2.8.1 Spectroelectrochemical Studies

Homopolymer film was potentiodynamically deposited on indium tin oxide (ITO) coated glass slides, sweeping the potential between 0.0 V and 1.0 V in the presence of 0.01 M DTTP and ACN/ NaClO₄/LiClO₄ (0.1 M) solvent-electrolyte couple. For the investigation of copolymer, same conditions were used while the solution contained 2 μL EDOT.

Spectroelectrochemical studies of the homopolymer film were carried out sweeping the potentials from 0.0 V to 0.6 V in the monomer free ACN/ NaClO₄/LiClO₄ (0.1 M) solution while spectroelectrochemical series are taken at the same time.

Spectroelectrochemical studies of the copolymer film were carried out sweeping the potentials from -0.6 V to 0.8 V in the monomer free ACN/ NaClO₄/LiClO₄ (0.1 M) solution while spectroelectrochemical series are taken at the same time.

2.8.2 Switching Properties of Polymers

After coating the polymers on ITO electrode, a potential square wave was applied in the monomer free ACN/ NaClO₄/LiClO₄ (0.1 M) solution while recording the percent transmittance between its neutral and doped states at the at a fixed maximum absorption wavelength.

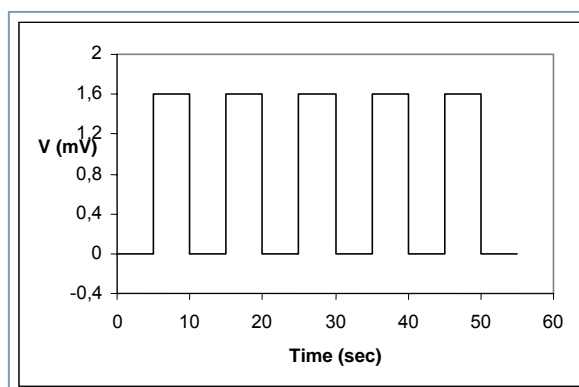


Figure 2.5 Square wave voltammetry

Switching properties of polymer films were investigated by application of potential square wave technique with a residence time of 5 seconds between 0.0 V and +0.6 V for homopolymer, between -0.6 V and +0.8 V for copolymer.

2.8.3 Colorimetry Studies of Polymers

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

2.9 Electrochromic Device (ECD) Construction

2.9.1 P(DTTP)/PEDOT Electrochromic Device

Cathodically coloring polymer, poly(3,4-ethylenedioxythiophene) (PEDOT), were electrochemically deposited onto the ITO-coated glass from a 0.1 M solution of EDOT in 0.1M ACN/NaClO₄/LiClO₄ at +1.5V versus Ag/Ag⁺. The anodically coloring polymer, P(DTTP) was potentiodynamically deposited onto the ITO-coated glass sweeping between 0.0 V and +1.0 V in the presence of 0.01 M DTTP in NaClO₄ (0.1 M) and LiClO₄ (0.1 M)/ACN solvent-electrolyte couple. Prior to construction,

the charge capacities of the electrochromic layers were balanced in order to achieve complete electrochromic reaction and eliminate the residual charge formation during the coloring/bleaching. The gel electrolyte was spread on the polymer-coated sides of the electrodes (one doped, the other neutral) and the electrodes were sandwiched under atmospheric conditions.

2.9.2 P(DTTP-co-EDOT)/PEDOT Electrochromic Device

The anodically coloring polymer P(DTTP-co-EDOT) was potentiodynamically deposited onto the ITO-coated glass sweeping between -0.5 V and +1.1 V 0.01 M DTTP and 20 μ L EDOT in NaClO₄ (0.1 M) and LiClO₄ (0.1 M)/ACN solvent-electrolyte couple. Cathodically coloring film which is PEDOT was fully reduced by polarizing to -1.5 V vs Ag/Ag⁺, anodically coloring films were fully oxidized by polarizing to +1.0 V vs Ag/Ag⁺, in the monomer free solution. The gel electrolyte was spread on the polymer-coated sides of the electrodes (one doped, the other neutral) and the electrodes were sandwiched under atmospheric conditions.

2.9.3 Preparation of the Gel Electrolyte

Gel electrolyte was prepared by using NaClO₄:LiClO₄: AN: PMMA: PC in the ratio of 1.5:1.5:70:7:20 by weight. After NaClO₄/LiClO₄ was dissolved in AN, PMMA was added into the solution. In order to dissolve PMMA, vigorous stirring and heating was required. Propylene carbonate (PC), as a plasticizer, was introduced to the reaction medium when all of the PMMA was completely dissolved. The mixture was stirred and heated until the highly conducting transparent gel was produced.

2.10 Characterization of Electrochromic Devices

2.10.1. Spectroelectrochemistry Studies of Electrochromic Devices

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

Spectroelectrochemical UV-Vis transmittance of electrochromic device of P(DTTP)/PEDOT measured under miscellaneous applied potentials between -0.6 V and +1.6 V while measuring the absorbance as a function of wavelength.

Spectroelectrochemical study of P(DTTP-co-EDOT)/PEDOT device was carried out varying the voltage between -0.6 V and + 2.0 V and absorbance was measured as a function of wavelength.

2.10.2 Switching Properties of Electrochromic Devices

Potential square wave technique (2.2.5) was used to determine switching properties of ECDs between -0.6 V and +1.6 V with a residence time of 5 s for P(DTTP)/PEDOT device and between -0.6 V and +2.0 V with a residence time of 5 s for P(DTTP-co-EDOT)/PEDOT device.

2.10.3 Open Circuit Memory

Open circuit memory of devices were tested by the application of potential to ECDs for 1 second for each 200 seconds time intervals while recording percent transmittance at a fixed wavelength. Open circuit memory of P(DTTP)/PEDOT ECD

was monitored simultaneously at 617 nm by an applied pulse ($0.0 \pm 1.6V$) for 1 s and kept under open-circuit conditions for 200 s.

Open circuit memory of P(DTTP-co-EDOT)/PEDOT ECD was monitored simultaneously at 615 nm by an applied pulse ($-0.6 \pm 2.0V$) for 1 s and kept under open-circuit conditions for 200 s.

2.10.4 Stability of the Electrochromic Devices

P(DTTP)/PEDOT device repeatedly switched up to 1000 cycles with CV sweeping voltage of $-0.6V$ and $+1.6 V$ range with 500 mV/s scan rate under atmospheric conditions. P(DTTP-co-EDOT)/PEDOT device were repeatedly switched up to 1000 cycles with CV voltage of $-1.0 V$ and $+1.5 V$.

2.10.5 Colorimetry Studies of Electrochromic Devices

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

CHAPTER III

RESULTS AND DISCUSSION

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

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of monomer and $^1\text{H-NMR}$ of polymer were investigated with CDCl_3 as the solvent and chemical shifts (δ) are given relative to tetramethylsilane as the internal standard.

Pale white powder; mp 161 °C; $^1\text{H-NMR}$ spectrum of monomer (Fig. 3.1): $\text{C}_{19}\text{H}_{15}\text{NS}_2$, δ_{H} (CDCl_3): 2.36 (s, 3H, H_g), 6.46 (dd, $J = 1.1$ and 3.7 Hz, 2H, H_c), 6.47 (s, 2H, H_d), 6.73 (dd, $J = 3.6$ and 5.1 Hz, 2H, H_b), 6.97 (dd, $J = 1.1$ and 5.1 Hz, 2H, H_a), 7.12 (d, $J = 8.7$ Hz, 2H, H_f), 7.14 (d, $J = 9$ Hz, 2H, H_e).

$^{13}\text{C-NMR}$ spectrum of the monomer $\text{C}_{19}\text{H}_{15}\text{NS}_2$ (Fig. 3.2): $^{13}\text{C-NMR}$ (δ , ppm): 20.2, 109.7, 123.8, 124.1, 126.9, 129.7, 129.8, 130.2, 135.1, 135.8, 139.1.

$^1\text{H-NMR}$ spectrum of chemically synthesized polymer (Fig. 3.3): δ_{H} (CDCl_3): 2.36 (s, 3H, H_g), 6.15-6.20 (broad s, 2H, H_c), 6.38-6.50 (broad s, 2H, H_d), 6.51-6.53 (broad s, 2H, H_b), 6.90-7.20 (broad s, 2H, H_f), 7.03-7.18 (broad s, 2H, H_e). The decrease in the intensity of H_a confirms the polymerization through position 2 of thiophene moiety of the monomer.

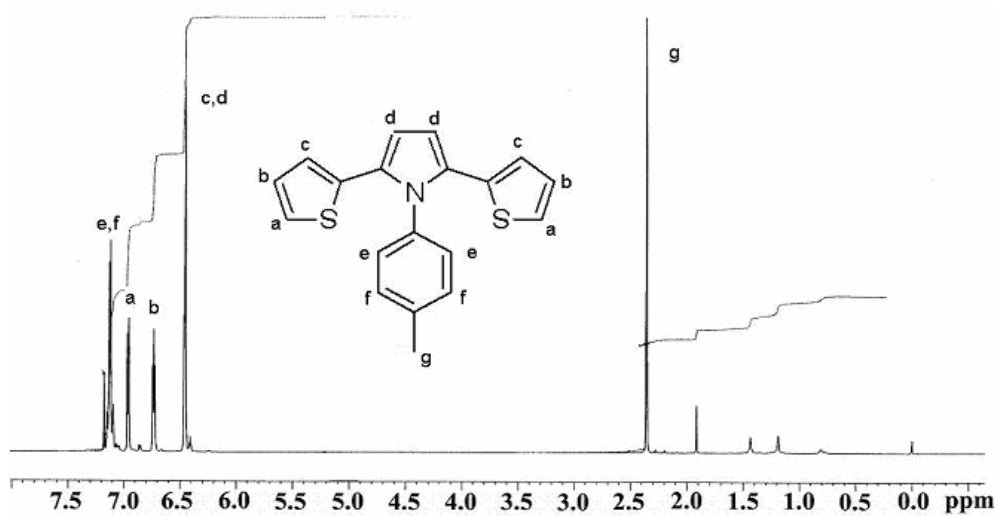


Figure 3.1 $^1\text{H-NMR}$ spectrum of the monomer.

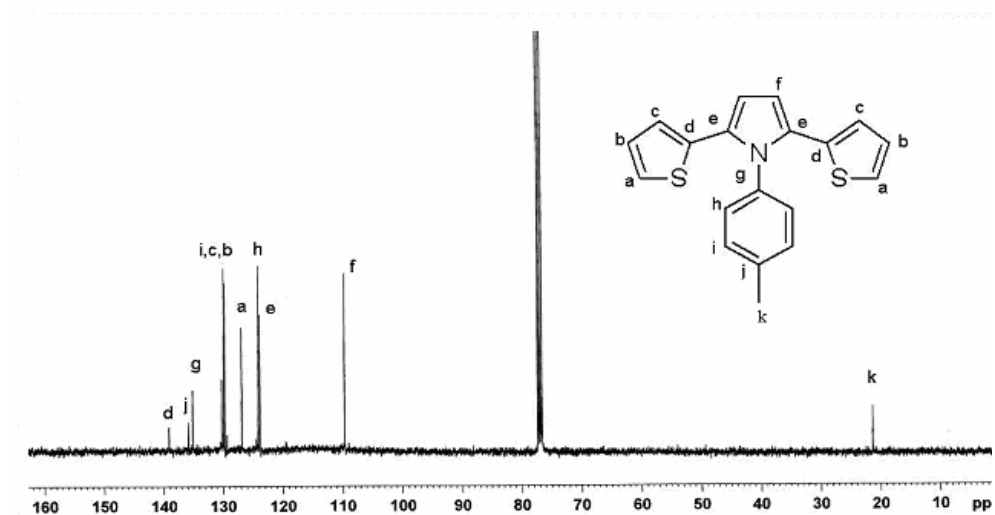


Figure 3.2 $^{13}\text{C-NMR}$ spectrum of the monomer.

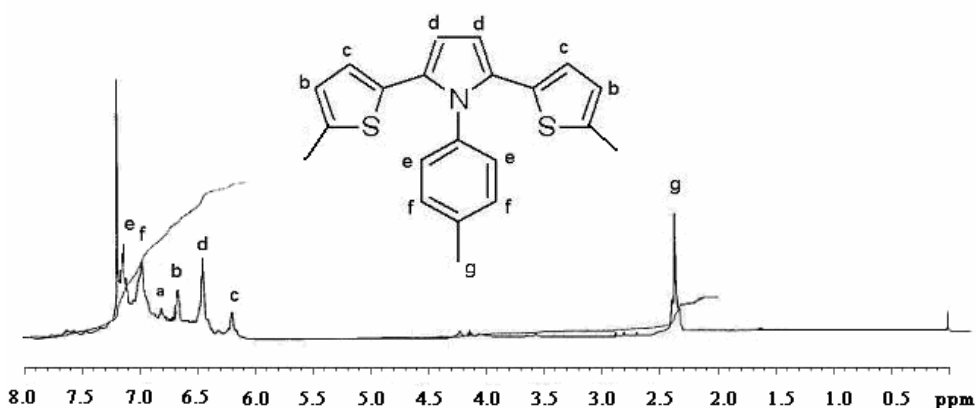


Figure 3.3 $^1\text{H-NMR}$ spectrum of the chemically synthesized P(DTTP).

3.2. FTIR Spectra

FTIR spectrum (Fig. 3.4a) of the DTTP indicated the following absorption peaks: 3033 cm^{-1} (C-H_α stretching of thiophene), 3099 cm^{-1} (aromatic C-H), 2926 cm^{-1} (aliphatic C-H), $1491\text{-}1350\text{ cm}^{-1}$ (aromatic C=C , C-N stretching due to pyrrole and benzene), 1043 cm^{-1} (C-H in plane bending of benzene), 765 cm^{-1} (C-H_α out of plane bending of thiophene) and 685 cm^{-1} (para- methyl substituted benzene).

FTIR spectra (Fig. 3.4b) of electrochemically synthesized P(DTTP) showed characteristic peaks of the monomer, such as aliphatic C-H (belonging to methyl group attached to benzene) at 2923 cm^{-1} . The peaks related to C-H_α stretching of thiophene disappeared completely. The new broad band at around 1428 cm^{-1} was due to polyconjugation. The strong absorption peak at 1109 and 636 cm^{-1} were attributed to the incorporation ClO_4^- ions into the polymer film during doping process. Results of the FTIR studies clearly indicated the polymerization of the monomer.

Most of the discriminative peaks of the monomer DTTP remained unvaried upon chemical polymerization. (Fig. 3.4c) The intensity absorption bands of the

monomer at 3033 cm^{-1} and 765 cm^{-1} due to C-H_α stretching of thiophene moiety disappeared entirely. This is the confirmation of the polymerization through 2,5 positions of thiophene moiety of the monomer. Formation of a new band related to polyconjugation appearing at 1605 cm^{-1} is also a good evidence of polymerization. The new peaks at 581 cm^{-1} denotes the presence of the dopant ion (Cl^-).

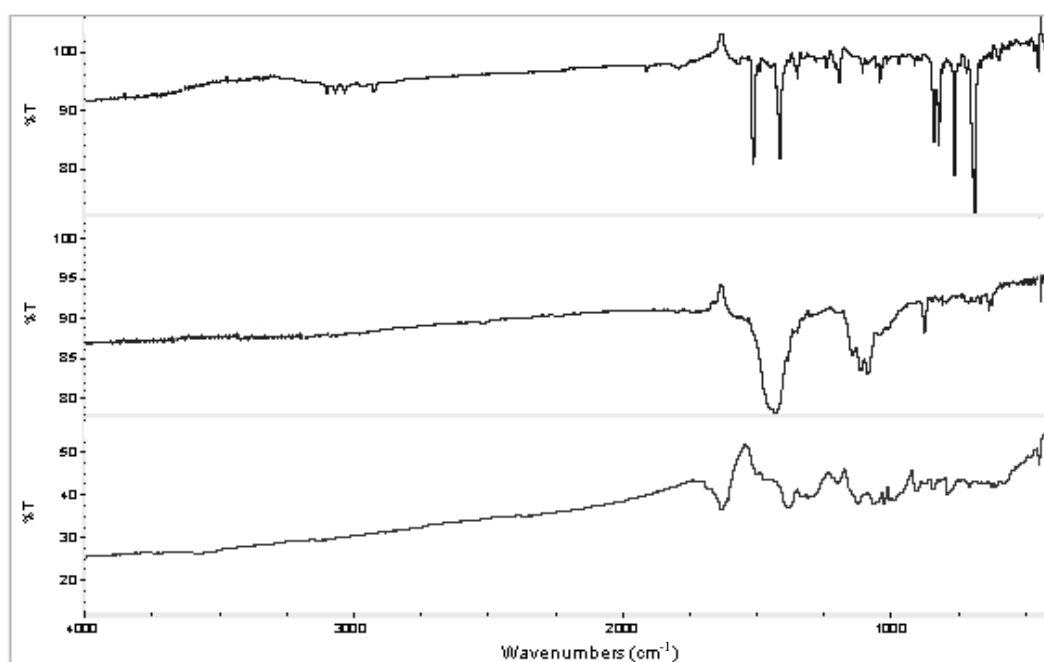


Figure 3.4 FTIR spectra of (a) DTTP, (b) electrochemically synthesized P(DTTP), and (c) chemically synthesized P(DTTP).

FTIR spectrum (Fig. 3.5) of electrochemically synthesized P(DTTP-co-EDOT) showed the characteristic peaks of the monomer. The peak at 1512 cm^{-1} was due to conjugated cyclic C=N stretching, the peak at 980 cm^{-1} and 847 cm^{-1} was due to 1,2,5 trisubstituted pyrrole and 2,5 disubstitue thiophene, respectively. The strong peak at 1073 cm^{-1} was CH_3 rocking vibration of CH_3 bonded to benzene ring. The peaks related to C-H_α stretching of thiophene disappeared completely. On the other hand, evolution of a new peak was observed at 1354 cm^{-1} , which is attributed to the

aromatic ethylene dioxy group belong to EDOT. The strong absorption peak at 1197 cm^{-1} was attributed to the incorporation of ClO_4^- ions into the polymer film during doping process. Results of the FTIR studies clearly indicated the copolymerization of the DTTP with EDOT.

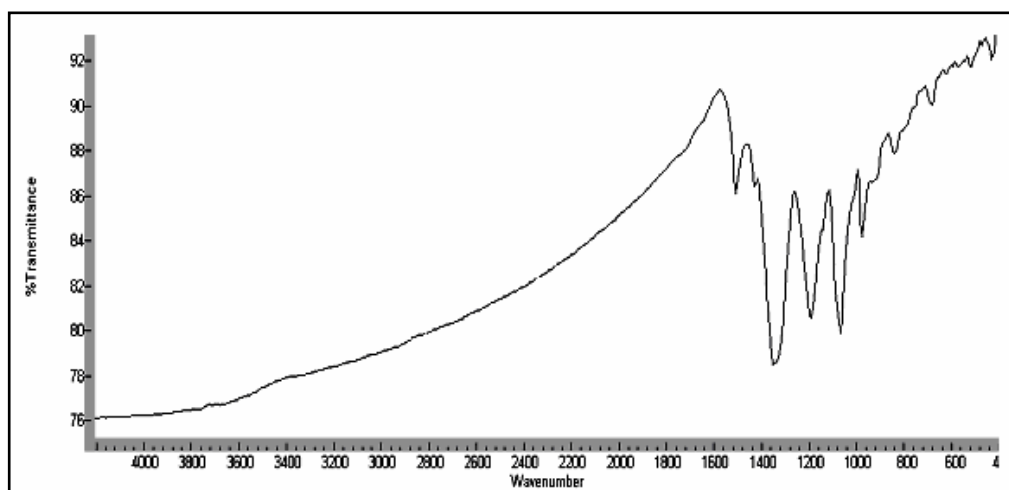


Figure 3.5 FTIR spectrum of P(DTTP-co-EDOT).

3.3. Cyclic Voltammograms

Cyclic voltammetry experiments were carried out in $\text{ACN}/\text{NaClO}_4/\text{LiClO}_4$ solvent electrolyte system on bare Pt electrode with a 500 mV/s scan rate. Homopolymer of DTTP in acetonitrile indicated an oxidation peak at +0.43 V and a reduction peak at +0.30 V, which implies the electroactivity of P(DTTP). On the other hand, with increasing scan number, a decrease at +0.57 V was due to the monomer consumption in diffusion layer. When the range between 0.00 V to +1.00 V (Fig. 3.6) was swept, it was observed that the electroactivity increases with increasing scan number and neutral linear oligomers partially dissolves in medium.

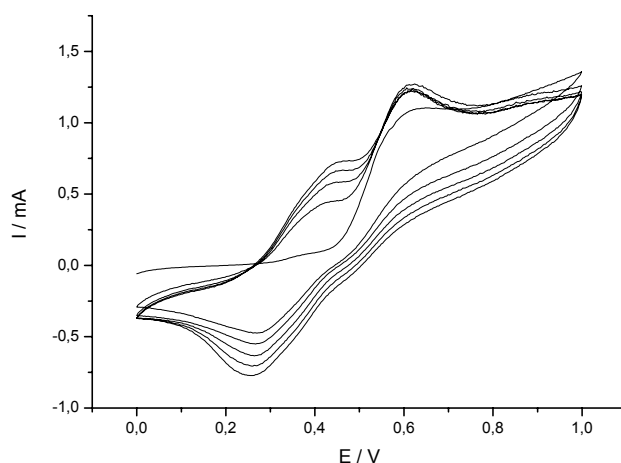


Figure 3.6 Cyclic Voltammogram of P(DTTP).

The redox behavior and the increments between consecutive cycles of DTTP in the presence of EDOT ($E_{p,a}$: -1.00 V and $E_{p,c}$: -0.21 V with scan rate 500 mV/s.) were completely different than that of P(DTTP) and PEDOT. This is an indication of reaction and formation of copolymer between DTTP and EDOT. The quality of film coated on Pt electrode during copolymerization were better than P(DTTP), since the polymer chain were growing steadily without getting dissolved partially in the medium. Figure 3.7b shows the redox behavior of DTTP in the presence of EDOT and of pure PEDOT. Pure EDOT in ACN/LiClO₄(0.1 M)/NaClO₄(0.1 M) reveals an oxidation peak at -0.17 V and a reduction peak at -0.88 V (Figure 3.7a) with a scan rate 500 mV/s.

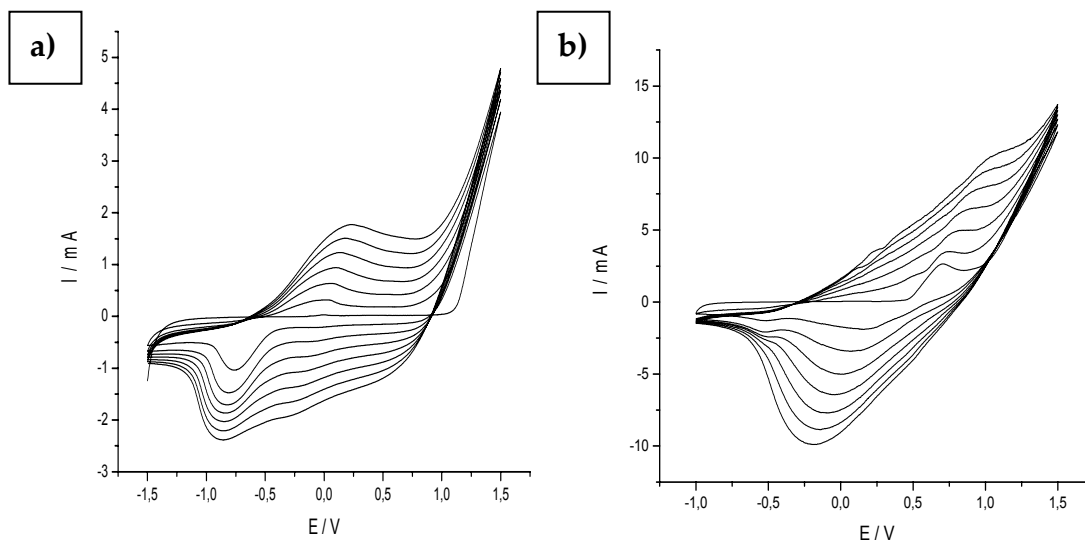


Figure 3.7 Cyclic Voltammograms of (a) pure PEDOT, (b) DTTP in the presence of EDOT, P(DTTP-co-EDOT).

3.4 Conductivities

The conductivities (Table 3.1) of electrochemically and chemically prepared P(DTTP) were measured as $1.07 \times 10^{-3} \text{ S.cm}^{-1}$ and $1 \times 10^{-3} \text{ S.cm}^{-1}$ respectively via four probe technique at room temperature. It is observed that the conductivity increased 10 orders of magnitude upon copolymerization due to increase in conjugation through DTTP and EDOT.

Table 3.1 Conductivities of P(DTTP) and P(DTTP-co-EDOT)

| Sample | Conductivity (S/cm) | |
|------------------------|----------------------------|-----------------------------------|
| | <i>Chemically Prepared</i> | <i>Electrochemically Prepared</i> |
| P(DTTP) | 1.07×10^{-3} | 1×10^{-3} |
| P(DTTP-co-EDOT) | 1.1×10^{-2} | |
| PEDOT | 1.0×10^{-2} | |

3.5 Morphologies of Films

Surface morphologies of P(DTTP), P(DTTP-co-EDOT) and PEDOT were examined by employing Scanning Electron Microscope. SEM micrograph of polymers designates the excellence of their film formation ability.

Spheroids like droplets were observed on the solution side of P(DTTP) film (Fig. 3.8a). The film also exhibited homogeneous and compact structure. As far as the SEM micrograph of copolymer of DTTP with EDOT is concerned (Fig. 3.8c), the solution side of copolymer film differs from SEM micrograph of PEDOT (Fig. 3.8b) and P(DTTP), considerably. At the solution side of P(DTTP-co-EDOT), popcorn-like structures were observed. The topology of PEDOT reveals globules.

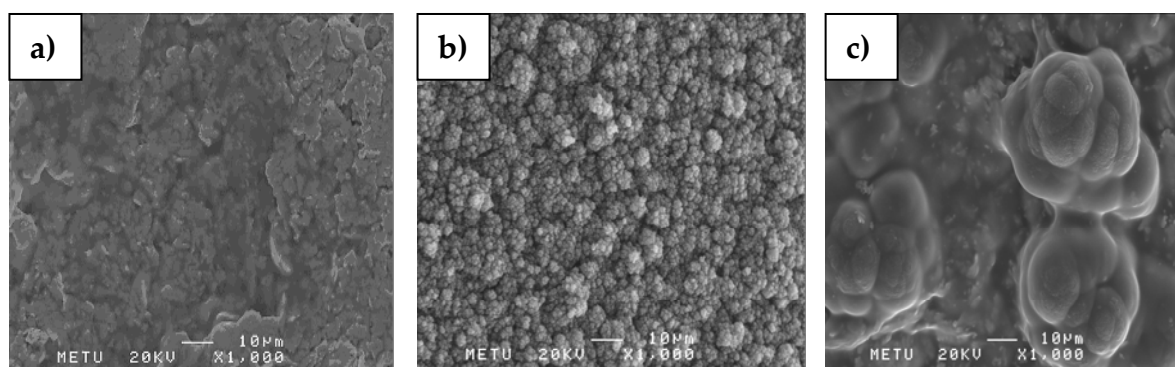


Figure 3.8 SEM micrographs of (a) solution side of P(DTTP), (b) solution side of PEDOT (c) solution side of P(DTTP-co-EDOT).

3.6 Gel Permeation Chromatography (GPC)

The weight average and number average molecular weight of chemically synthesized P(DTTP) were determined by GPC. The polydispersity (M_w/M_n) of P(DTTP) was found as 1.08 which means all polymer chain have almost same

number of repeating units. The number of repeating unit is determined as 8. The results of GPC studies are given in Table 3.2.

Table 3.2. GPC Results.

| | |
|----------------------|---------------------------|
| M₀ | 223 g/mol |
| M_n | 2.5x10 ³ g/mol |
| M_w | 2.7x10 ³ g/mol |
| PD | 1.08 |

3.7. Investigation of Electrochromic Properties of Polymers

3.7.1 Spectroelectrochemistry

Spectroelectrochemistry is the best way of examining the changes in optical properties of a polymer on ITO upon applied potentials. It also provides information on the properties of conjugated polymers, such as band gap (E_g) and the intergap states that appear upon doping. P(DTTP) film was potentiodynamically synthesized on ITO electrode in the presence of 0.01 M DTTP, sweeping the potential between 0.0 V and 1.0 V in the presence of ACN/ NaClO₄/LiClO₄ (0.1 M) solvent-electrolyte couple.

Spectroelectrochemical studies of the resulting homopolymer were carried out sweeping the potentials from 0.0 V to 0.6 V in the monomer free ACN/ NaClO₄/LiClO₄ (0.1 M) solution. The wavelength at which homopolymer shows π - π^* transition is defined as the maximum wavelength (λ_{max}) which was 428 nm for the homopolymer at 0.0 V. The band gap (E_g) was calculated as 2.14 eV. As the potential was varied, a decrease in the intensity of π - π^* transition and new bands

related to charge carriers were observed. Thus, appearance of a peak around 620 nm is attributed to the evolution of polaron band (Fig. 3.9).

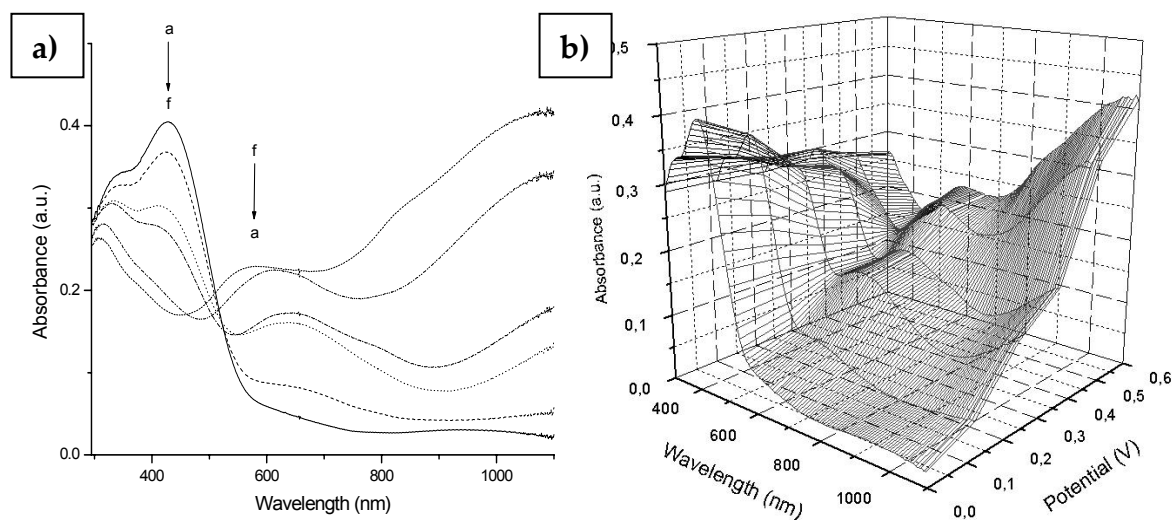


Figure 3.9 (a) 2D Spectroelectrochemical spectrum of P(DTTP) with applied potentials between 0.0 and +0.6 V in ACN/NaClO₄/LiClO₄ (0.1 M); (a) 0.0 V, (b) +0.2 V, (c) +0.3V, (d) 0.4 V, (e) 0.5 V, (f) 0.6 V. (b) 3D Spectroelectrochemical spectrum of P(DTTP) with applied potentials between 0.0 and +0.6 V in ACN/NaClO₄/LiClO₄ (0.1 M).

P(DTTP-co-EDOT) coated ITO was swept between 0.0 V and -0.8 V in a monomer free ACN/NaClO₄/LiClO₄ (0.1 M) solution. The λ_{\max} value for the π - π^* transition in neutral state at 0.0 V was found to be 448 nm and the electronic band gap (E_g) was calculated as 1.8 eV at λ_{\max} (Fig. 3.10). As the copolymer gets oxidized, the intensity of the π - π^* transition decreases while the charge carrier bands at longer wavelengths increases in intensity. Polaron band between 600 nm and 1000 nm and bipolaron band beyond 1000 nm are observed.

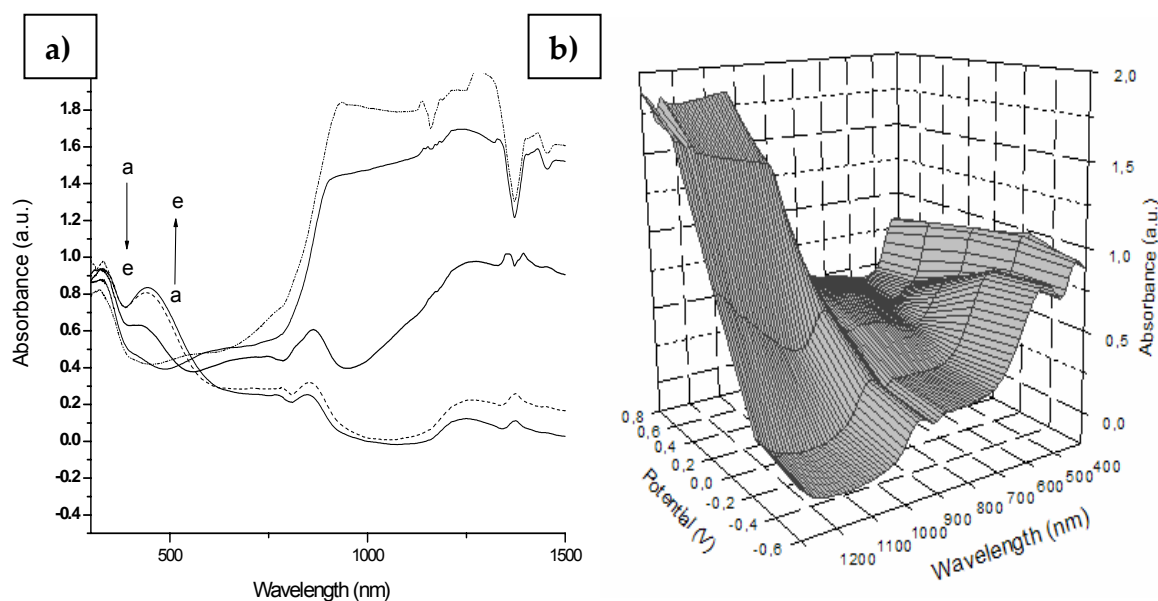


Figure 3.10 (a) 2D Spectroelectrochemical spectrum of P(DTTP-co-EDOT) with applied potentials between -0.6 V and +0.8 V in ACN/NaClO₄/LiClO₄ (0.1 M), a) - 0.6 V, (b) 0.0 V, (c) +0.4 V, (d) 0.6 V, (e) 0.8 V. (b) 3D Spectroelectrochemical spectrum of P(DTTP-co-EDOT) with applied potentials between -0.6 and +0.8 V in ACN/NaClO₄/LiClO₄ (0.1 M).

3.7.2 Electrochromic Switching

For electrochromic applications, the ability of a polymer to switch immediately and exhibit a noteworthy color change is significant. Electrochromic switching studies can supervise these types of properties.

The experiments carried out by spectroelectrochemistry shows the ability of P(DTTP) to switch between its neutral and doped states with a change in transmittance at a fixed wavelength. During the experiment, the % transmittance (%T) at 428 nm of the polymer is measured using a UV-Vis spectrophotometer. The polymer films were synthesized on ITO-coated glass slides. The %T of P(DTTP) was then monitored at λ_{\max} (428 nm) while the polymer was switched between 0.0 V and

+0.6 V. The contrast is measured as the difference between %T in the reduced and oxidized forms and noted as 10 %T at 428 nm. As seen in Fig. 3.11, homopolymer has reasonable stability and switching time (less than 2 sec.).

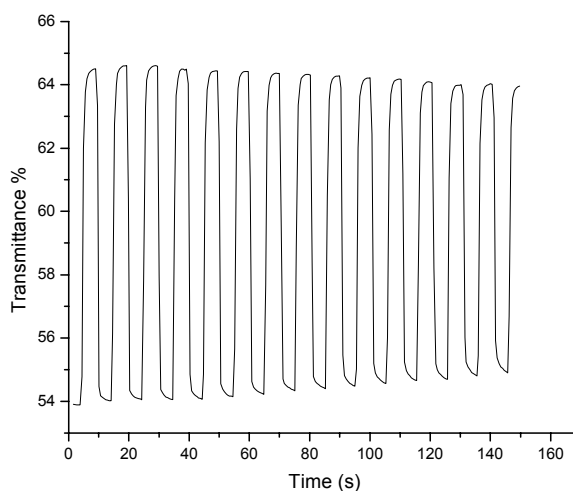


Figure 3.11 Electrochromic switching, optical absorbance change monitored at 428 nm for P(DTTP) between 0.0 V and 0.6 V.

Experiments for P(DTTP-co-EDOT) were carried out at 448 nm via switching the potential between -0.6 V and +0.8 V with a residence time of 5 seconds. Optical contrast and the time needed to reach 95% of the total transmittance change for the copolymers were found to have 10 % optical contrast with a switching time of 2.0 s. (Fig. 3.12)

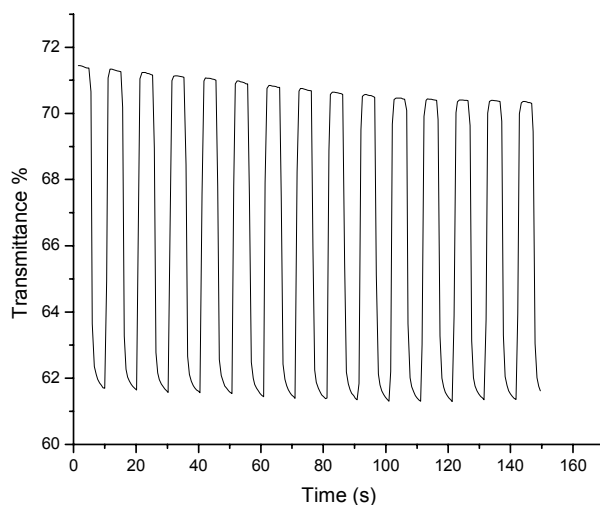


Figure 3.12 Electrochromic switching, optical absorbance change monitored at 448 nm for P(DTTP-co-EDOT) between -0.6V and +0.8 V.

3.7.3 Colorimetry of Polymers

L^*a^*b values of the films were measured at the fully oxidized and reduced states and the results were recorded in Table 3.3. The P(DTTP) film was yellow (0.0 V) in the reduced state and gray (0.6 V) in the oxidized state.

The P(DTTP-co-EDOT) film switches between blue color (in the oxidized state) and red color (in the reduced state). L^*a^*b values of the films were measured at the fully oxidized and the fully reduced states in addition to a state in between and the results were recorded in Table 3.4. Upon stepwise increase of the applied potential from -0.6 V to +0.8 V, alternations of the three different colors were observed, red, green and blue. In all copolymer compositions, the films pass from a green intermediate state to a blue fully oxidized state [67].

Table 3.3 Electrochromic properties of P(DTTP)

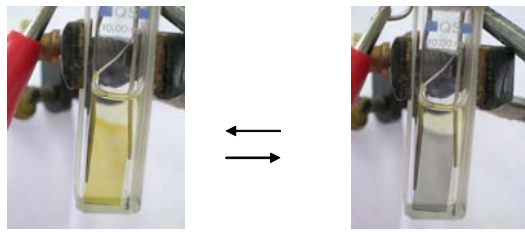
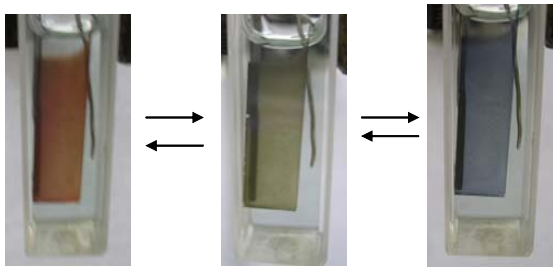
| | | | | | | | | |
|---|---------|---------|-------|-------|--------|-------|-------|--------|
|  | | | | | | | | |
| <table border="0"> <tr> <td>(0.0 V)</td> <td>(0.6 V)</td> </tr> <tr> <td>L= 79</td> <td>L= 57</td> </tr> <tr> <td>a= -10</td> <td>a= -5</td> </tr> <tr> <td>b= 59</td> <td>b= -14</td> </tr> </table> | (0.0 V) | (0.6 V) | L= 79 | L= 57 | a= -10 | a= -5 | b= 59 | b= -14 |
| (0.0 V) | (0.6 V) | | | | | | | |
| L= 79 | L= 57 | | | | | | | |
| a= -10 | a= -5 | | | | | | | |
| b= 59 | b= -14 | | | | | | | |

Table 3.4 Electrochromic properties of P(DTTP-co-EDOT)

| | | | | | | | | | | | | |
|---|----------|---------|---------|--------|-------|-------|-------|-------|------|-------|-------|--------|
|  | | | | | | | | | | | | |
| <table border="0"> <tr> <td>(-0.6 V)</td> <td>(0.2 V)</td> <td>(0.8 V)</td> </tr> <tr> <td>L = 33</td> <td>L= 62</td> <td>L= 34</td> </tr> <tr> <td>a= 24</td> <td>a= -6</td> <td>a= 2</td> </tr> <tr> <td>b= 21</td> <td>b= 26</td> <td>b= -21</td> </tr> </table> | (-0.6 V) | (0.2 V) | (0.8 V) | L = 33 | L= 62 | L= 34 | a= 24 | a= -6 | a= 2 | b= 21 | b= 26 | b= -21 |
| (-0.6 V) | (0.2 V) | (0.8 V) | | | | | | | | | | |
| L = 33 | L= 62 | L= 34 | | | | | | | | | | |
| a= 24 | a= -6 | a= 2 | | | | | | | | | | |
| b= 21 | b= 26 | b= -21 | | | | | | | | | | |

3.8 Characterization of Electrochromic Devices (ECDs)

3.8.1 Spectroelectrochemistry of ECDs

ECD were assembled with a configuration of ITO/P(DTTP) || gel electrolyte || PEDOT/ITO and its characteristics were examined. Fig. 3.13 exhibits spectroelectrochemical UV-Vis transmittance of electrochromic device of P(DTTP)/PEDOT under miscellaneous applied potentials between -0.6 V and +1.6 V. Maximum absorption at 431 nm revealing yellow color was observed due to π - π^* transition upon application of negative voltages. At that state, PEDOT did not show an obvious absorption at the UV-Vis region of the spectrum and device revealed yellow color. When the applied potential increased, due to reduction of PEDOT layer, blue color became dominant and a new absorption was observed at 617 nm.

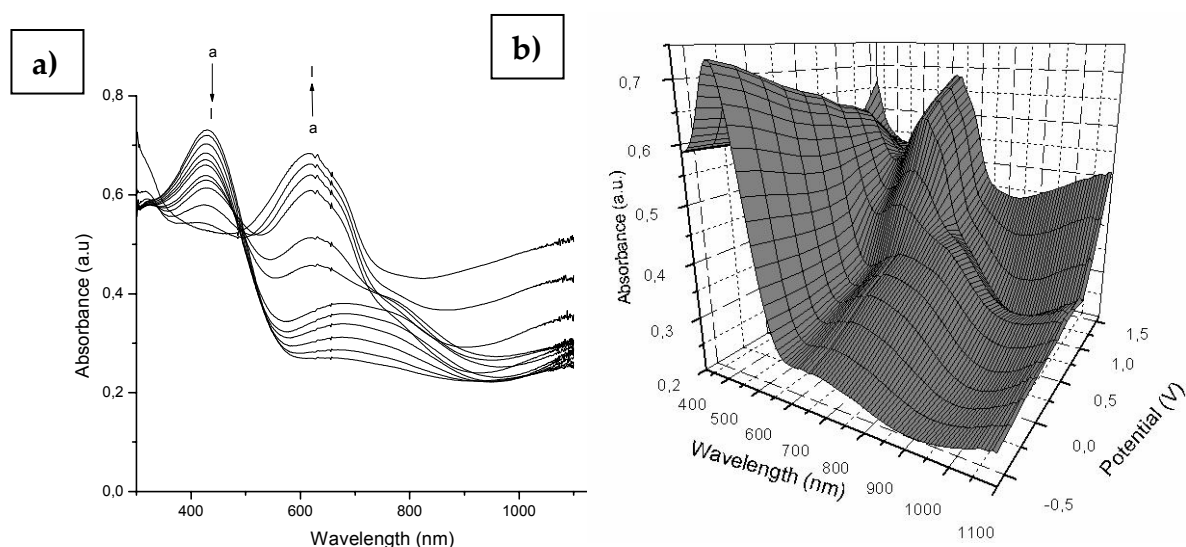


Figure 3.13. (a) 2D Spectroelectrochemical spectrum of the device with applied potentials between -0.6 and +1.6 V (a) -0.6 V, (b) -0.4 V, (c) -0.2 V, (d) 0.0 V, (e) .2 V, (f) 0.4 V, (g) 0.6 V, (h) 0.8 V, (i) 1.0 V, (j) 1.2 V, (k) 1.4 V, (l) 1.6
(b) 3D Spectroelectrochemical spectrum of the device with applied potentials between -0.6 and +1.6 V.

The same configuration was used to assemble ECD for copolymer ITO/P(DTTP-co-EDOT) || gel electrolyte || PEDOT/ITO. Fig. 3.14 shows the spectroelectrochemical spectrum of P(DTTP-co-EDOT)/ PEDOT device at voltages varying between -0.6 V and 2.0 V. When a voltage of -0.6 V applied to P(DTTP-co-EDOT) layer, the copolymer was in its neutral state with the interband π - π^* transition at 448 nm and PEDOT layer is in its oxidized state revealing a transparent color. A new π - π^* transition was observed at 615 nm due to the π - π^* transition of PEDOT in its reduced state while the intensity of π - π^* transition peak of anodically coloring P(DTTP-co-EDOT) was decreasing.

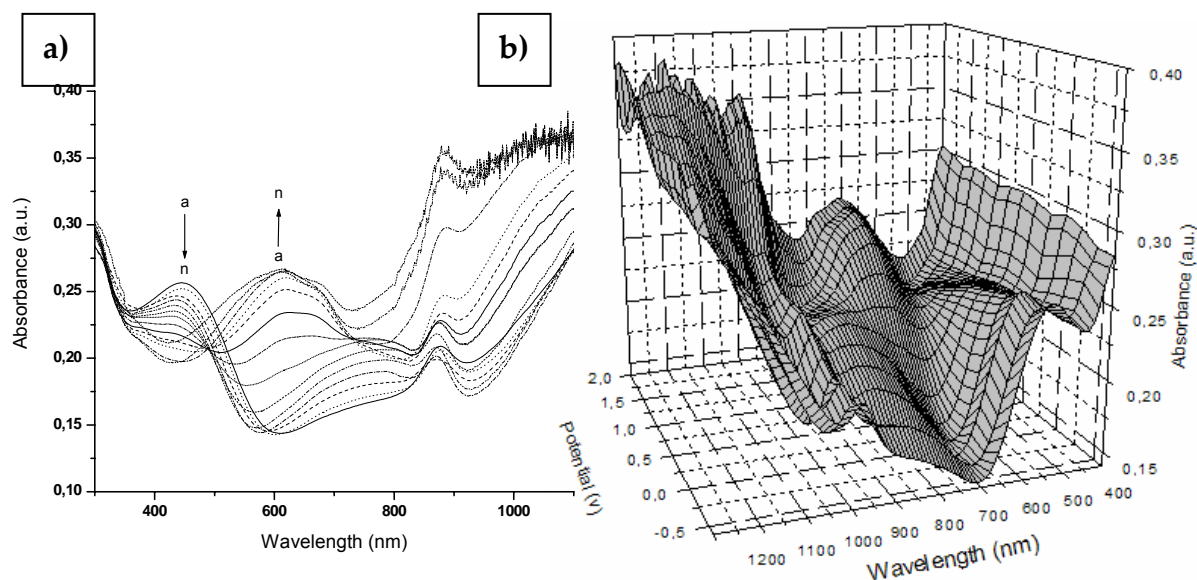


Figure 3.14 (a) 2D Spectroelectrochemical spectrum of the device with applied potentials between -0.6 and +1.6 V (a) -0.6 V, (b) -0.4 V, (c) -0.2 V, (d) 0.0 V, (e) .2 V, (f) 0.4 V, (g) 0.6 V, (h) 0.8 V, (i) 1.0 V, (j) 1.2 V, (k) 1.4 V, (l) 1.6
(b) 3D Spectroelectrochemical spectrum of the device with applied potentials between -0.6 and +1.6 V.

3.8.2 Switching of ECDs

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

Switching square wave potentials between -0.6 and $+1.6$ V with a residence time of 5 s, the optical contrast (ΔT %) at 617 nm were found 29% with 1.5 s switching time by UV-Vis spectrophotometer (Fig. 3.15).

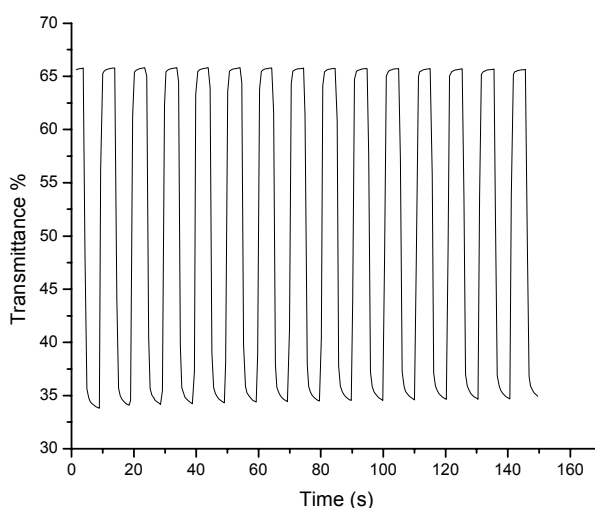


Figure 3.15 Electrochromic switching, optical absorbance change monitored at 617 nm for device between -0.6 V and 1.6 V.

Switching properties and optical contrast (ΔT %) of P(DTTP-co-EDOT)/PEDOT device at the wavelength of maximum contrast (448 nm and 615 nm) were measured (Fig 3.16). Switching square wave potentials between -0.6 and $+2.0$ V with a residence time of 5 s, the optical contrast (ΔT %) at 448 nm were found as 9% and it is calculated that the ECD switches rapidly in about 1 s to reach 95% of

the total transmission change. The optical contrast (ΔT %) at 615 nm was found to be 18 % and time required to reach 95% of the ultimate T was 1.5 s.

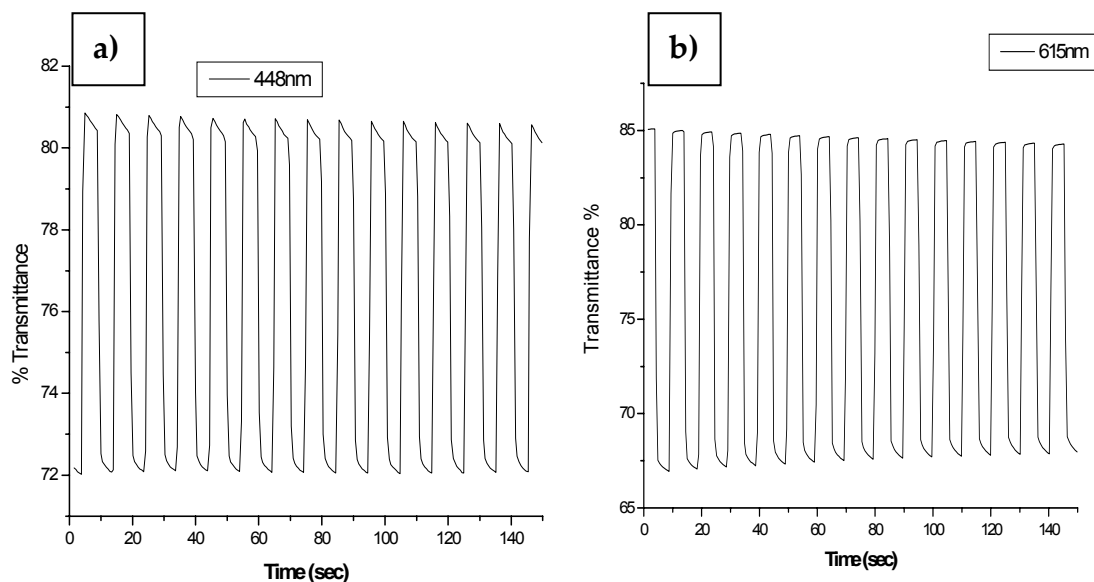




Figure 3.16 Electrochromic switching, optical absorbance change monitored at 448 and 615 nm for device between -0.6 V and 2.0 V.

3.8.3 Colorimetry of ECDs




L, a, b values of the ECDs were measured at the fully oxidized and the fully reduced states of devices and the results were recorded. The P(DTTP)/PEDOT ECD was yellow-green at -0.6 V when the P(DTTP) layer was in its reduced and PEDOT was in its oxidized state. Blue color was observed at 1.6 V when PEDOT was in its reduced state and P(DTTP) layer in its oxidized state. L, a, b values of P(DTTP)/PEDOT ECD are given in Table 3.5.

Table 3.5 Electrochromic properties of P(DTTP)/PEDOT ECD

| | |
|---|--|
|  |  |
| -0.6 V | 1.6 V |
| L= 46 | L= 42 |
| a= -20 | a= -6 |
| b= 37 | b= -25 |

The P(DTTP-co-EDOT)/PEDOT ECD was red-brown at -0.6 V when the P(DTTP-co-EDOT) layer was in its reduced and PEDOT was in its oxidized state (transparent). Blue color was observed at 2.0 V when PEDOT was in its reduced state and P(DTTP-co-EDOT) layer in its oxidized state. At 0.2 V intermediate green state was observed [67]. L, a, b values of P(DTTP-co-EDOT)/PEDOT ECD are given in Table 3.6.

Table 3.6 Electrochromic properties of P(DTTP-co-EDOT)/PEDOT ECD

| | | |
|---|---|---|
|  |  |  |
| -0.6 V | 0.2 V | 2.0 V |
| L= 37 | L= 35 | L= 27 |
| a= 12 | a= -15 | a= -3 |
| b= 18 | b= 21 | b= 30 |

3.8.4 Open Circuit Stability

The optical memory of an electrochromic material is defined as the time elapsed during which this material retains its color without applying potential [68]. The color persistence in the electrochromic devices is an important feature since it is directly related to aspects involved in its maintenance without decomposition and energy consumption during use [69].

Open circuit memory of P(DTTP)/PEDOT ECD was monitored simultaneously at 617 nm ($0.0 \pm 1.6V$, green/blue-colored state, respectively) by applying potential for one second for each 200 seconds time interval. As seen in Fig. 3.17. P(DTTP)/PEDOT device shows quite good optical memories both in oxidized state (with only 1% transmittance change) and reduced state (with almost no transmittance change).

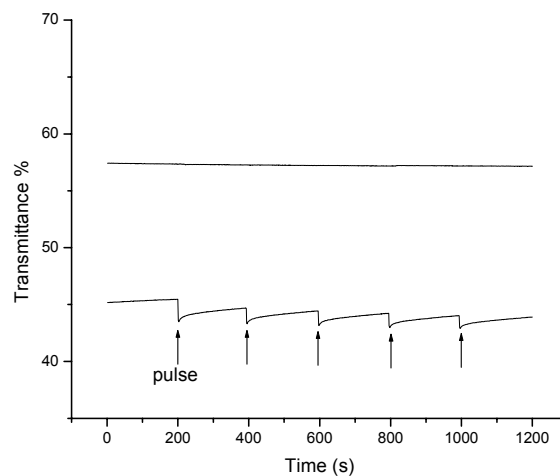


Figure 3.17 Open circuit memory of P(DTTP)/PEDOT ECD monitored at 0.0 V and +1.6 V potentials applied for one second for every 200 seconds time interval.

The optical spectrum for P(DTTP-co-EDOT)/PEDOT ECD was monitored at 448 nm and 615 nm as a function of time at -0.6 V and 2.0 V by applying potential for one second for each 200 seconds time interval,. As seen in Fig. 3.18b P(DTTP-co-EDOT)/PEDOT device shows quite good optical memories both in oxidized (with only 1% transmittance change) and reduced states (with almost no transmittance change) at 615 nm. It is observed that the transmittance of the red-brown state of the P(DTTP-co-EDOT)/PEDOT device is highly stable at 448 nm while blue state exhibits a 3 %T loss.

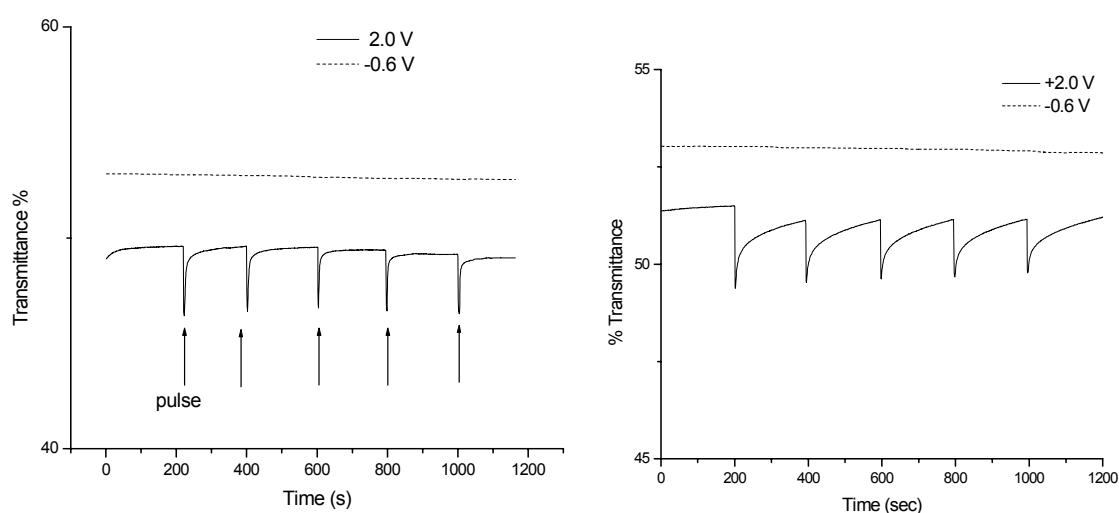


Figure 3.18 Open circuit memory of P(DTTP-co-EDOT)/PEDOT ECD monitored at -0.6 V and +2.0 V potentials at a) 448 nm and b) 615 nm.

3.8.5 Stability of the ECDs

Cyclic voltammetry is employed by monitoring current change to figure out the long-term stability for devices. Cyclic voltammetry studies showed that the electrochromic devices perfectly operated with applied voltages of -0.6V and +1.6 V with 500 mV/s scan rate under atmospheric conditions. Fig. 3.19 shows that

P(DTTP)/PEDOT device could be repeatedly switched up to 1000 cycles retaining 83% of its electroactivity.

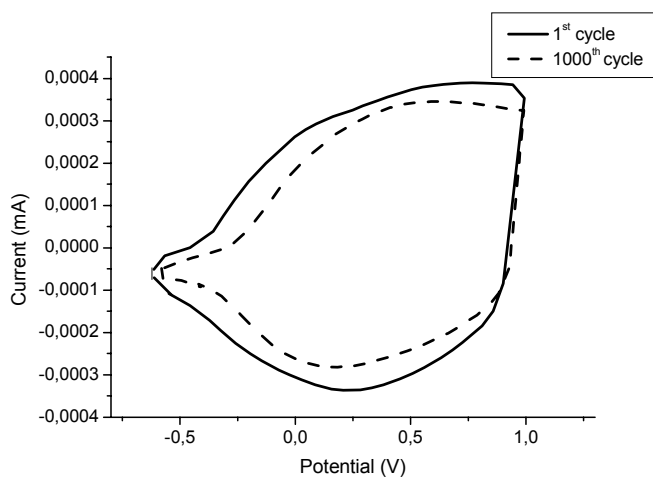


Figure 3.19. Cyclic voltammogram of the P(DTTP)/PEDOT device as a function of repeated scans 500 mV/s: after 1st cycle (plain), after 1000 cycles (dash).

The stability measurements for P(DTTP-co-EDOT)/PEDOT device were also carried out by cyclic voltammetry. The device was subjected to -1.0 V and +1.5 V with 500 mV/s scan rate under atmospheric conditions. The results (Fig. 3.20) show that P(DTTP-co-EDOT)/PEDOT ECD could be repeatedly switched up to 1000 cycles retaining 75 % of its electroactivity.

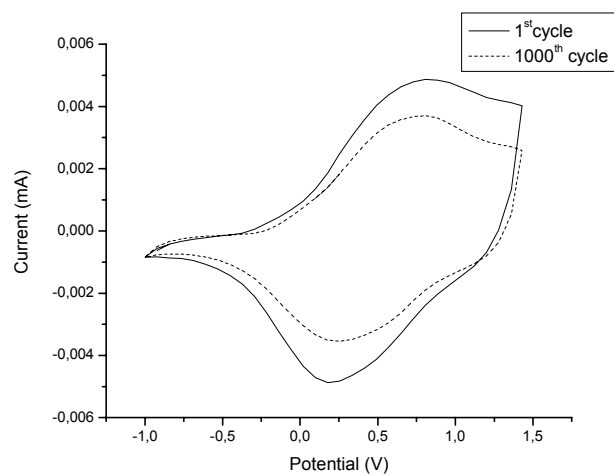


Figure 3.20 Cyclic voltammogram of P(DTTP-co-EDOT)/PEDOT device as a function of repeated scans 500 mV/s: after 1st cycle (plain), after 1000 cycles (dash).

CHAPTER IV

CONCLUSION

Synthesis of a novel full conjugated monomer, 2,5-di(thiophen-2-yl)-1-p-tolyl-1H-pyrrole (DTTP) was successfully accomplished. Oxidative polymerization was achieved via both electrochemical and chemical methods. Soluble P(DTTP) obtained by chemical polymerization method was characterized by NMR and GPC. Conducting copolymer of DTTP with EDOT was synthesized electrochemically. Cyclic voltammetry studies showed the electroactivity of DTTP. Copolymers P(DTTP-co-EDOT) revealed different redox behavior than that of both monomers and pure EDOT. Copolymerization was also proved by FTIR and SEM studies. They were found to have reasonable conductivities. Spectroelectrochemical analyses revealed that P(DTTP) and P(DTTP-co-EDOT) can be switched between their fully oxidized and fully reduced states with distinct color changes. Spectroelectrochemistry experiments showed that π to π^* transition occurs at 428 nm with a band gap 2.4 eV, for P(DTTP) on the other hand λ_{max} for P(TTMT-co-Py) was found as 448 nm and the band gap was calculated as 1.8 eV. Electrochromic investigations showed that P(DTTP) switches between greenish yellow and blue while P(DTTP-co-EDOT) was found to be multichromic material switching between red, yellow and blue.

Dual-type P(DTTP)/PEDOT and P(DTTP-co-EDOT)/PEDOT electrochromic devices were assembled with a configuration ITO coated glass/anodically coloring polymer ||gel electrolyte||cathodically coloring polymer (PEDOT)/ITO coated glass. The color of P(DTTP) device changed between greenish yellow and blue upon applied potential, while color of P(DTTP-co-EDOT) device can be changed between red, green and blue. Spectroelectrochemistry, electrochromic switching and open circuit stability of the devices were studied. ECDs were found to have reasonable switching times, contrasts and optical memories. Considering these results, P(DTTP) and P(DTTP-co-EDOT) are promising candidates for electrochromic layers in ECDs.

REFERENCES

- [1] H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, A. J. Heeger, *J. Chem. Soc. Chem. Commun.* (1977) 578.
- [2] C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger, and H. Shirakawa, E. J. Louis, S. C. Gau, A. G. Macdiarmid, *Phys. Rev. Letters*, 39 (1977) 1098.
- [3] M. Hatano, S. Kambara, S. Okamoto, *J. Polym. Sci.*, 51 (1961) S26.
- [4] V.V. Walatka, M. M. Labes, J. H. Perlstein, *Phys. Rev. Lett.*, 31 (1973) 1139.
- [5] H. Shirakawa, in *Handbook of Conducting Polymers*, 2nd ed.; T.A. Skotheim, R.L. Elsenbaumer, J.R. Reynolds, Eds.; Marcel Dekker: New York, 1998, pp.197-208.
- [6] A. F. Diaz, K. K. Kanazawa, G.P. Gardini, *J. Chem. Soc., Chem. Commun.*, (1979) 635.
- [7] K. Kaneto, K. Yoshino, Y. Inushi, *Solid State Comm.*, 46 (1983) 389.
- [8] A. G. MacDiarmid, J. C. Chiang, A. F. Richter, A. J. Epstein, *Synth Met.*, 18 (1987) 285.
- [9] P. Kovacic, A. Kyriakis, *J. Am. Chem. Soc.*, 85 (1963) 454.
- [10] G.E. Wnek, J.C. Chine, F.E. Karasz, C.P. Lillya, *Polymer* 20 (1979) 1441.

- [11] L. B. Gronendaal, F. Jonas, D. Freitag, H. Pielartzik, J. R. Reynolds, *Adv.Mater*, 12(7) (2000) 481.
- [12] J. L. Dai, *Rev. Macromol. Chem. Phys.*, C39(2) (1999) 273–387.
- [13] L. Bredas, G. B. Street, *Acc. Chem. Res.*, 18 (1985) 309.
- [14] J. Roncali, P. Blanchard, P. Frere, *J. Mater. Chem.*, 15 (2005) 1589.
- [15] K. Gurunathan, A.V. Murugan, R. Marimuthu, U.P. Mulik, D.P. Amalnerkar, *Mater. Chem. Phys.* 61 (1999) 173.
- [16] A. G. Macdiarmid, *Angew. Chem. Int. Ed.*, 40 (2001) 2581.
- [17] P. J. Nigrey, A. G. MacDiarmid, and A. J. Heeger, *Chem. Commun.*, 96 (1979) 594.
- [18] A. J. Heeger, *Reviews of Modern Physics.*, 73 (2001) 681.
- [19] J. van Hapert, PhD thesis, Utrecht University, 2002.
- [20] D. Kumar, R.C. Sharma, *Eur. Polym. J.*, 34 (1998) 1053
- [21] T. Okada, T. Ogata, M. Ueda, *Macromolecules* 40 (1996) 3963
- [22] G. Zotti, *Handbook of Organic Conductive Molecules and Polymers*, ed. H. S. Nalwa, Wiley, Chichester, 1997, Vol. 2, Ch. 4.
- [23] R. Sugimoto, S. Takeda, H.B. Gu, K. Yoshino, *Chem. Express* 1 (1986) 635.

- [24] N. Toshima, S. Hara, Prog. Polym. Sci. 20 (1995) 155.
- [25] A. Malinauskas, Polymer 42 (2001) 3957.
- [26] J. R.Reynolds, S. G. Hsu, H. J. Arnott, J. Polym. Sci. Pol. 27 (1989) 2081.
- [27] S. Asavapiriyonont, G.K. Chandler, G.A. Gunawardena, D. Pletcher, J. Electroanal. Chem., 177 (1984) 229.
- [28] J. D. Strenger-Smith, Prog. Polym. Sci., 23 (1998) 57.
- [29] Ali Çırpan, Phd Thesis, METU, 2004
- [30] K. Kaeriyama, Handbook of Organic Conductive Molecules and Polymers, ed. H. S. Nalwa, Wiley, Chichester, 1997, Vol. 2, Ch. 3.
- [31] J. Roncali, R. Garreau, A. Yassar, P. Marque, F. Garnier, and M. Lemaire J. Phys. Chem.; 91 (1987) 6706 .
- [32] E. Kalaycioğlu, L. Toppare, Y. Yağci, Valeria Harabagiu, Mariana Pintela, Rodinel Ardelean and Bogdan C. Simionescu Synth. Met. 97 (1998)7.
- [33] R. Gumbs, Handbook of Organic Conductive Molecules and Polymers, ed. H. S. Nalwa, Wiley, Chichester, 1997, Vol. 2, Ch. 5
- [34] P. Manisankar, C. Vedhi, G. Selvanathan, R. M. Somasundaram, Chem. Mater., 17 (2005) 1722.
- [35] E. Kalaycioğlu, L. Toppare and Y. Yağci Synth. Met., 108 (2000) 1.

- [36] E. Sahin, P. Camurlu, L. Toppare, V. M. Mercore, I. Cianga, Y. Yağcı J. Electroanal.Chem.,579(2005)189.
- [37] J. Roncali, P. Blanchard, P. Frere J. Mater. Chem., 15 (2005) 1589.
- [38] R. Struè Mpler, J. Glatz-Reichenbac, J. Of Electroceramics 3:4, (1999) 329.
- [39] M. A. DePaoli, R. J. Waltman, A. F. DiazBargon, J. J Chem Soc Chem Commun (1984) 1015.
- [40] S. E Lindsey, G. B Street, Synth Met 85 (1984) 1067.
- [41] S. Yigit, J. Hacaloglu, U.Akbulut, L. Toppare, Synth. Met., 79 (1996) 11.
- [42] E. Sahin, P. Camurlu, L. Toppare Synth. Met., 156 (2006) 124.
- [43] H. Hoppe, T. Glatzel, M. Niggemann, A. Hinsch, , M. Ch. Lux-Steiner, N. S. Sariciftci, Nano Lett., 5 (2005) 269.
- [44] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. MacKay, R. H. Friend, P. L. Burn, A. B. Holmes, Nature 347, (1990) 539.
- [45]A. Star, Y. Lu, K. Bradley, G. Gruner, Nano Lett. 4 (2004) 1587.
- [46] G. Inzelt, M. Pineri, J.W. Schultze, M.A. Vorotyntsev, Electrochim. Acta 45 (2000) 2403.
- [47] J.W. Schultze, H. Karabulut, Electrochim. Acta 50 (2005) 1739.
- [48] S. Wang, E. K. Todd, M. Birau, J. Zhang, X. Wan, Z. Y. Wang, Chem. Mater. 17 (2005) 6388.

- [49] C. G. Granqvist, *Electrochim. Acta* 44 (1999) 3005.
- [50] N. R. de Tacconi, K. Rajeshwar, R. O. Lezna, *Chem. Mater.* (2003), 15(16), 3046-3062.
- [51] U. H. Yildiz, E. Sahin, I. M. Akhmedov, C. Tanyeli, L. Toppare *J. Polym. Sci. Pol. Chem* 44(2006) 2215.
- [52] G. Sönmez, *Chem Commun* 42 (2005) 5251.
- [53] R. J. Mortimer, A. L. Dyer, J. R. Reynolds, *Displays*, 27 (2006) 2.
- [54] A. A. Argun, P.H. Aubert, B. C. Thompson, I. Schwendeman, C. L. Gaupp, J. Hwang, P. Jungseek, J. Nicholas, D. B. Tanner, A. G. MacDiarmid, J. R. Reynolds, *Chem. Mater* 16 (2004) 4401.
- [55] D. Witker, J.R. Reynolds, *Macromolecules*, 383 (2005) 7636.
- [56] U. Bulut, A. Çirpan, *Synth. Met.*, 148 (2005) 65.
- [57] M.A. De Paoli, W. A. Gazotti, *J. Braz. Chem. Soc.*, 13, (2002) 4.
- [58] B. C. Thompson, P. Schottland, K. Zong, J. R. Reynolds *Chem. Mater.* 2000, 12 (2000) 1563.
- [59] H.J. Kooreman, H. Wynberg, *Rec. Trav. Chim. Pays-Bas.* 86 (1967) 37.
- [60] H. Stetter, B. Rajh, *Chem.* 5 (1968) 454.
- [61] J. Kagan , S.K. Arora, *Heterocycles*, 20 (1983) 1941.

- [62] J. Kagan, S.K. Arora, *Heterocycles*, 20 (1983) 1937.
- [63] H. Wynberg,; J. Metselaar, *Synth. Commun.*, 14 (1984) 1.
- [64] W.Y. Leung, E. Legoff, *Synth. Commun.*, 19 (1989) 787.
- [65] A. Merz, F. Ellinger, *Synthesis*, 6 (1991) 463.
- [66] L.H. Chen,; C.Y. Wang, T.M. H. Luo, *Heterocycles*, 38 (1994) 1393.
- [67] C.L. Gaupp, J.R. Reynolds, *Macromolecules* 36 (2003) 6305.
- [68] W.A. Gazotti, J.R.G. Casalbore-Micelli, A. Geri, M.A De-Paoli. *Adv. Mater.* 10 (1998) 60.
- [69] B.C. Thompson, P. Schottland, K. Zong, J.R. Reynolds, *Chem. Mater.* 12 (2000) 1563.