

SYNTHESIS AND CHARACTERIZATION OF POLY(OXALIC ACID
DITHIOPHEN-3-YL METHYL ESTER) AND THIOPHENE ENDED
POLY- ϵ -CAPROLACTONE

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İPEK KERMAN

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Prof. Dr. Canan Özgen
Director

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

Prof. Dr. Hüseyin İşçi
Head of the 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 for the degree of Master of Sciences.

Prof. Dr. Levent Toppare
Supervisor

Examining Committee Members

Prof. Dr. Levent Toppare (METU, CHEM)

Prof. Dr. Jale Hacaloğlu (METU, CHEM)

Prof. Dr. Leyla Aras (METU, CHEM)

Prof. Dr. Ahmet Önal (METU, CHEM)

Prof. Dr. Mustafa Güllü (Ankara Un., CHEM)

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF POLY (OXALIC ACID DITHIOPHEN-3-YL METHYL ESTER) AND THIOPHENE ENDED POLY- ϵ - CAPROLACTONE

Kerman, İpek

M.Sc., Department of Chemistry

Supervisor: Prof. Dr. Levent Toppare

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Synthesis and characterization of thiophene ended poly- ϵ -caprolactone (PCL) and oxalic acid dithiophen-3-yl methyl ester (ODME) and their copolymers with both pyrrole and thiophene were achieved. Chemical structure of the precursor polymer and monomer were investigated. Redox behavior of polymer and monomers were determined by Cyclic Voltammetry (CV). Structural characterization of samples were carried out by ^1H , ^{13}C Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared Spectroscopy (FTIR). Conductivities of the films were measured by using four probe technique. Thermal analyses of conducting copolymers were

investigated via Differential Scanning Calorimetry (DSC) and Thermal Gravimetry Analysis (TGA). The morphologies of the copolymer films were examined by Scanning Electron Microscopy (SEM). Electrochromic and spectroelectrochemical behavior of the copolymers were investigated, and their ability of employment in device construction has been examined.

Keywords: Conducting copolymers, electrochemical polymerization, electrochromic properties, thiophene, pyrrole, electrochromic devices

ÖZ

POLİ (OKSALİK ASİT DİTİYOFEN-3-İL METİL ESTER) VE TİYOFENLE SONLANDIRILMIŞ POLİ-ε-KAPROLAKTONUN SENTEZ VE TANIMLANMASI

Kerman, İpek

Yüksek Lisans, Kimya Bölümü

Tez Yöneticisi: Prof. Dr. Levent Toppare

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Oksalik asit ditiyofen-3-il metil ester (ODME) ve tiyofenle sonlandırılmış poli-ε-kaprolaktonun (PCL), pirol ve tiyofen varlığında kopolimerizasyonu gerçekleştirilmiştir. Öncül monomer ve polimerin kimyasal yapısı incelenmiştir. Polimer, monomer ve kopolimerlerin yükseltgenme-indirgenme davranışları Dönüşümlü Voltametri tekniğiyle belirlenmiştir. Numunelerin yapısal tanımlanması için Nükleer Manyetik Rezonans Spektroskopisi (¹H-NMR ve ¹³C-NMR) ve Fourier Transform Infrared Spektroskopisi (FTIR) kullanılmıştır. Filmlerin iletkenlikleri dört-nokta tekniği ile belirlenmiştir. İletken kopolimerlerin termal analizleri DSC ve TGA ile incelenmiştir. Kopolimer

filmlerinin yüzey yapısı Taramalı Elektron Mikroskopisi (SEM) ile incelenmiştir. Tiyofenli kopolimerlerin elektrokromik ve spektroeletrokimyasal davranışları çalışılmış, ve elektrokromik cihaz yapımında kullanılmaya uygun olup olmadığı incelenmiştir.

Anahtar Kelimeler: İletken polimerler, elektrokimyasal polimerizasyon, elektrokromik özellikler, tiyofen, pirol, elektrokromik cihazlar.

Dedicated to My Family

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LIST OF ABBREVIATIONS

PCL.....	Thiophene ended Poly- ϵ -caprolactone
ODME.....	Oxalic Acid Dithiophen-3-yl Ester
PPy.....	Polypyrrole
PTh.....	Polythiophene
Py	Pyrrole
Th	Thiophene
VB.....	Valence band
CB.....	Conductance band
CV.....	Cyclic Voltammetry
PC.....	Propylene carbonate
PMMA.....	Poly (methyl methacrylate)
ACN	Acetonitrile
DCM.....	Dichloromethane
BFEE.....	Boron trifluoro-diethyl etherate
TBAFB.....	Tetrabutylammonium tetrafluoroborate
TEA	Triethyl amine
EDOT.....	Ethylenedioxythiophene
PEDOT.....	Poly-ethylenedioxythiophene
ECD's.....	Electrochromic devices
ITO.....	Indium doped tin oxide

CHAPTER I

INTRODUCTION

1.1 Conducting Polymers

1.1.1 Brief History of Conducting Polymers

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

A key discovery in the development of conducting polymers was the finding in 1973 that the inorganic polymer sulfur nitride, $(SN)_x$, showed properties very close to those of a metal. The room temperature conductivity of $(SN)_x$ was of the order of 10³ S/cm. [1]. As a comparison, copper has a conductivity of 1×10^6 S/cm, and polyethylene, 10^{-14} S/cm. Although it's other physical properties, such as its explosive nature, prevented it from becoming commercially important, it proved the existence of highly conducting polymers, and led to the discovery of an entirely new class of conducting polymers.

Polyacetylene (PAC) was known as a black powder in 1974. Later, it was prepared as a film by Shirakawa and co-workers; unfortunately it was not a conductor. In 1977, it was discovered that PAC films can be made conductive when treated with iodine, chlorine or bromine vapor, and “doped” form of PAC was found to possess a conductivity of 10^3 S/cm [2].

Besides doping, presence of conjugated double bonds in the backbone is required for conducting polymers. In conjugated polymers, bonds between the carbon atoms are alternately single and double. Every bond contains a localized sigma bond, which is responsible for holding the polymer together, in addition to less strongly localized π bond which is weaker. These π -bonded unsaturated polymers have small ionization potentials and high electron affinities which provides the ease of oxidation-reduction reactions. In order to provide the conduction, the deficiency or excess π electrons must exist in the polyconjugated chain [3, 4]

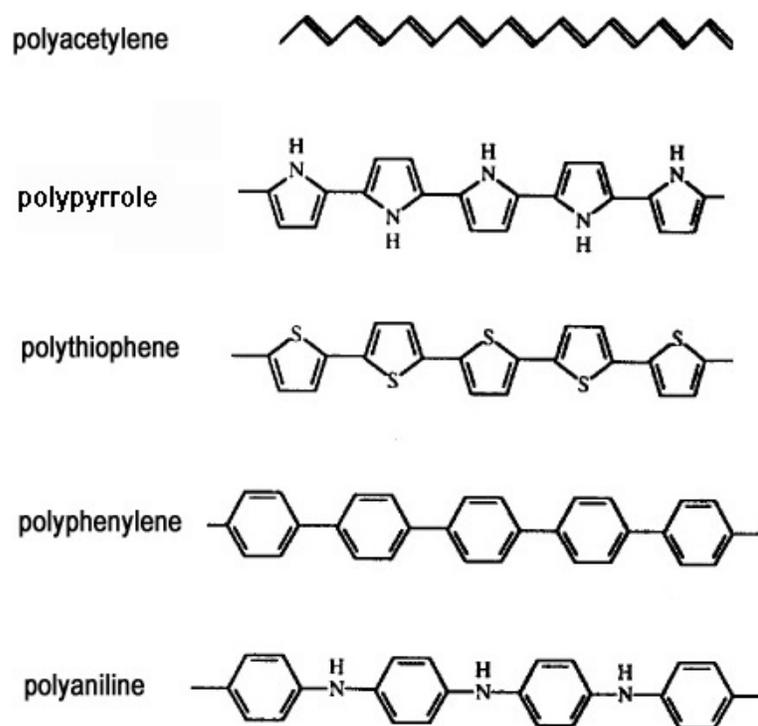


Figure 1.1 Some common conducting polymers.

The discoverers of PAc; Shirakawa, MacDiarmid and Heeger were awarded the Nobel Prize in Chemistry in 2000.

PAc initially was the most studied conducting polymer from both scientific and practical points of view. However, poor physical and mechanical properties, and instability of doped PAc has prevented their widespread applications, but has also prompted studies of other organic polymers.

One of the most popular methods of producing conjugated electronically conducting polymers is via the polymerization of resonance-stabilized aromatic molecules. Study of this type of polymer was prompted by the discovery that oxidation of pyrrole at a platinum electrode in the presence of a supporting electrolyte produced free-standing electrically conductive films. The reasons polypyrrole (PPy) has been occupied in a great deal of research lies in the fact that it is easily oxidized, has excellent thermal stability in air and good redox properties [5]. Many other systems have been studied since, such as polythiophene (PTh) [6], polyaniline (PANI) [7] poly (p-phenylene) [8], poly (p-phenylenevinylene) [9] and lately poly (3,4-ethylenedioxythiophene) (PEDOT) [10–12].

1.1.2 Applications of Conducting Polymers

The recent developments towards the syntheses of new and processable as well as discovering the broad range of chemical flexibility opens up opportunities for new technological applications. The higher environmental stability and modification of properties to suit a given end use and processibility achieved with the polymers derived from acetylene, pyrrole, thiophene, aniline and their derivatives, polyphenylene, poly(phenylene vinylenes) have emerged as materials to replace metals and semiconductors in electrical and electronics industry. Applications of conducting polymers include, plastic rechargeable batteries, circuit boards,

EMI shielding, corrosion protection, sensors, controlled-release applications, radar applications, infrared polarizers, light emitting diodes and electrochromic devices.[13,14]

Electrochromic devices (ECDs) are designed to modulate the reflectance and absorbance/transmittance of incident electromagnetic radiation by applying an external potential. ECDs have been developed for mirrors, optical displays, camouflage materials, spacecraft thermal control and solar control glazing for “smart” building windows [15].

Electrochromism has become the recent focus of research in the field of conducting polymers since every conducting polymer is a potential electrochromic material. The use of conducting polymers as potential electrochromic materials is the most pertinent to the work in this thesis.

1.2. Electrical Conduction in Conducting Polymers

1.2.1 Conductivity and Electronic Structure of Conducting Polymers

The electrical properties of conventional materials depend on the electronic band structure and on the distribution of available electrons in the bands. In a polymer, the interaction of a polymer unit cell with all its neighbors leads to the formation of electronic bands. The highest occupied electronic levels constitute the valence band (VB), and the lowest unoccupied levels, the conduction band (CB).

The energy spacing between the highest occupied and lowest unoccupied band is called the band gap. The width of the band gap determines the intrinsic electrical properties of the material that is whether a material is an insulator, semiconductor or a conductor.

In a metal, the valence orbitals are not filled. The conductivity of the metal is due either to partly-filled valence or conduction bands, or to the band gap being near zero, so that with even a weak electric field the electrons easily excited.

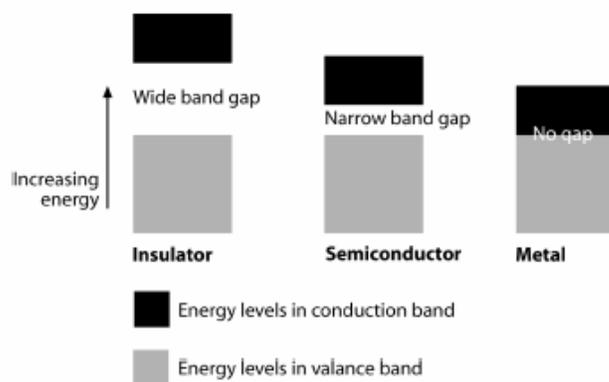


Figure 1.2 Schematic representations of band structures

In semiconductors, valence band is filled and a conduction band is empty. They are separated by a band gap, making conduction slightly more difficult. Introduction of dopants into semiconductor materials increases conductivity by producing states which lie loose to either the conduction or valence bands. The conduction band can be populated at the expense of the valence band by exciting electrons across the band gap either thermally or photochemically. Semiconductors can be doped which increases the conductivity of the material and depending on the type of dopant used either holes (*p-type*) or electrons (*n-type*) are the charge carriers.

The semi-conducting neutral polymer is converted into an ionic complex consisting of a polymeric cation (or anion) and a counter ion which

is the reduced form of the oxidizing agent (or the oxidized form of the reducing agent). The use of an oxidizing agent corresponds to p-type doping and that of a reducing agent to n-type doping.

In organic polymeric materials, conduction may occur through the movement of either the electrons or these ions. In each case, conductivity δ , is equal to the product of the carrier mobility μ , its charge q and the number of carriers or the concentration n , so that ;

$$\delta = n \cdot \mu \cdot q \quad (5)$$

In the case of insulators, separation between two bands is large which lowers the probability of the promotion of the electron to the conduction band. Insulators exhibit poor conductivities.

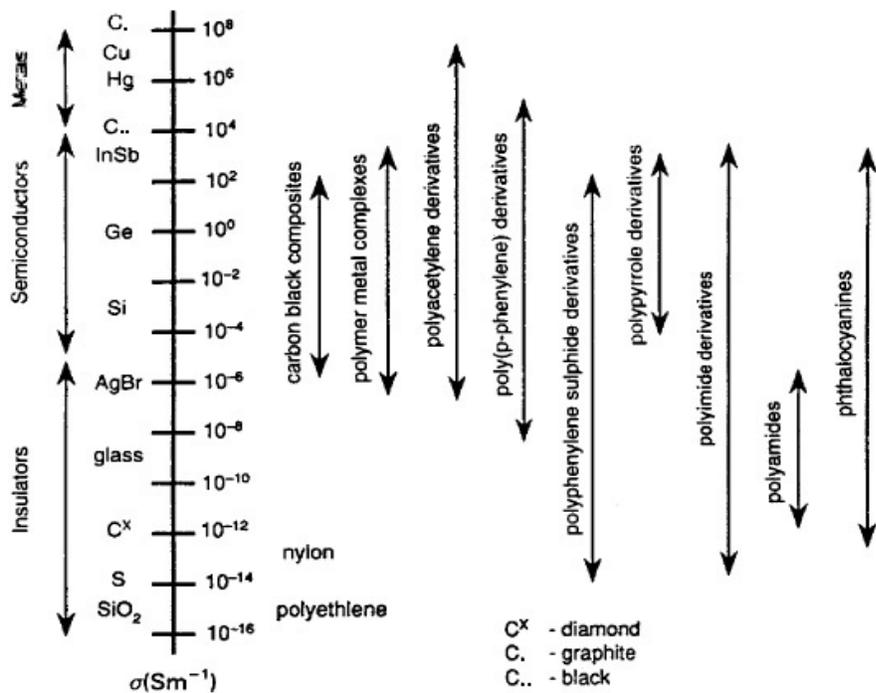


Figure 1.3 Conductivity range

1.2.2 Charge Carriers in Conducting Polymers

Conjugated double bonds act collectively. It has been predicted that for polyacetylene, π electrons are delocalized over the entire chain and that the band gap becomes vanishingly small for a long enough chain. So, PAc may be considered as quasi-one-dimensional system with one exactly half filled band, but Peierls found that such a material would be unstable and that the bond lengths alternate. It has been found that two geometric structures of PAc, which are alternating and equal bond lengths, correspond to exactly same total energy. The only difference is the exchange of the carbon-carbon double bonds. Therefore, structural defects, that are interfaces between these two structures, may occur. This defect is called soliton [16].

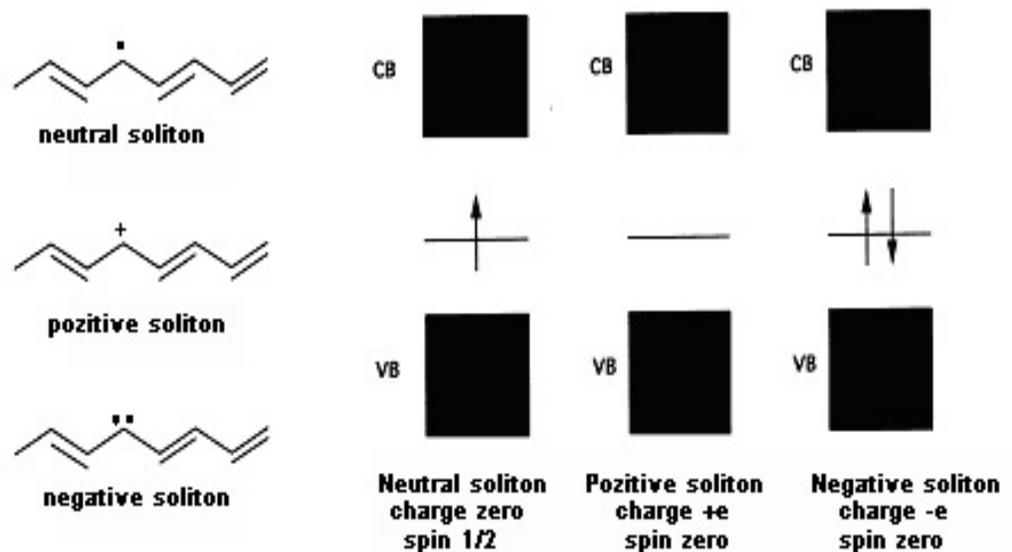


Figure 1.4 Schematic representations of solitons

For a neutral system, in which, a chain contains odd number of conjugated carbons, there remains an unpaired π electron, a radical, and it is called a neutral soliton. Upon oxidation or reduction, a radical cation or anion is generated which moves along a polymer chain by the mechanism shown in Figure 1.4., the positively charged soliton is diamagnetic, and obtained by p-type doping or electrochemical oxidation where an electron is removed. When the electron is added by n-type doping or electrochemical reduction, a negatively charged soliton is formed.

The presence of a soliton leads to the appearance of a localized electronic level at mid-gap, which is half occupied in the case of neutral soliton, empty in the case of positively charged soliton and doubly occupied in the case of a negatively charged soliton. Systems other than PAc, possess a non-degenerate ground state since their ground state corresponds to a single geometrical structure, which is aromatic-like. For PPy or PTh a quinoid-like structure can be predicted which has a higher total energy [17].

Polarons and bipolarons are defect states created during oxidation or reduction of most of the polymers. In chemical language, they can be described as radical cations and dications [18]

When an electron is removed from the top of the valence band by oxidation, a vacancy is created, but it does not delocalize completely. A radical cation that is partially delocalized over some polymer segment is called a polaron. Polarons have to overcome an energy barrier to move, thus, it undergoes a hopping process along or between the chains. The polaronic defects can be delocalized over approximately five ring units in the chain. In the case of polaron formation, the VB remains full and CB is empty. There is no appearance of metallic character since the half-occupied energy level is localized in the gap. When a second electron is removed from the polymer chain, bipolaron formation is observed. Bipolarons are extended over four rings. They transport charge via

interchain hopping and responsible for the spinless conductivity. It has been stated that bipolaron formation is favored over two polaron formations [17].

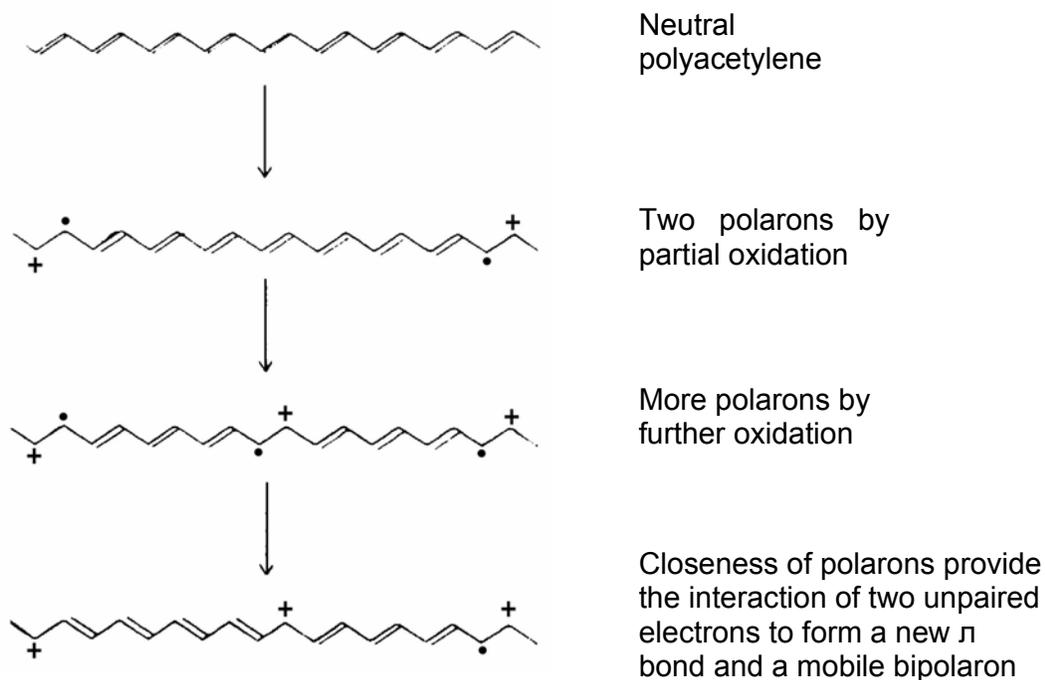


Figure 1.5 Formation of polaron and bipolaron for polyacetylene

In highly doped cases, bipolarons overlap, and a wide bipolaron band occurs. This band structure supports the fact that upon application of an electric field, the spinless bipolarons could become mobile at high dopant concentrations.

1.2.3 Hopping Process

Band theory is only applicable to a crystal lattice. Although an amorphous material will have similar bandwidths and band gaps to its

crystalline counterpart, it is found that the band edges are smeared out into the band gap and that mobility gets much lower. This is because the disorder causes localized states which act as traps or defects, either delaying the transit of the charge carrier or scattering it [19]. The electrical conduction in polyheterocyclics results from the mobility of the charge through the means below:

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

Cases b and c are called hopping processes.

1.3 Dopping

Conjugated organic polymers in their pure (undoped) state are best described as insulators. Due to the relatively large band gaps in conjugated polymers, the concentration of charge carriers at low temperatures is very low. The doping of conducting polymers generates high conductivities primarily by increasing the carrier concentration [20]. Doping is reversible to produce the original polymer with little or no degradation of the polymer backbone. Both doping and undoping processes, involving dopant counterions which stabilize the doped state, may be carried out chemically or electrochemically. By controllably adjusting the doping level, conductivity anywhere between that of the non-doped (insulating or semiconductor) and that of the fully doped (conducting) form of the polymer is easily obtained. In the doped state, the backbone of a conducting polymer consists of a delocalized π system. In the undoped state, the polymer may have a conjugated backbone which is

retained in a modified form after doping, or it may have a non-conjugated backbone which becomes truly conjugated only after p-doping [21]

p-Doping is the partial oxidation of the π backbone of an organic polymer. The basic process involves removing electrons to form a positively charged repeat unit



where P presents the basic monomeric repeat unit in the polymer. Furthermore if the polymer chain is partially reduced, the process is n type doping



1.4 Synthesis of Conducting Polymers

The purposes of conducting polymer synthesis are, synthesizing new and novel structures, increasing the order of the polymer backbone as well as conductivity, good processability, easier synthesis, more defined three dimensional structure, stability in both conducting and non-conducting states, solubility in certain solvents such as water and many other application unique properties.

Conducting polymers can be either synthesized directly by electro- or oxidative polymerization or polymerized and then oxidized chemically or electrochemically.

1.4.1 Chemical Polymerization

Chemical polymerization by using an oxidizing agent, in other words, oxidative chemical polymerization involves the oxidation of monomers to a cation radical, and their coupling to form dications and the repetition of this process. In this method, stoichiometric amount of

oxidizing agent is used to form polymer that is in its conducting (doped) form. The choice of solvent is limited to one that dissolves both the monomer and the oxidant. The product is usually obtained as a powdery, insoluble precipitate. Since polymerization is very rapid, no film formation is observed, and lower conductivity product is obtained. However, chemical polymerization is the most useful and cheap technique for the preparation of large amounts of conducting polymers. Polyheterocyclics are usually made with FeCl_3 as the chemical oxidant although other oxidants can also be used [22, 23]. Reduction to the neutral state is accomplished by addition of a strong base such as ammonium hydroxide or hydrazine.

1.4.2 Electrochemical Polymerization

The electrochemical polymerization of conducting polymers is preferred over chemical polymerization because of its simplicity and the frequently higher polymer conductivity obtained. As the electrical potential needed for oxidation of monomer is significantly higher than the doping of the formed polymer, the polymer is directly obtained in its conducting state. In this procedure, the oxidation potential at which the system polymerizes is well defined and finely controlled and the properties of the deposited polymer allows for the preparation of a variety of different conducting polymers prepared from the same monomer system by simply varying specific electrochemical parameters such as applied potential, electrolyte, temperature, electrode [24]

The electrochemical synthesis of polyheterocyclics can be made with anodic and cathodic coupling. Anodic coupling provides the oxidation of monomer to a polymer with proton elimination whereas the cathodic coupling is based on the reduction of the dihalogen-substituted (usually dibromo substituted) monomer to a polymer with halogenide release.

Anodic coupling is preferred because it uses the unmodified monomer and the formed 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.

Polymerizations by electrochemical techniques have some advantages:

- Simple
- Selective
- Reproducible
- Reactions are done at room temperature
- Thickness of the films can be controlled
- It is possible to produce homogenous polymers
- Doping of the polymer can be achieved with the desired ion simultaneously
- The molecular weight distributions can be controlled
- Films are directly formed at the electrode surface
- Graft and block copolymers can be easily obtained

Monomers used in electrochemical polymerization are aromatic and can be oxidized at relatively low anodic potentials. This removes the complications arising from the oxidative decomposition of the solvent and electrolyte. The stability of the cation is another important parameter. Film formation results from cation intermediates with intermediate stability which favors the radical coupling reaction.

Since the polymerization involves the radical cation intermediates, the reaction will be sensitive to the nucleophilicity of the environment, thus, some limitations arise in terms of the choice of the solvent and electrolyte. For this reason, experiments are performed in aprotic solvents. With regards to the electrolyte salt, the main considerations are the solubility,

preferred salts are tertaalkylammonium salts, since they are soluble in aprotic solvents and are highly dissociated.

The choice of the electrodes is another important parameter in electrochemical synthesis of conducting polymers. Since films are produced by an oxidative process, it is important that electrode does not oxidize concurrently with the monomer. That's why; mostly platinum or gold electrodes are employed.

The reactions are carried out in a single or dual compartment cells by adopting a standard three-electrode configuration where counter electrode is separated from the working and reference electrodes [19].

1.5 Electrochemical Polymerization Techniques

1.5.1 Constant Current Electrolysis

Constant current electrolysis (CCE) is carried out in a cell equipped with two electrodes. Current is kept constant during the electrolysis and the potential is allowed to change. It is simple in application but it has some disadvantages. The nature of the generated species may be unknown because of the variations in potential which is caused by the increase in the film resistance. Complications may arise in the initiation and propagation step since the involvement of species present in the system in addition to the monomer is generally inevitable [25].

1.5.2 Constant Potential Electrolysis

Constant potential electrolysis is carried out in a three compartment cell to maintain the potential on the working electrode and to prevent the excessive current flowing through reference electrode. The potential of the working electrode with respect to a reference is adjusted and kept constant while current is allowed to vary. Cyclic voltammetry is used in determination of the applied potential. The voltage between the working and the reference electrodes may be called the polymerization potential (E_{pot}). By keeping the potential constant, unwanted species can be eliminated [25].

1.5.3 Cyclic Voltammetry

The most common electrochemical method employed for characterization is cyclic voltammetry. Cyclic voltammetry (CV) is an electrolysis method that uses microelectrodes and an unstirred solution so that the measured current is limited by analyte diffusion at the electrode surface. The electrode potential is ramped linearly to a more positive (or negative) potential, and then ramped in reverse back to the starting voltage. The current flow as a function of this potential is measured and redox behavior of the material is investigated. A voltammogram of a material provides us to understand its electroactivity, redox potential, mechanism of the electrochemical reaction, it is reversible or irreversible and whether reaction products are further reduced or oxidized.

1.5.4 The Mechanism of Electropolymerization

Polymerization is initiated by removal of two electrons from a neutral monomer molecule to produce a reactive intermediate, followed by a rapid dimerization with another neutral molecule. The former step is considered as the rate determining step [26]. Another mechanism is suggested in the literature which involves the coupling of two radical cations to form a dimer followed by elimination of two protons and formation of neutral dimer [27]. Then, one monomer unit of the dimer is again oxidized to a radical cation, and it undergoes further coupling with monomeric radical cation to form a trimer. Since the polymerization reaction proceeds when oxidation potential is high enough to form a radical cation, and cannot continue further when potential is not applied, the coupling reaction must involve the reaction of two radical cations. This coupling reaction is likely to occur between the radical cations of oligomers, since it is easier to oxidize dimer, trimer etc. than the monomer.

The chain growth is terminated either when the radical cation of the growing chain becomes unreactive or, most likely, when the reactive end of the chain becomes sterically blocked from further reaction. The final polymer chain carries a charge of unity for every three to four pyrrole rings, this charge being counterbalanced by the anion of the electrolyte salt [28].

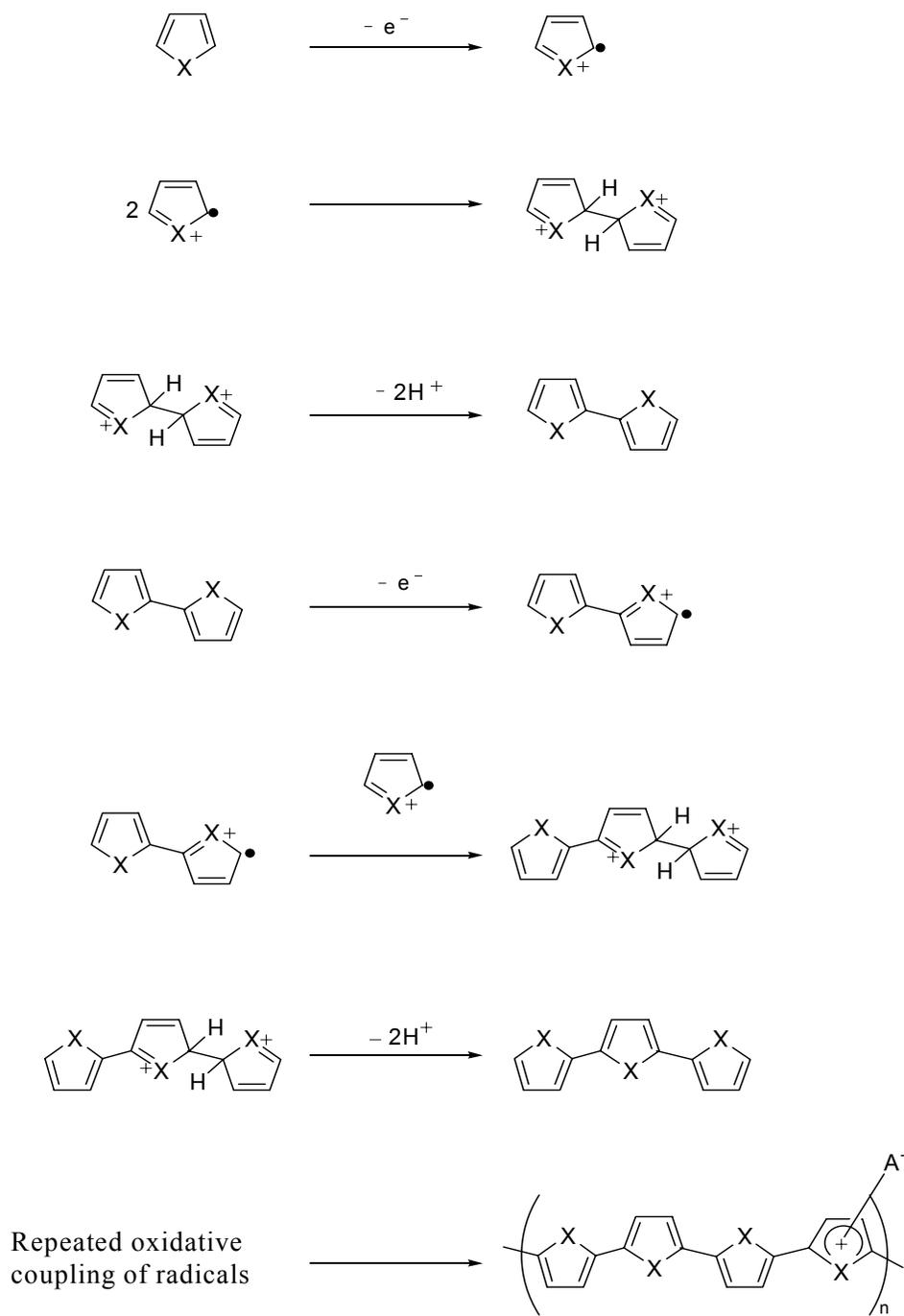


Figure 1.6 Mechanism of electrochemical polymerization

1.6 Conducting Copolymers, Blends and Composites

Conducting polymers have become very promising materials for numerous applications because they can be formed into thin, mechanically strong films, and it is desirable to confer the additional property of electrical conductivity on polymers that already benefit from being flexible and compact. These materials also stand out as an excellent class of materials due to their high conductivity, stability against environmental conditions and the ease of preparation. However, their poor mechanical properties and processability constitute major obstacle to their applications. Various methods such as the introduction of alkyl groups into the main chain, the synthesis of soluble precursors and preparation of conducting polymer composites, blends and copolymers can be used to improve mechanical properties [29].

Common approach for the preparation of conducting composites and copolymers is electropolymerization of the conducting component on electrode previously coated with the insulating polymer. In these cases, monomer and solvent molecules and electrolyte anions swell the polymer film as they diffuse into the polymer coating and polymerization starts in the interface between the electrode surface and the insulating polymer film and finally a conducting polymer film is obtained.

Polycarbonate and polystyrene [30], poly (methyl methacrylate) [31,32,33], polyimide [34], polyamide [35], polysiloxanes [36], polytetrahydrofuran [37, 38], were previously used as the host matrices.

1.7 Electrochromism

Electrochromism can be defined as a reversible and visible change in the transmittance and/or reflectance of a material as the result of electrochemical oxidation and reduction [39] An electrochromic material is

one that changes color in a persistent but reversible manner by an electrochemical reaction. Accordingly, conjugated polymers that can be repeatedly driven from insulating to conductive states electrochemically with high contrast in color are promising materials for electrochromic device (ECD) technology [40, 41]

Switchable windows and mirrors, active advertising displays, and dynamic camouflage, electrochromic devices based on conductive polymers have become a recent focus of research. This is due in part of the fact that all electroactive and conducting polymers are potentially electrochromic materials, are more processible than inorganic electrochromic materials, and offer the advantage of a high degree of color tailorability [39].

This tailorability is achieved by creating electronic states with electronic transitions at lower energies than that exhibited by $\pi\text{-}\pi^*$ transition. The color exhibited by the polymer is closely related to the band gap. By varying the electronic nature of the backbone, and the steric interactions between repeat units, the band gap, ultimately, the coloration of the polymer can be tailored [42].

The incorporation of electron donating substituents onto a conjugated chain is a commonly employed strategy to decrease the polymers oxidation potential by raising the energy of the valence band electrons (HOMO of the conjugated chain). At the same time, there is a small perturbation on the energy of the conduction band (LUMO of the conjugated chain), which leads to a decrease in the polymer's electronic band gap [43].

The electrochemical p-doping-undoping process, which switches conjugated polymers between insulating and conducting states and causes the color changes, is an oxidation-reduction reaction involving ion transport into and out of the polymer matrix to balance the electronic

charge. The overall process can be rendered as shown below with polythiophene as the conjugated polymer.

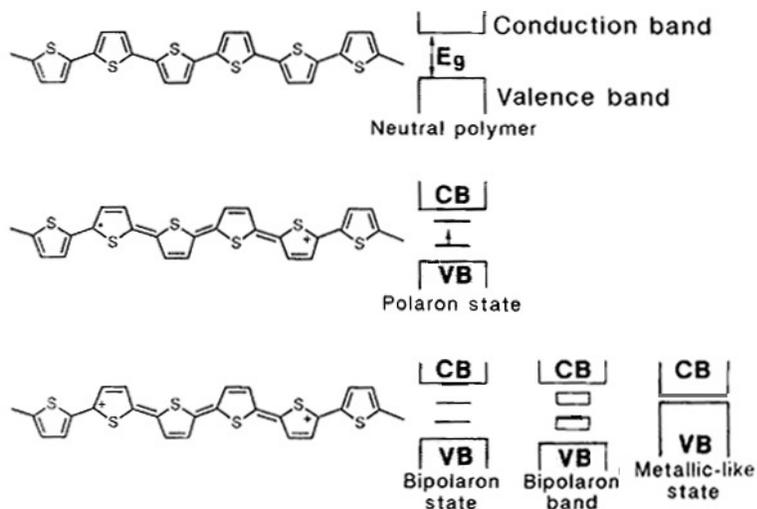


Figure 1.7 Evolution of electronic band structure with p-doping for conjugated polymer with non-degenerate ground state.

Conducting polymers are thus a class of ion insertion electrochromic materials that act during an electrochromic process as mixed electronic and ionic conductors.

The color changes elicited by doping are due to the modification of the polymer's band electronic structure. The unidimensional character of the polymer system energetically favors the localization on the chain of the charge created by doping and the relaxation of the lattice around this charge. This confinement of the charge then creates the defects that produce new electronic transitions in the band gap which causes the color change. In polymers with a non-degenerate ground state and an aromatic-

like structure the lattice relaxation is towards the quinoid structure and the defects, polarons (single charged of the spin $\frac{1}{2}$) and bipolarons (double charged, spinless), are related to the amount of the stored charge in the polymer, usually indicated as the doping level. As the doping level increases, the bipolaron states overlap in bipolaron bands, leading to a metallic-like state.

The evolution of the electrochromic band structure with p-doping can be easily monitored by UV-Vis spectrophotometry. The undoped polymer exhibits strong absorption band, which is characteristic of $\pi-\pi^*$ interband transition. This interband transition decreases upon doping and two new optical transitions appear below the interband transition, as is consistent with the presence of bipolaron bands. A pair of polarons is unstable with respect to the formation of bipolaron, and in thiophene based polymers, bipolaron states appear even at low doping levels [44].

1.8 Colorimetry

The color is a subjective phenomenon causing the description of color, or the comparison of two colors, to be difficult. Much effort has been given to transforming the description of color from a subjective matter to an objective, quantitative nature, which is the focus of colorimetry. There are three attributes that are used to describe color. The first attribute identifies the color by its location in the spectral sequence: i.e., what wavelength of light is associated with that color. This is known as “hue”, dominant wavelength or chromatic color. The second attribute is known as saturation, chroma, tone, intensity or purity. This attribute deals with the level of white and/or black. The third attribute is the brightness of the color, and it is also referred to as value, lightness, or luminance. To assign a quantitative scale to color measurement, these three basic attributes must be defined in a given color system. Many color systems exist but the most

systematic manner in which the human eye perceives color. Three most commonly used CIE color spaces are the 1931 Yxy , the 1976 $L^* u^* v^*$ and the 1976 $L^* a^* b^*$ systems. Because of the common use in the industry, 1976 $L^* a^* b^*$ system is used in determination of color in this thesis [39].

The figure below is the color space used to determine the color of the copolymers. On this chart, x-axis corresponds to a , which is hue, y-axis corresponds to b which is intensity and z-axis corresponds to L , luminance.

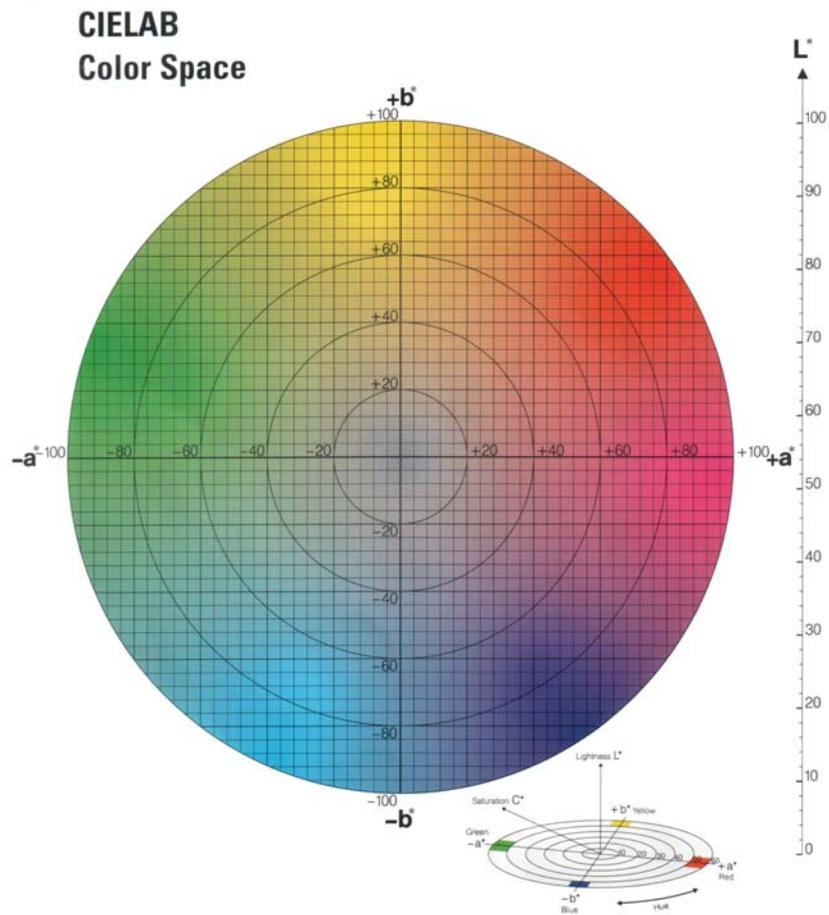


Figure 1.8 CIELAB color space

1.9 Electrochromic Devices

An ECD is essentially a rechargeable battery in which the electrochromic electrode is separated by a suitable solid or liquid electrolyte from a charge balancing counter electrode, and the color change occurs by charging and discharging the electrochromic cell with applied potential. These types of devices are called single-type ECD's.

ECD's are made of two indium-tin oxide coated glass electrodes (ITO) facing each other. One of them is coated with a cathodically coloring material, which means, it is colored in its reduced state. The other is coated with an anodically coloring material, which means, it is colored in its oxidized state. At least one of these states should be colorless or should have high transmittance, for an efficient device. These two electrodes are separated by a gel electrode which is sandwiched in between.

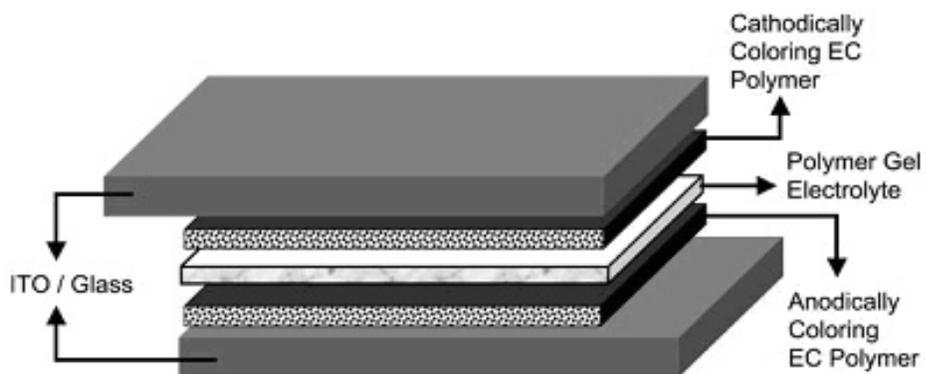


Figure 1.9 Construction of an electrochromic device

Construction of a dual polymer sandwich type device, as shown schematically in the figure above is carried out with one polymer doped while the other is neutral, making both either transmissive or absorptive, and the device can be viewed as colored or bleached. Reversal of the bias

potential oxidizes the neutral polymer with concurrent reduction (charge neutralization) of the oxidized polymer, inducing the color formation or bleaching. The optical switching rate is much faster in a dual-type ECD, than that of a single-type ECD. Because the capacitive charging of each bare ITO electrode in the single-type ECD partially compensates the applied voltage while in the dual-type ECD, both electrodes participate in the oxidation-reduction process. The ability to match the redox sites in each film leads to a high electrochromic contrast in the device as the extremes of absorption and transmission can be attained [42]. Otherwise, the complete oxidation or reduction of the materials could not be achieved, the remaining charges leads to the coloration of the polymer which curtails the actual value of the electrochromic contrast.

Before assembling the device, it is necessary to equilibrate the charge of the electrodes to improve the optical stability during repetitive charge/discharge processes [45].

1.10 Polymer electrochromic performance

The requirements for high performance electrochromic devices are:

- a) High electrochromic efficiency, expressed in $\text{cm}^2 \text{C}^{-1}$ and related to the injected charge in the material to change its color;
- b) Short electronic response time;
- c) Good stability;
- d) Optical memory, defined as the color stability under open circuit potential conditions;
- e) Optical contrast, also called write-erase efficiency
- f) Color uniformity [46].

Electrochromic efficiency, expressed as, $\text{cm}^2 \text{C}^{-1}$, is the ratio of the variation of optical density to the injected charge as a function of unit area, and it is a wavelength-dependent quality. The electrical power needed to

operate an ECD is related to the electrochromic efficiency, an important parameter to discriminate among the electrochromic materials for large-area devices.

Electronic response time is the time that the polymer takes in response to the potential pulse to go to fully colored state to another fully colored state. As conducting polymers are ion-insertion electrochromic materials, very fast electrochromic response times cannot be expected when polymer films are made thick enough to achieve sufficiently high differences in optical density between doped and undoped forms.

Optical memory is the persistence of the colored state even when the driving voltage is removed. For polymer-based electrochromic materials, it is related to the stability in the electrolytic medium of the doped and undoped forms of the polymer [44].

Aims of the work

- To synthesize thiophene ended poly- ϵ -caprolactone (PCL) and oxalic acid dithiophen-3-yl methyl ester (ODME) precursor polymer and monomer
- To perform electrochemical syntheses of PCL-co-PPy, PCL-co-PTh, ODME-co-PPy and ODME-co-PTh copolymers with better physical properties
- To characterize the copolymer films with various techniques.
- To investigate electrochromic and spectroelectrochemical properties of PCL/PTh and ODME/PTh copolymers.
- To examine their use in an electrochromic device

CHAPTER II

EXPERIMENTAL

2.1 Materials

Pyrrole (Py) and thiophene (Th) (Aldrich) were distilled before use. Acetonitrile (ACN) (Merck), dichloromethane (DCM) and borontrifluoride-ethylether (BFEE) (Sigma) were used without further purification. Tetrabutylammonium tetrafluoroborate (TBAFB) (Aldrich) was used as received. ϵ -Caprolactone, 3-thiophenemethanol, triethylamine (TEA) ethylenedioxythiophene (EDOT) and oxalyl chloride were purchased from Aldrich.

2.2 Instrumentation

2.2.1 Potentiostat

Wenking POS 73 potentiostat was used to supply a constant potential in electrochemical polymerizations.

Potentiostat keeps the voltage difference between working electrode and reference electrode at a constant value despite the changes in the current passing through the electrolytic cell, the concentration of the

electroactive substance, and the solution resistance. The current supplied by the potentiostat can be determined by measuring the voltage drop across a resistance connected to the counter electrode in series. To compensate the changes in potential of working electrode, potentiostat continuously checks the potential of working electrode measured with respect to reference electrode, and changes the potential difference in between to maintain the desired potential value that was set.

For device characterizations Solatron 1285 Potentiostat connected to a PC and operated by an appropriate software.

2.2.2 Electrolysis Cell

Electrochemical polymerization was carried out both in an H-shaped cell and one compartment cell. Platinum electrodes with area of 1.5cm^2 were used as working and the counter electrodes.

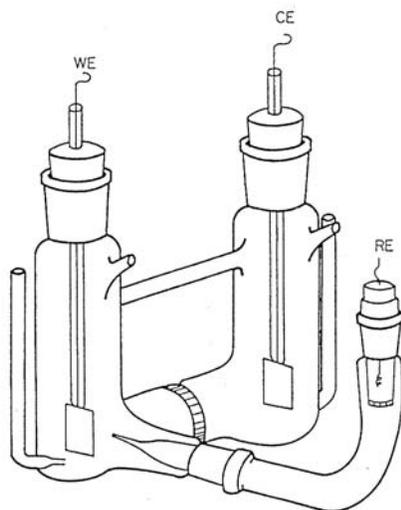


Figure 2.1 H-shaped electrolysis cell

H-shaped cell is a three-compartment one which is divided into two compartments as catholyte and anolyte with a medium porosity sintered glass disc of 2.0 cm in diameter. Reference electrode was inserted in a way that it faces the working electrode. And an Ag/Ag^+ (10^{-2} M) was utilized as the reference electrode. The cell has gas inlets to allow the passage of N_2 gas through the solution, which provides an inert atmosphere.

2.2.3 Cyclic Voltammetry System

Oxidation-reduction behavior of the precursor materials were examined by cyclic voltammetry (CV). The CV cell consists of a platinum bead working electrode 1 cm in length, a platinum spiral counter electrode made from a 3 cm wire, and an Ag/Ag^+ reference electrode. The volume of the cell was about 20 mL. The same potentiostat with an XY recorder was used to obtain the voltammograms.

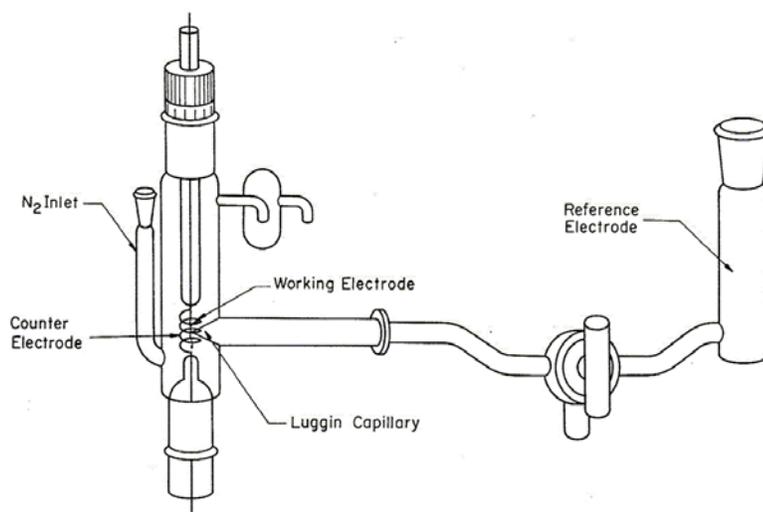


Figure 2.2 Cyclic Voltammetry cell

2.2.4 Fourier Transform Infrared Spectrophotometer (FTIR)

Nicolet 510 FTIR Spectrophotometer was used for FTIR studies

2.2.5 Differential Scanning Calorimetry (DSC)

A Du Pont 2000 instrument was used to perform thermal analysis.

2.2.6 Thermal Gravimetry Analysis (TGA)

Du Pont 2000 Thermal Gravimetry Analyzer was used to investigate the thermal behavior of polymers and monomers.

2.2.7 Nuclear Magnetic Resonance Spectroscopy (NMR)

^1H -NMR and ^{13}C -NMR spectra were obtained by Bruker-Instrument-NMR Spectrometer (DPX-400).

2.2.8 Scanning Electron Microscope (SEM)

Surface morphologies of conducting polymer films were inspected by a JEOL JSM-6400 scanning electron microscope.

2.2.9 Four Probe Conductivity Measurements

Conductivity measurements were done by four-probe technique because it is more dependable than two-probe technique since no contact resistance is created. In four-probe technique, four equally spaced osmium tips were placed on a head. The head was lowered to the sample until the four probes touch but not tear the sample.

A constant source was used to pass a steady current through the outermost probes and voltage drop across the inner two was measured. This is why it eliminates the contact resistance.

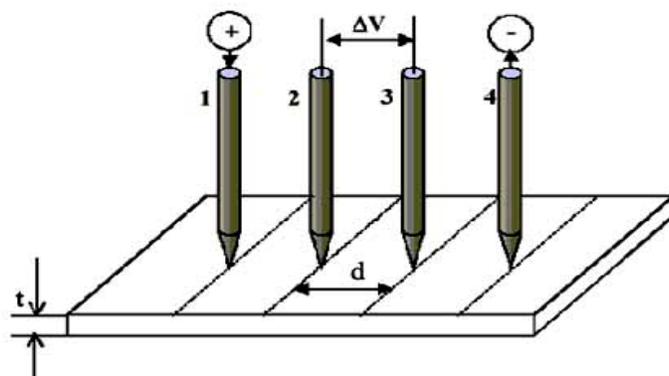


Figure 2.3 Four-probe conductivity measurement

Conductivity was given by the equation:

$$\sigma = \ln 2 / (\pi d \times i / V)$$

σ : Conductivity

i : current applied through the outer probes

V : voltage drop measured across the inner probes and

d : sample thickness.

2.2.10 Colorimetry analysis

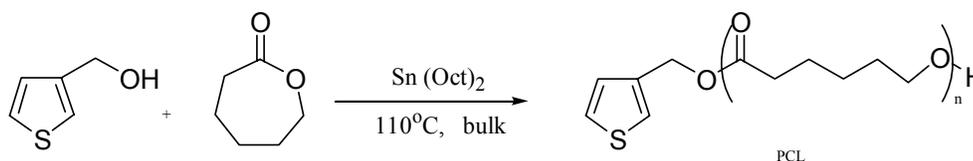
Colors were estimated by GretagMacbeth Color-eye XTH.

2.2.11 Spectroelectrochemistry

Agilent 8453 UV-Vis spectrometer was used to monitor the electrochemical behavior of the polymers.

2.3 Procedure

2.3.1 Synthesis of thiophene functionalized poly- ϵ -caprolactone (PCL)



Scheme 2.1 **Synthesis of PCL**

The synthesis of PCL involved the reaction of thiophene methanol (0.41 M) with ϵ -caprolactone (8.5 M), in the presence of stannous 2-ethylhexanoate (stannous octoate) as the catalyst (scheme1). Ingredients were added into a previously flamed and nitrogen purged schlank tube, equipped with a magnetic stirrer. Polymerization of ϵ -caprolactone was carried out in bulk, at 110 °C. After a given time, mixture is diluted with CH_2Cl_2 and poured into ten-fold excess of cold methanol and the polymer precipitated. The precipitate was allowed to dry at room temperature in vacuum for three days. Data concerning the product is given in Table 1.

Table 2.1. Synthesis of thiophene ended poly - ϵ -caprolactone

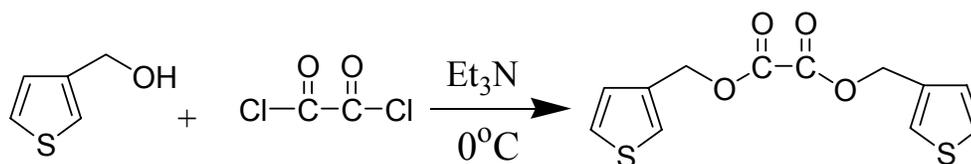
$[\text{I}] \times 10^{-2}$ (mol/L)	Time (hour)	Conversion (%)	Mn_{theo}	Mn_{GPC}	Mw/Mn	$\text{Mn}_{\text{H-NMR}}$
41	140	100	2300	2100	1.37	2350

^a Temp. 110 °C, $[\epsilon\text{-CL}] = 8.5 \text{ mol/L}$ (in bulk),

$[\text{I}] / [\epsilon\text{-CL}]$: 1/20 and $[\text{Sn}(\text{Oct})_2] / [\text{I}]$: 1/400

2.3.2 Synthesis of Oxalic Acid Dithiophen-3-yl methylester

The synthesis of Oxalic Acid Dithiophen-3-yl methyl ester (ODME) is achieved by the reaction of thiophene methanol with oxalyl chloride in DCM with the mole ratio of 2:1(Scheme 2).



Scheme 2.2 Synthesis of ODME

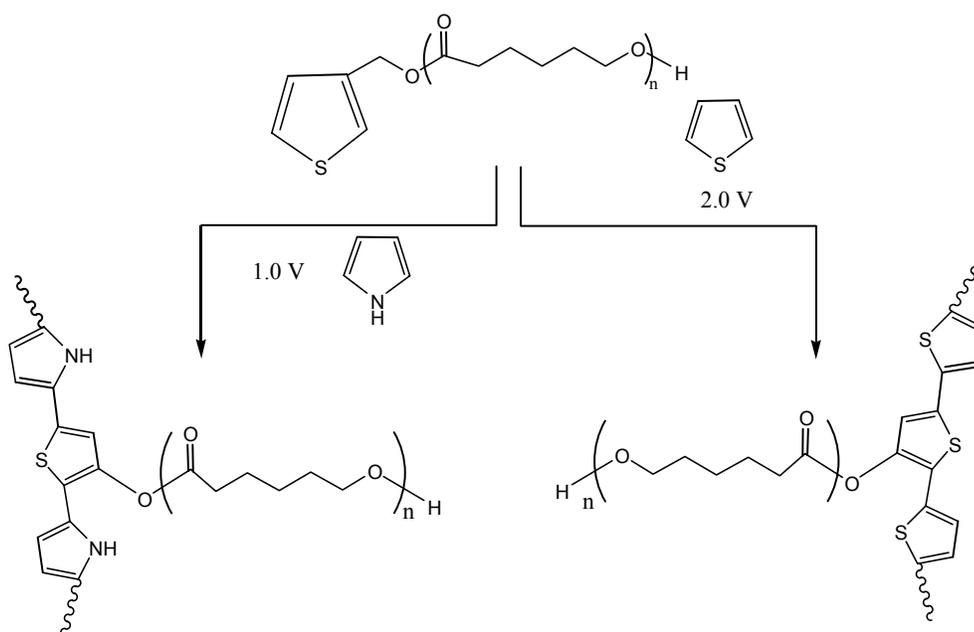
Oxalyl chloride was added dropwise, into the thiophenemethanol solution in DCM at 0 °C and by-product HCl was neutralized with TEA. The mixture was allowed to stir overnight. Then the white solid was filtered off and the solution was washed with HCl %1 solution (three times) and water (three times). The organic layer was dried over and the Na₂SO₄, and the solvent was removed via rotary evaporator.

2.3.3 Syntheses of conducting copolymers of PCL with pyrrole and thiophene

Copolymer films of PCL were synthesized by constant potential electrolysis, using platinum working and counter electrodes and Ag/Ag⁺ reference electrode.

The synthesis of PCL-co-Py was performed in ACN/TBAFB solvent/electrolyte system, using 0.02M Py, 0.05 M supporting electrolyte and 0.44 M PCL. Electrolysis was performed at +1.0 V. Electrolyses in the

presence of 0.02 M thiophene were conducted at +2.0 V in a medium consisting of 0.44 M PCL, 0.05 M TBAFB in ACN. After polymerizations, films were washed intensively with ACN, in order to remove unreacted PCL, and excess supporting electrolyte.

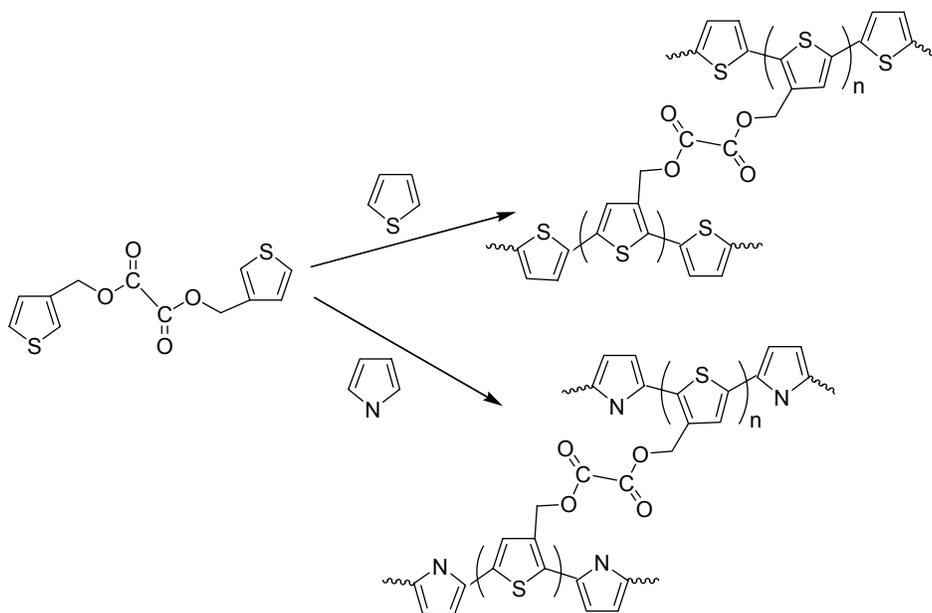


Scheme 2.3 Synthesis of PCL-co-PPy and PCL-co-PTh

2.3.4 Synthesis of conducting polymers of ODME with pyrrole and thiophene

Copolymer films of ODME with pyrrole and thiophene were synthesized via constant potential electrolysis. Electrolyses were performed in ACN/TBAFB solvent/electrolyte couple, by applying +1.0 V and +2.0 V respectively.

The polymer films were washed with ACN for the removal of unreacted ODME and supporting electrolyte. 0.02 M Py (or Th), 0.05 M supporting electrolyte (TBAFB) and ~ 30mg ODME were used.



Scheme 2.4 Synthesis of ODME/PPy and ODME/PTh

2.3.5 Galvanostatic Polymerization of PCL and ODME

100 mg PCL and 0.2 M TBAFB were dissolved in 15 ml of DCM. Constant current electrolysis was carried out in one-compartment cell equipped with Pt working and counter electrodes, allowing the passage of 0.02 mA current at 0 °C. A brown, greasy, insoluble polymer grew on the electrode surface. It was washed with DCM and dried at room temperature. The galvanostatical polymerization of ODME is achieved by applying the same procedure. A small amount of brown and poor quality film was obtained.

2.3.6 Chemical polymerization of ODME

Chemical polymerization of ODME was carried out as follows: 1 mmol ODME was dissolved in 5 ml CCl_4 while another solution of 4 mmol FeCl_3 in 10 ml nitromethane was prepared. Latter solution was added to former dropwise; in 0°C . The mixture was allowed to wait overnight. Then the ingredients were poured into excess methanol and the polymer precipitated.

2.3.7 Spectroelectrochemistry

For spectroelectrochemistry, indium doped-tin oxide (ITO) coated glass slides were used as the working electrode while using Pt wire as counter, and Ag/Ag^+ as reference electrodes.

2 mM PCL and $2\mu\text{l}$ Th were dissolved in BFEE. Films were coated onto ITO-electrodes in this medium, using a UV cuvette as an electrolysis cell, at +1.6 V constant potential. Spectroelectrochemical studies were carried out by recording UV-Vis spectra of the copolymer film at various potentials, in ACN/TBAFB system.

Spectroelectrochemical studies for ODME were done by using the same cell construction, using 3mM ODME and $2\mu\text{L}$ Th, in BFEE. The applied potential was +1.6 V.

2.4 Device Applications

2.4.1 Preparation of electrodes

2 mM PCL and 3mM ODME with $2\mu\text{l}$ Th were deposited onto ITO electrodes as stated above, and EDOT was polymerized by CV applying potentials from -0.5V to $+1.6\text{V}$.

2.4.2 Preparation of gel electrolyte

The gel electrolyte based on poly (methyl methacrylate) (PMMA) and TBAFB was prepared by using ACN as the high vapor pressure solvent. TBAFB was dissolved in ACN, then PMMA was added. With vigorous stirring and mild heating at 60 °C , dissolution of PMMA and homogeneity of the solution was achieved. The acetonitrile was slowly evaporated under stirring and a few drops of propylene carbonate were added as a plasticiser. Heating was continued until honey-like, highly conducting gel electrolyte is formed. The ratio of the composition of TBAFB-PMMA-PC-ACN was 3:7:20:70 by weight.

2.4.3 Construction of ECD's

The redox sites of the polymers were matched by applying square wave potentials stepping between $-0.5V$ and $+1.6V$. The electrodes are arranged by doping one of the polymers while leaving the other in neutral form, and faced each other, sandwiching the gel electrolyte in between. When the excess ACN is evaporated, the gel electrolyte seals itself and the construction is not ruined.

CHAPTER III

RESULTS AND DISCUSSIONS

3.1. Characterization of Thiophene ended Poly- ϵ -caprolactone (PCL)

Homopolymerization of PCL was only achieved by galvanostatic polymerization. Electropolymerization of PCL with thiophene and pyrrole were achieved in ACN/TBAFB medium.

3.1.1. $^1\text{H-NMR}$ Spectroscopy

$^1\text{H-NMR}$ spectrum of PCL was taken in CDCl_3 by using TMS as the initial standard. $^1\text{H-NMR}$ spectrum is shown in figure 3.1.1.

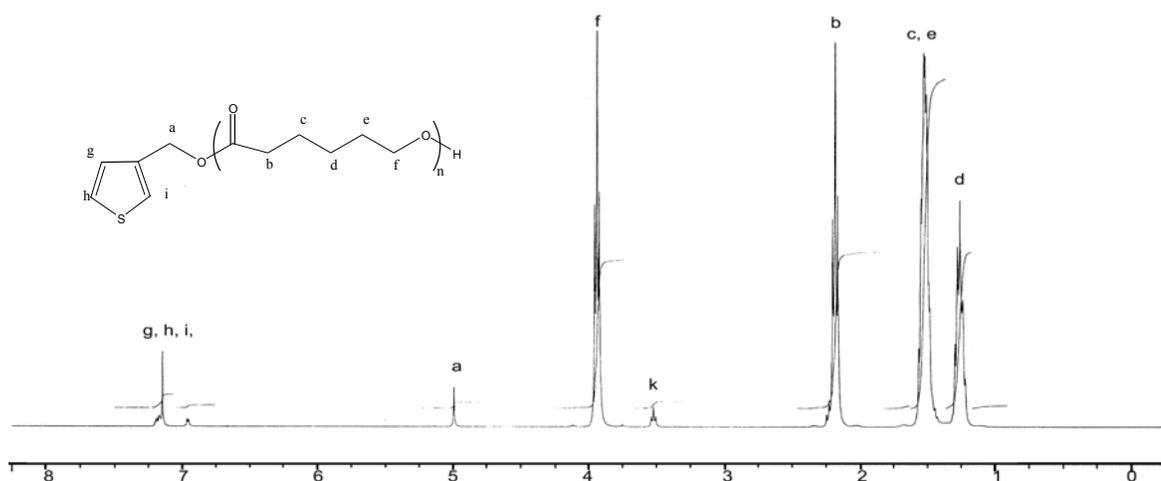


Figure 3.1.1 $^1\text{H-NMR}$ spectrum of PCL

$^1\text{H-NMR}$ spectra for PCL (δ , ppm): 7.3 (m), from thiophene ring, 5.0 (s) from β -methylene protons of thiophene, 3.9 (t) from $-(\text{C}=\text{O})\text{OCH}_2$ and 2.3 (t) from $-\text{O}(\text{C}=\text{O})\text{CH}_2$, 1.5 (m) and 1.3 (m) inner methylene groups.

3.1.2 Cyclic Voltammetry

Redox behavior of PCL was investigated via cyclic voltammetry. CV's of PCL in ACN-TBAFB system implied that our precursor polymer is not electroactive since it lacks the existence of any redox peaks. Upon addition of Py into the reaction medium, an increasing redox peak with increasing scan number was observed (Figure 3.1.2).

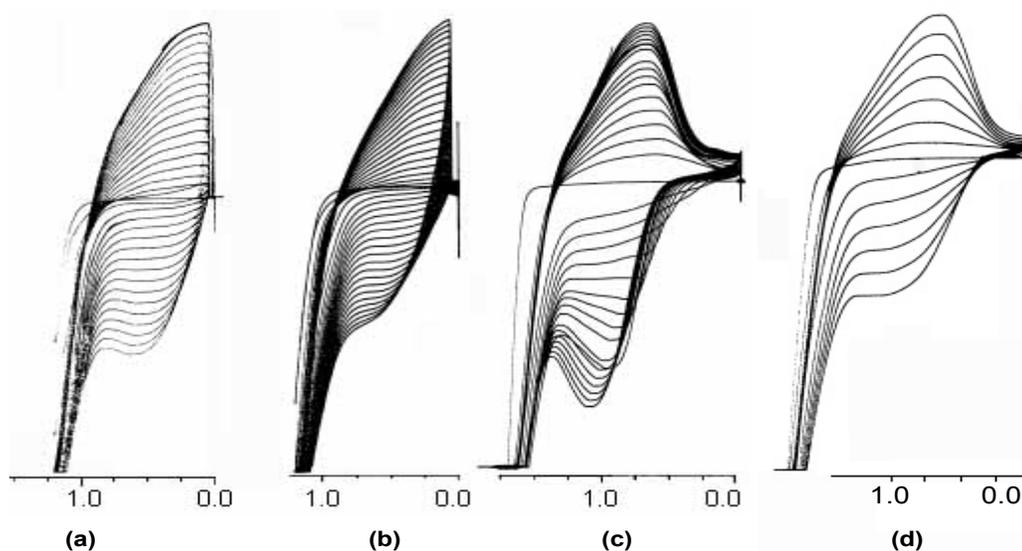


Figure 3.1.2 Cyclic Voltammograms of (a) PPy, (b) PCL-co-PPy, (c) PCL-co-Th, (d) PTh

The number of cycles observed up to a certain current value was different than that of pure polypyrrole (PPy). Moreover, the well-defined oxidation peak at +0.65 V for PPy ceased to exist, and a sharpening of the reduction peak was observed.

When the CV's of PCL was investigated in the presence of Th, a well-defined, oxidation peak at +1.1 V and a reduction peak at +0.6 V were observed. As seen in Figure 3.1.2c, it is sharper than the peak for PTh. Also, the number of cycles within the same interval of current values is different than of PTh. Moreover, the rate of current increase with continuous cycles was decreased, implying that polymerization through the thiophene moieties stop after some extent.

Another CV experiment was conducted with PCL and Th in propylene carbonate (PC)/TBAFB solvent/electrolyte couple.

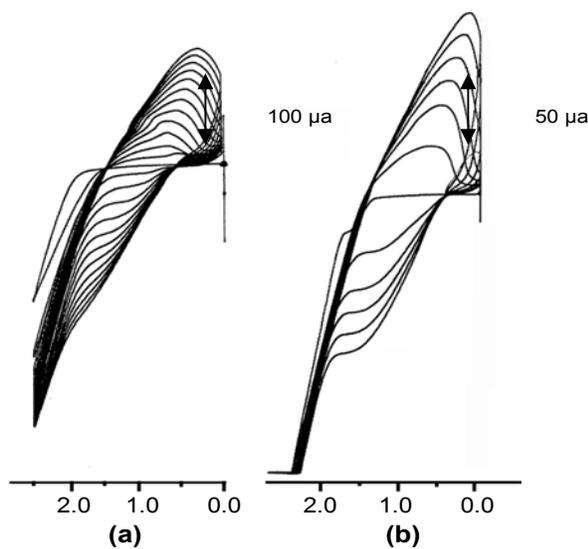


Figure 3.1.3 Cyclic voltammograms of (a) PCL-co-PTh,
(b) PTh in PC/ACN system

The precursor polymer is coated on the electrode. This was done in order to make sure that radical-cation of PCL is formed in the diffusion layer. The difference observed in the voltammogram, in terms of the general appearance and the number of cycles, is the proof of the formation of a copolymer.

3.1.3 FTIR

FTIR studies for PCL showed a characteristic, intense peak at 1727 cm^{-1} , which belongs to C=O stretching vibrations (Figure 3.1.4). Two peaks at 2948 cm^{-1} and 2867 cm^{-1} belong to aliphatic methylene stretching. Peaks between 1296 cm^{-1} to 1046 cm^{-1} can be attributed to C–O–C ester group vibrations. The peak at 732 cm^{-1} is the result of aromatic C–H_α stretching of thiophene units.

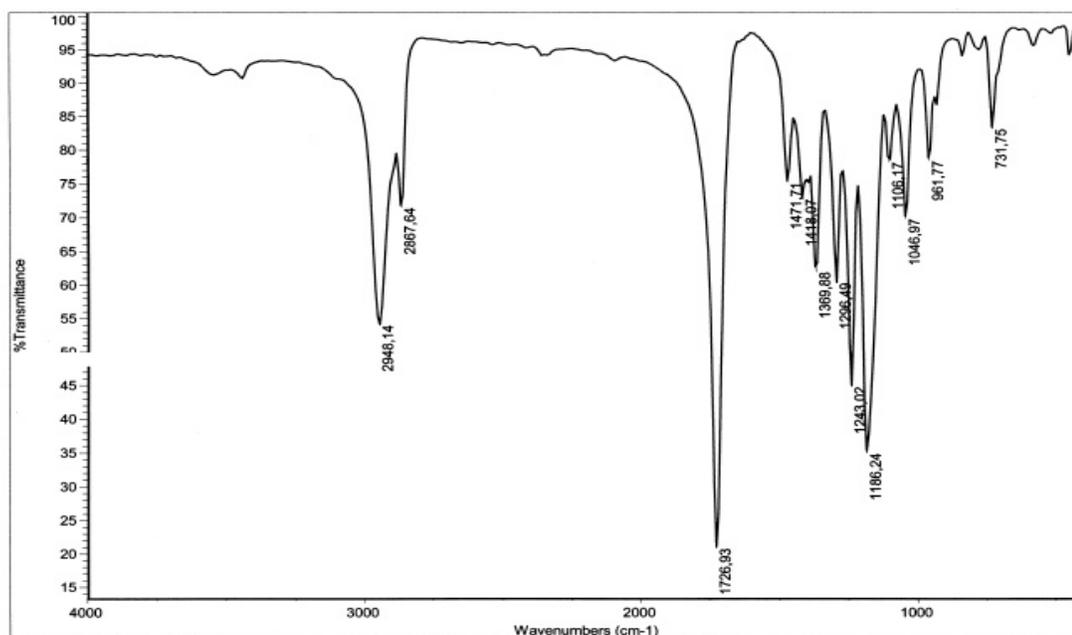


Figure 3.1.4 IR spectrum of PCL

When IR spectrum of galvanostatically polymerized PCL was investigated, the presence of carbonyl stretching at 1724 cm^{-1} , C–O–C ester group vibrations between 1295 cm^{-1} to 1192 cm^{-1} can be seen. Additionally, dopant peaks emerged around 1047 cm^{-1} indicating the conductivity of the polymer. Appearance of C-H $_{\beta}$ stretching peak at 884 cm^{-1} is the result of polymerization through 2-5 positions of thiophene ring. Another peak appeared at 1620 cm^{-1} is the proof of conjugation (Figure 3.1.5).

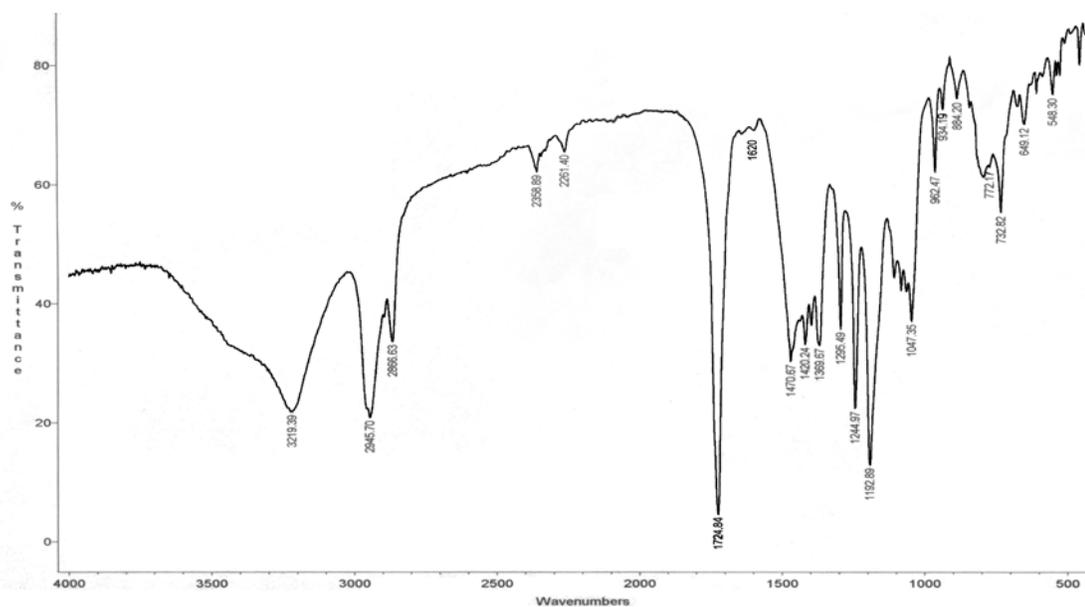


Figure 3.1.5 IR Spectrum of galvanostatically polymerized PCL

The IR spectrum of PCL-co-PTh reveals the presence of carbonyl stretching at 1727 cm^{-1} , and the peak at 1083 cm^{-1} can be attributed to dopant anion. C–H stretching seen at 732 cm^{-1} in the polymer itself, was seen to be decreased in intensity. A new peak emerged at 847 cm^{-1} , indicating that the polymerization proceeds through 2-5 positions of the thiophene rings. The

peak at 1659 cm^{-1} can be attributed to the presence of conjugation (Figure 3.1.6).

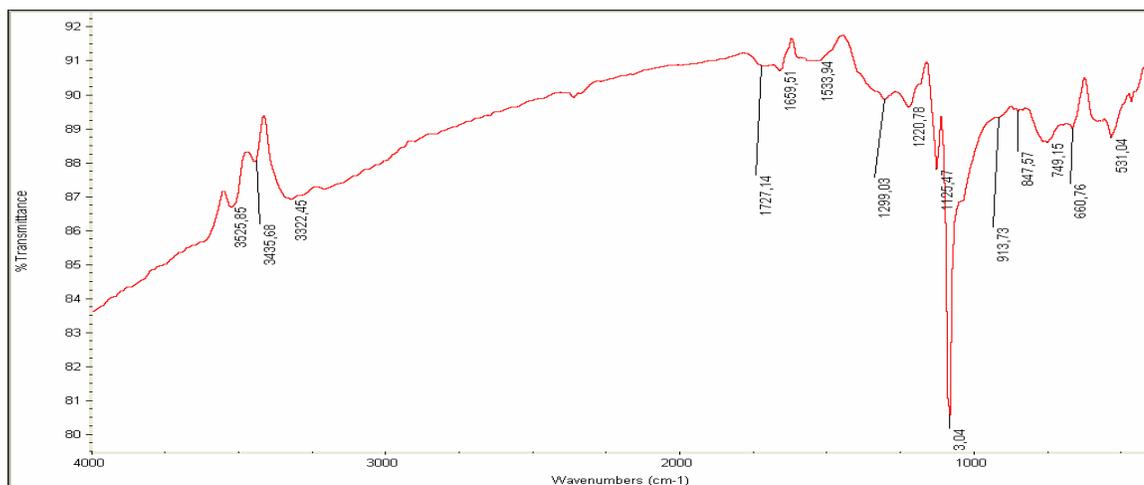


Figure 3.1.6 IR Spectrum of PCL-co-PTh

IR spectrum of PCL-co-PPy film revealed a carbonyl peak at 1731 cm^{-1} . This proves the presence of PCL in the resultant polymer since the carbonyl is specific to the precursor polymer.

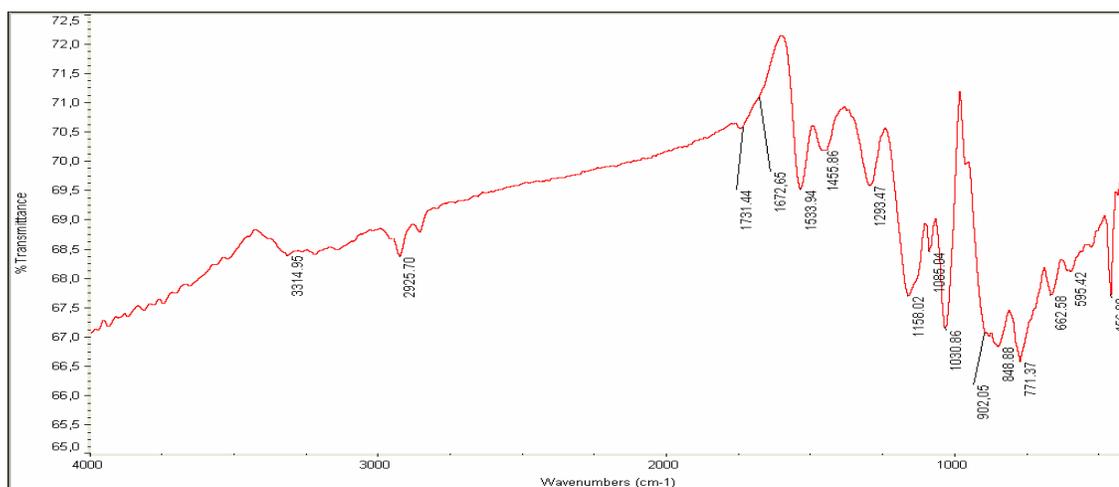


Figure 3.1.7 IR Spectrum of PCL-co-PPy

The peaks at 1293 to 1030 cm^{-1} are related to C–O–C stretching, and dopant anion. 902 cm^{-1} belongs to N–H wagging, proving the presence of Py in the structure. The peak belonging to C–H $_{\alpha}$ stretching at 732 cm^{-1} was decreased in intensity, and a new peak emerged at 848 cm^{-1} , proving the polymerization through 2-5 positions on Th ring (Figure 3.1.7).

3.1.4 Conductivities of the films

Standard four-probe technique was used to estimate the conductivities of copolymers, which were both doped with BF_4^- . Conductivity of PCL-co-Py was found to be 10.5 S/cm, and that of PCL-co-Th was found to be 1.4×10^{-2} S/cm. For both copolymers, conductivities of the solution sides and electrode sides were in the same order of magnitude, revealing the homogeneity of the films in terms of conductivity.

3.1.5 Thermal Analysis

DSC thermogram was obtained under nitrogen atmosphere, in the range of 25 °C to 450 °C at a heating rate of 10 °C / min.

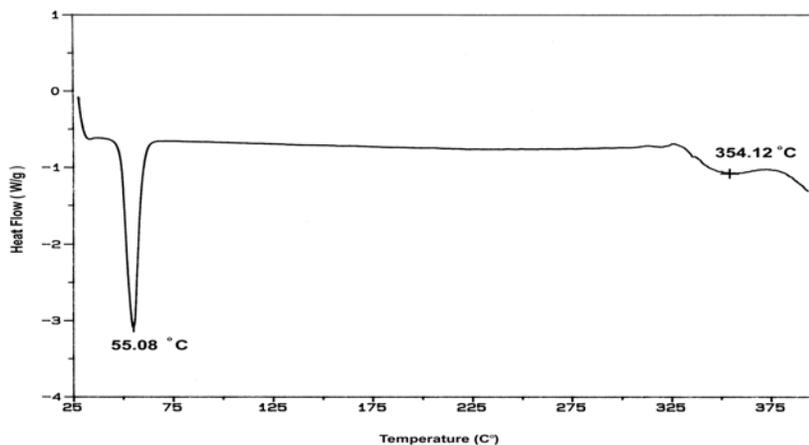


Figure 3.1.8 DSC, thermogram of PCL

DSC thermogram of PCL shows a sharp melting point at 55.08 °C and it is stable up to 312 °C. A second endotherm is observed at 354 °C.

TGA thermogram of PCL showed two weight losses at 350.0 °C and 429.12 °C (Figure 3.1.9). The weight loss at 350 °C was seen to start at around 330 °C, which is also supported by DSC thermogram. This is due to the thermal degradation of PCL which degrades by specific chain end scission in bulk, at 280-330 °C [47]. The other weight loss at 429 °C corresponds to decomposition of PCL. After the process, only 2.85 % of the polymer is left.

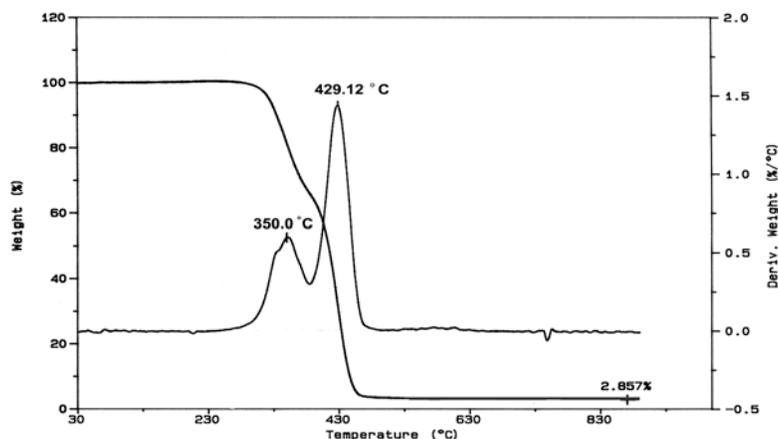
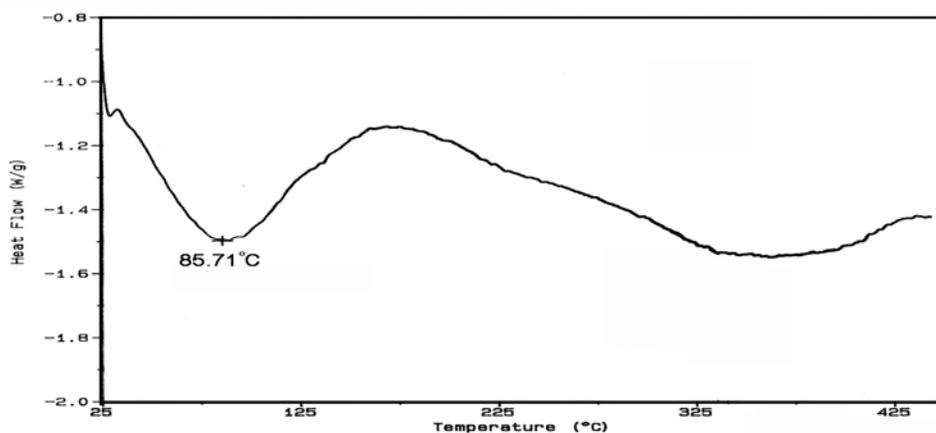


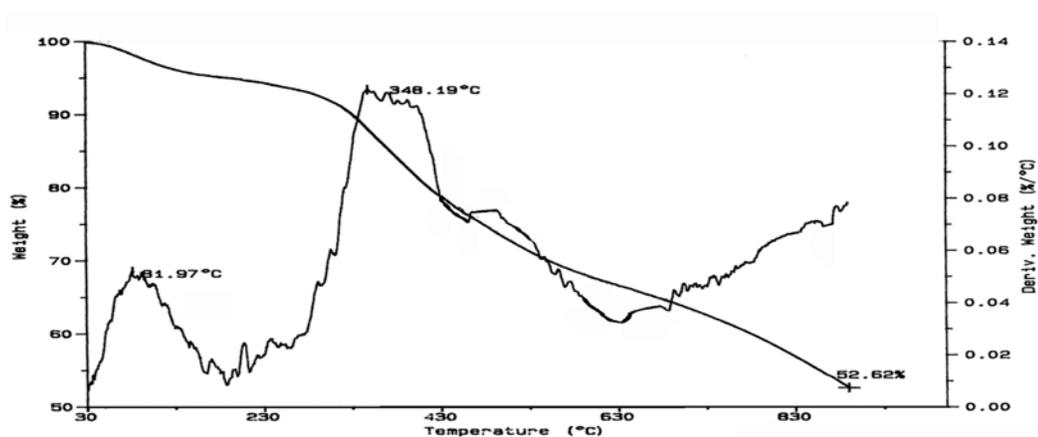
Figure 3.1.9 TGA thermogram of PCL

The DSC thermogram of PCL-co-PPy revealed two endotherms at 86 °C and 345 °C, former can be attributed to solvent removal and the latter can be the decomposition of copolymer. The TGA thermogram is consistent with DSC, since two weight losses are seen at 82 °C and 348 °C, while the 52% of the copolymer remained unaffected. Pure PPy yields two endotherms at 107 °C and 277 °C. These data show that, introduction of a bulky precursor polymer yields to a less compact matrix that, solvent removal is easier for the copolymer. And the higher decomposition temperature of the copolymer

compared to pure PPy may be attributed to the contribution of PCL, since the value is in between those of pure PPy and pure PCL.



(a)

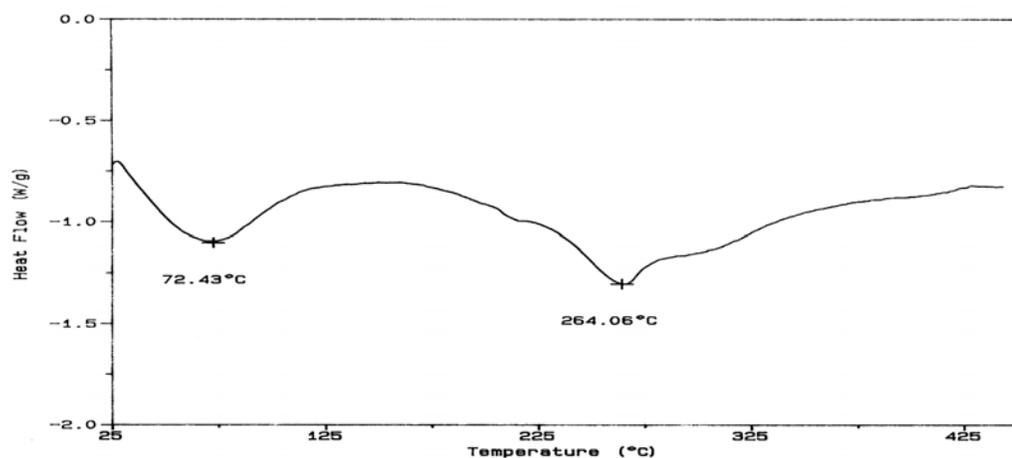


(b)

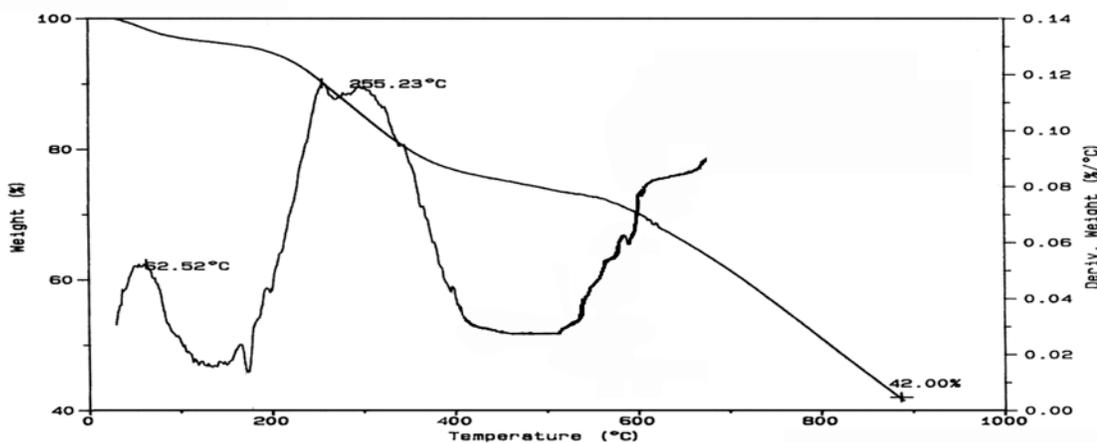
Figure 3.1.10 (a) DSC, (b) TGA thermograms of PCL-co-PPy

The DSC thermogram of PCL-co-PTh shows two endotherms at 72 °C and 246 °C, corresponding to solvent removal and decomposition respectively. TGA thermogram shows two weight losses at 62 °C and 255 °C, which is in accordance with DSC thermograms. DSC thermogram of pure PTh shows solvent removal at 91 °C while it decomposes at 296 °C, both of which

are higher than the copolymer. The disturbance of the compactness of PTh with the introduction of PCL may result in such a decrease in the resistance against heat. When TGA thermograms are examined, a 52% residue is seen for our polymer, while this value is 15% in pure PTh, PCL may cause a less compact structure that, solvent and dopant removal are at lower temperatures, but we can say that PCL strengthens the un-doped backbone of the polymer



(a)



(b)

Figure 3.1.11 (a) DSC, (b) TGA thermogram of PCL-co-PTh

3.1.6 Morphologies of the films

JEOL JSM-6400 scanning electron microscope was used for surface analysis. It can be seen from the SEM micrograph that, the electrode surface of the PCL/PPy film is far different than that of Py, which is smooth on the electrode side (Figure 3.1.12a).

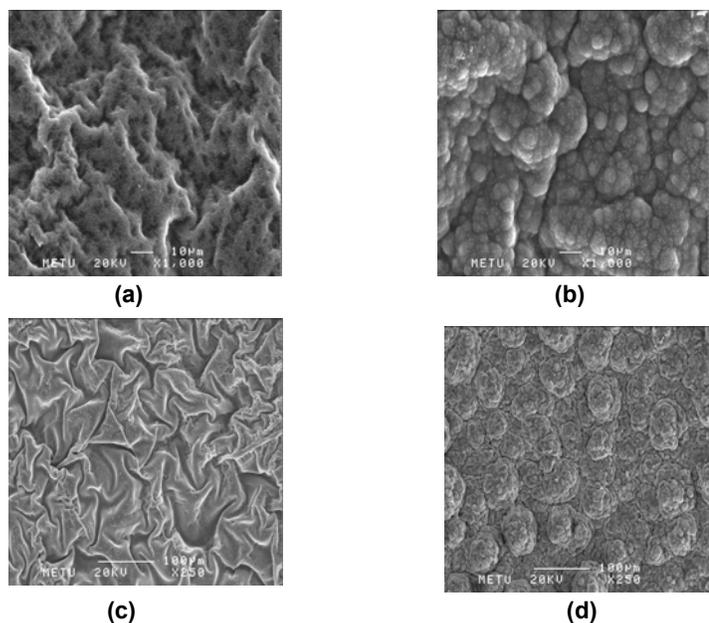


Figure 3.1.12 (a) electrode side of PCL-co-PPy, (b) Solution side of PCL-co-PPy, (c) electrode side of PCL-co-PTh (d) Solution side of PCL-co-PTh,

When the solution side of the PCL-co-PPy film was concerned, it is completely different than the well-known cauliflower structure of PPy (Figure 3.12 b). Cauliflowers were replaced by droplet-like structures, indicating the formation of a new material.

When PCL-co-PTh films were investigated, the difference from pure PTh can be seen (Figures 3.1.12 c and d). The electrode side had star-shaped wrinkles, while the solution side bears a flowery pattern both of which are completely different than that of PTh.

3.1.7 Spectroelectrochemistry

In-situ electrochemical copolymerization of PCL and PTh was investigated under +1.4 V, in BFEE, at every 10 second time intervals.

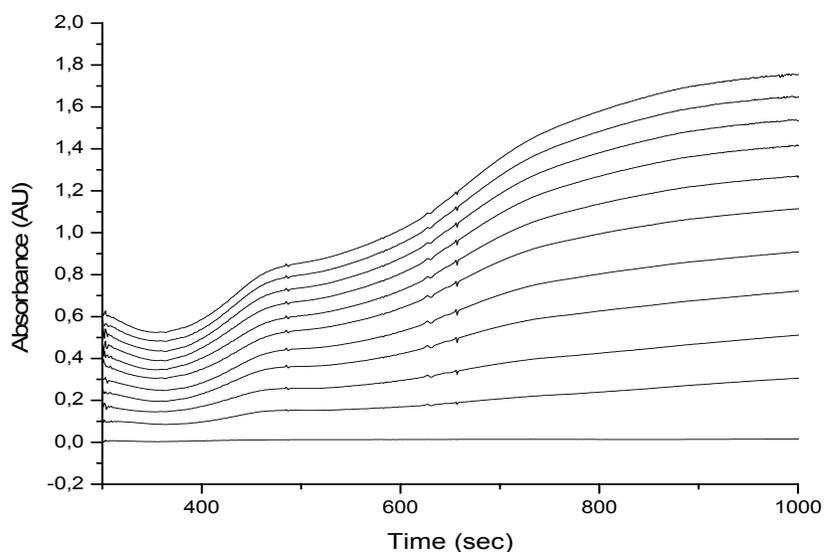


Figure 3.1.13 Spectrum of in situ polymerization of PCL-co-PTh

The intensities of peaks 473 nm and 750 nm gradually increased, revealing the formation of the charge carriers of a typical p-type conducting polymer (Fig3.1.13)

The copolymer was synthesized onto ITO electrode, via CV, sweeping between -0.5V and +1.7V. The spectroelectrochemical spectrum of PCL-co-PTh can be seen in (Fig 3.1.14).

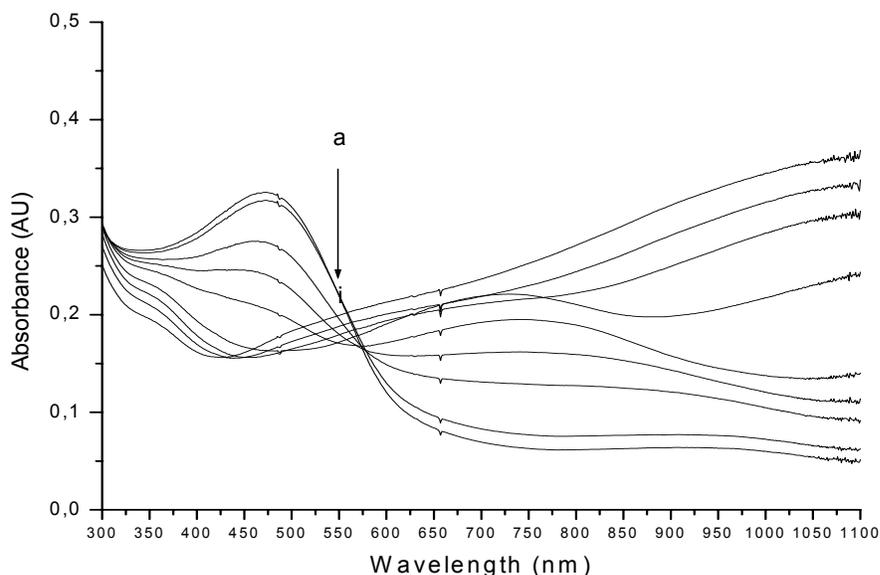


Figure 3.1.14 Spectroelectrochemistry of PCL-co-PTh

The absorption band at 475 nm corresponds to the $\pi \rightarrow \pi^*$ transition and the color of the copolymer at neutral state is pale red. The band gap of PCL-co-PTh estimated at the edge of the $\pi \rightarrow \pi^*$ transition is found to be 1.83 eV. When the applied voltage gradually increased, upon doping, lower energy transitions emerged while $\pi \rightarrow \pi^*$ transitions were ceased. These low energy transitions lead to the evolution of a new absorption band; the polaron charge carrier bands at 720 nm, which can be clearly observed in figure 3.1.14. This strong shift of the maximum absorption upon applied voltage is related to the electrochromic property of the polymer.

These lower transitions lead to the production of a second color, grayish-blue. When the film was further oxidized, this 720 nm band has also decreased, and in the near-IR region, bipolaron charge carrier bands were seen to emerge. The experiment was repeated, by decreasing the applied potential this time, and no change in band gap or λ_{\max} values were observed. The spectroelectrochemistry results showed that, PCL/PTh reversibly changes color between red and blue upon doping-dedoping processes, and the results obtained are different from those of PTh, indicating the formation of PCL/PTh copolymer [48]

3.1.8 Colorimetry Analyses

L*a*b values of the film were measured at the fully reduced and fully oxidized states and the data is given in Table 2. PCL/PTh copolymer was grayish-blue at its fully oxidized state, somewhat paler than PTh, but when the color of reduced states are concerned, this difference is more distinctive. This variation in color as well as band gap values, may point to the formation of a new copolymer

Table 3.1 Electrochemical, electronic and electrochromic properties of PTh and PCL-co-PTh.

	Epa*	Epc*	λ_{\max} (nm)	L	a	b	Color (red)	Color (ox)	Eg (eV)
PTh	0.63	0.58	495	(ox) 57 (red) 51	(ox)-7 (red) 52	(ox)-2 (red) 46	bright red	Pale blue	1.92
PCL/PT h	1.1	0.6	475	(ox) 53 (red) 63	(ox) -5 (red) 47	(ox) 7 (red) 25	red	Gray-blue	1.83

Volts vs. Ag/Ag⁺
(ox) oxidized state, (red) reduced state

Below, the extreme states, that is, fully oxidized and fully reduced states of PCL-co-PTh, with the corresponding colors can be seen.

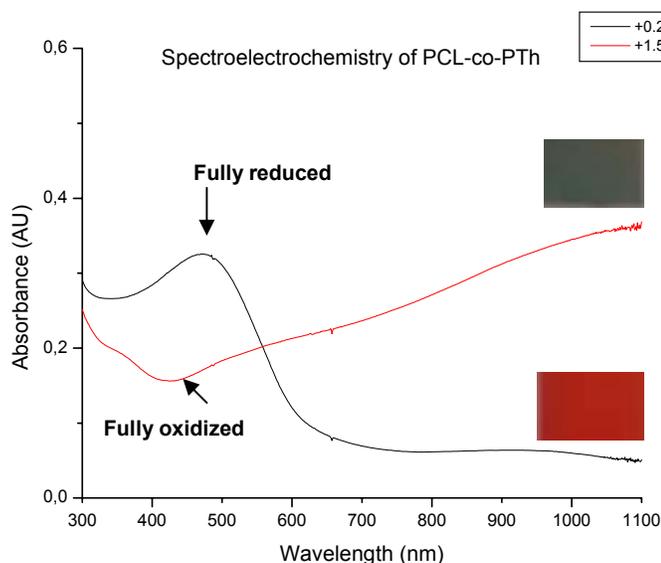


Figure 3.1.15 Extreme states of PCL-co-PTh

3.1.9 Electrochromic switching

Spectroelectrochemistry results showed the ability of PCL/PTh copolymer to switch between its neutral and doped states with a change in transmittance in a fixed wavelength. Electrochromic switching behavior of the film was investigated by recording absorption spectra while stepping the potential between -0.5 V and +1.7 V, for a switching time of 5 seconds (Figure 3.1.16)

Successful but gradually decreasing steps were observed. The contrast of PCL was measured as 6.5 % and 21 % at 610 nm and 900 nm respectively. Switching time was 0.6 s. These wavelengths were set by

the spectroelectrochemistry data, to the point where the transmittance difference is maximum.

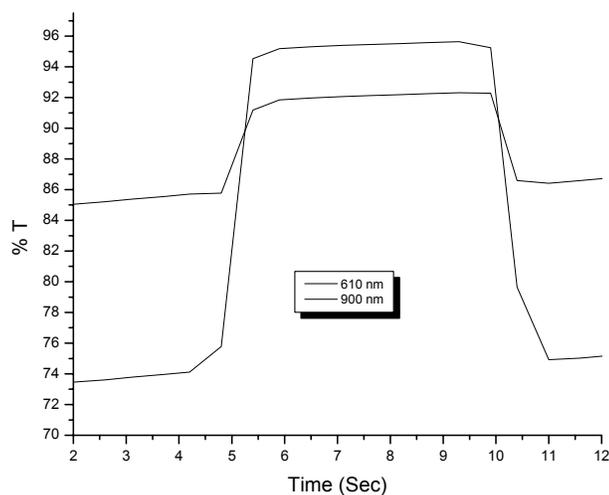


Figure 3.1.16 Electrochemical switching of PCL/PTh in BFEE

3.2 Characterization of Oxalic Acid Dithiophen-3-yl Ester (ODME)

Homopolymerization of ODME was both achieved by galvanostatic and chemical polymerization. Electropolymerization of ODME with thiophene and pyrrole were achieved in ACN/TBAFB medium.

3.2.1 $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ Spectra

$^1\text{H-NMR}$ spectrum of ODME was taken in CDCl_3 by using TMS as the initial standard. $^1\text{H-NMR}$ can be seen below (Figure 3.2.1.). $^1\text{H-NMR}$ for ODME (δ , ppm): 7.0 (d), 7.2 (q) and 7.3 (s), from thiophene ring, 5.3 (s) from β -methylene protons of thiophene.

ODME was successfully synthesized, since the expected peaks were seen. But in order to detect whether any oxalyl chloride was left, ^{13}C -NMR was needed since it has no hydrogen atoms.

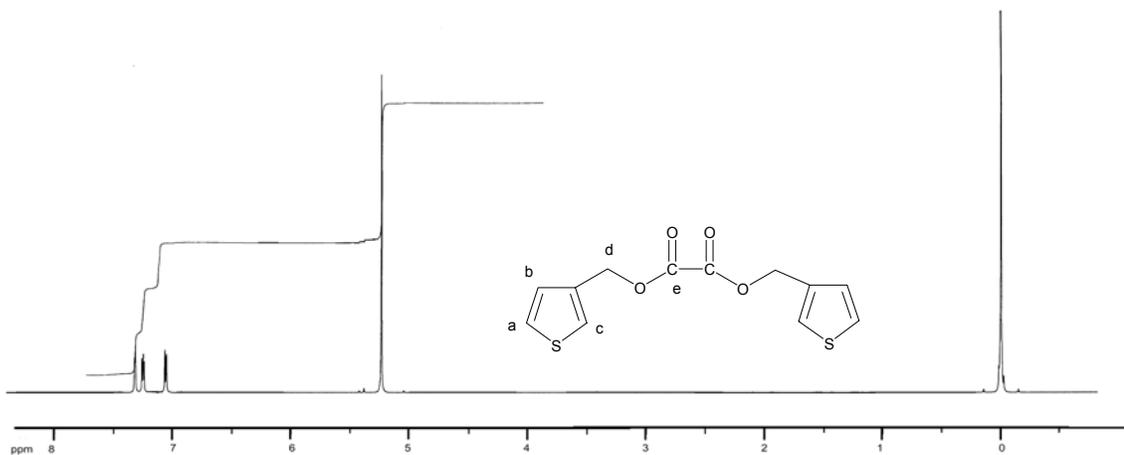


Figure 3.2.1 ^1H -NMR spectrum of ODME

^{13}C -NMR spectra of ODME (Figure 3.2.2) (δ , ppm): 155 from $\text{C}=\text{O}$, peaks between 120 and 140 from thiophene ring, 63 from methylenic groups.

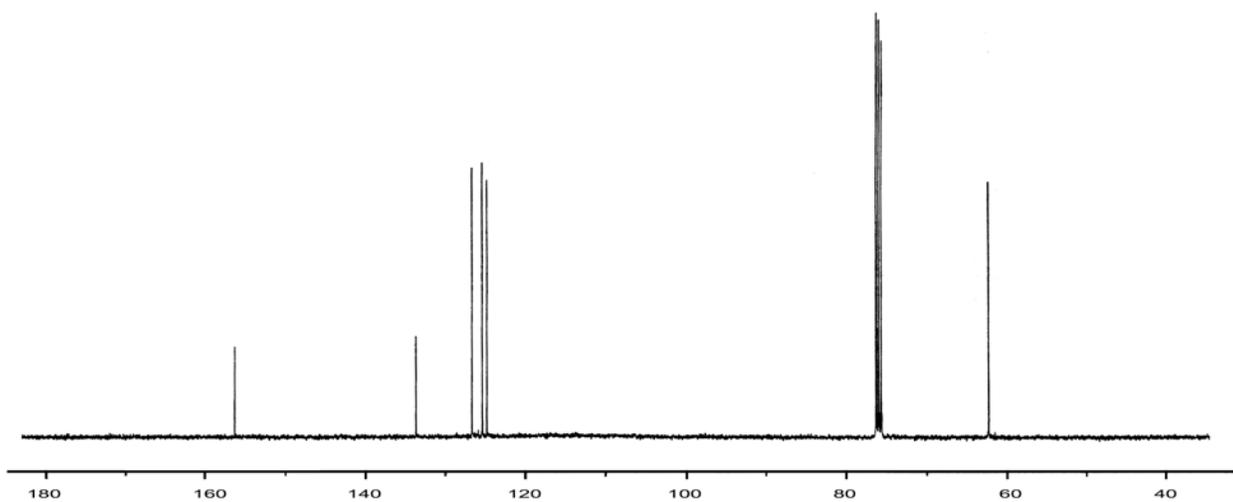


Figure 3.2.2 ^{13}C -NMR Spectrum of ODME

Six different carbon atoms of ODME are seen at the appropriate regions, so we may conclude that there is no impurity left, and ODME is successfully synthesized.

3.2.2 Cyclic Voltammetry

Redox behavior of ODME was investigated by cyclic voltammetry. CV of ODME in ACN/TBAFB system shows an oxidation peak at +2.1V. But a decrease in the electroactivity with the increasing number of cycles can be attributed to the lack of ability of homopolymerization (Figure 3.2.3 a). With the addition of Py into the medium, an increase in the cycles, in terms of peak height and number was occurred.

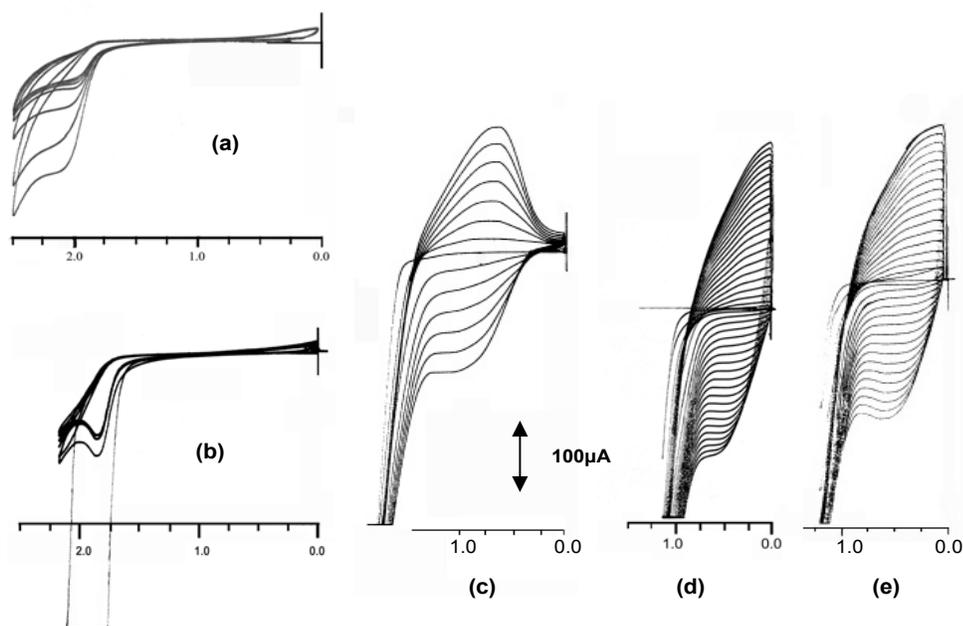


Figure 3.2.3 Cyclic Voltammograms of (a) ODME (b) ODME-co-PTh (c)PTh, (d) ODME-co-PPy, (e)PPy

Being similar to CV of the Py, the CV of ODME-co-PPy is narrower than that of PPy. In addition to that, the well-defined oxidation peak of PPy cannot be seen anymore (Figure 3.2.3 d).

A drastic difference is seen when copolymerization process is continued with thiophene (Figure 3.2.3.b). CV of ODME-co-PTh shows completely different behavior. The oxidation and reduction peaks of thiophene ceased to exist and a new oxidation peak at +1,85V emerged. This behavior is reasonable since it surely points to the formation of a new material.

3.2.3 FTIR

FTIR spectrum of ODME has revealed following characteristic peaks: C=O stretching at 1751 cm^{-1} , C-O-C ester stretching peaks at 1211 cm^{-1} , C-H_β and C-H_α stretchings from 921 to 700 cm^{-1} , aliphatic C-H stretchings at $2958, 3097\text{ cm}^{-1}$ (Figure 3.2.4).

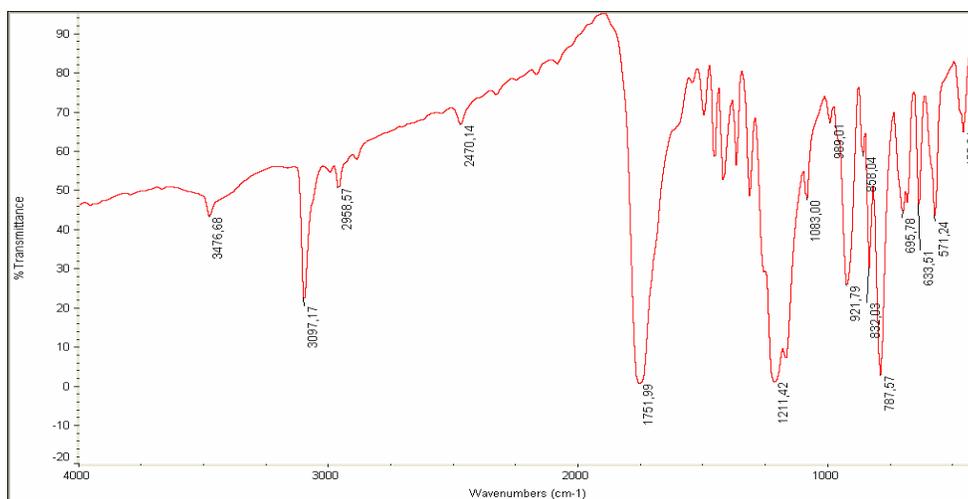


Figure 3.2.4 FTIR spectrum of ODME

FTIR spectrum of chemically polymerized ODME shows a peak at 1709 cm^{-1} which belongs to C=O stretching vibrations.

Since carbonyl vibrations are specific to ODME, this peak indicates the presence of monomer in the matrix [49]. The indication of polyconjugation can be seen at 1676 cm^{-1} .

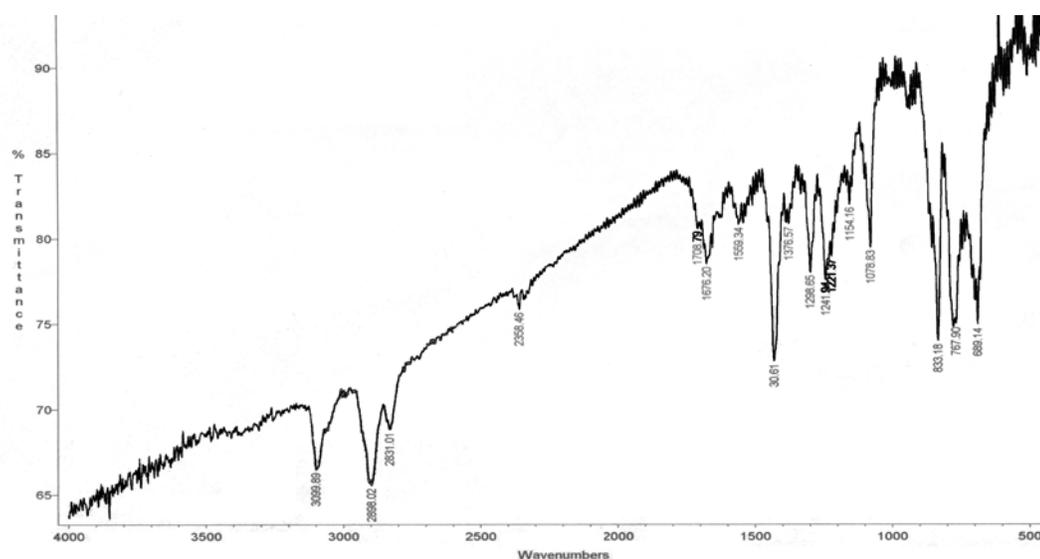


Figure 3.2.5 FTIR spectrum of chemically polymerized ODME

Two peaks at 2898 cm^{-1} and 2831 cm^{-1} are because of aliphatic methylene stretchings. 1078 cm^{-1} can be attributed to dopant ions. The peak at 833 cm^{-1} is the result of aromatic C-H_β stretching of thiophene units. (Figure 3.2.5)

When IR spectrum of galvanostatically polymerized ODME is in question, a 1725 cm^{-1} peak can be seen which belongs to carbonyl stretchings. 1763 cm^{-1} can also be attributed to C=O stretching, because

substitution of an electronegative group increases the frequency of carbonyl absorption [50].

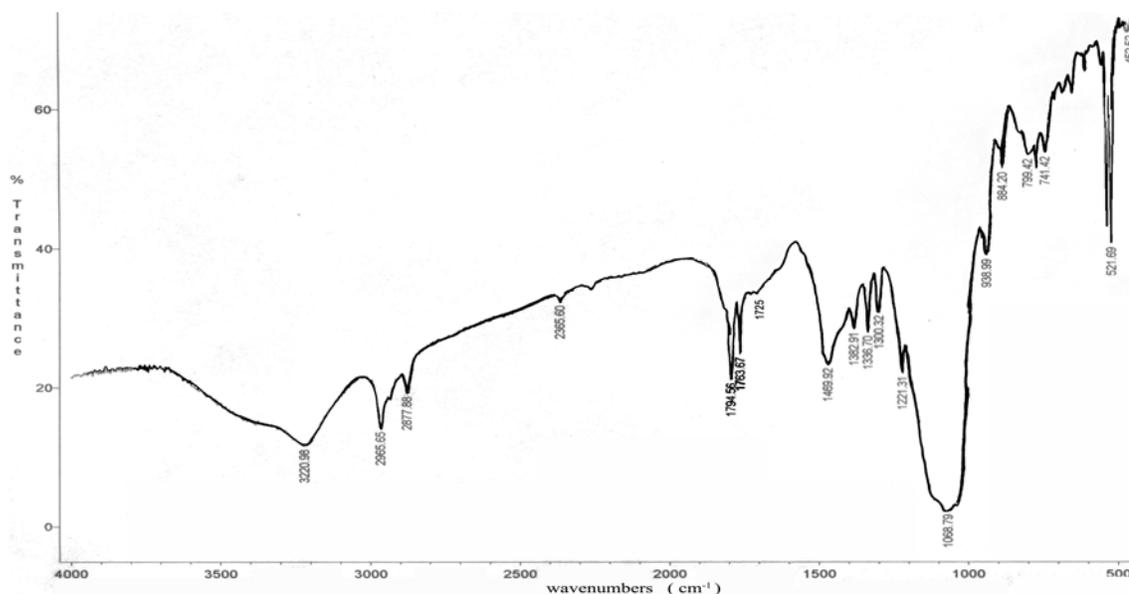


Figure 3.2.6 FTIR spectrum of galvanostatically polymerized ODME

1794 cm⁻¹ peak may be attributed to over-oxidation, since polymerization is done under harsh conditions. 1068 cm⁻¹ can be attributed to dopant ion. 2965 and 2877 cm⁻¹ are of aliphatic C-H stretchings. C-H_β stretching of thiophene units reveal themselves at 844 cm⁻¹. 1068 cm⁻¹ peak belongs to dopant ions.

The shoulder at ~1650 cm⁻¹ may be an indication of conjugation. This discussion supports the poor quality of the material deposited on the electrode surface. (Figure 3.2.6)

When ODME-co-PPY spectrum is examined, all the expected peaks can be seen. 1726 cm⁻¹ carbonyl peak, accompanied with other characteristic peaks at 2922, 1668, 1125-1035 cm⁻¹ are reasonable results, supporting

copolymer formation. The additional peak at 902 cm⁻¹ comes from N-H wagging indicating the presence of Py in the matrix (Figure 3.2.7).

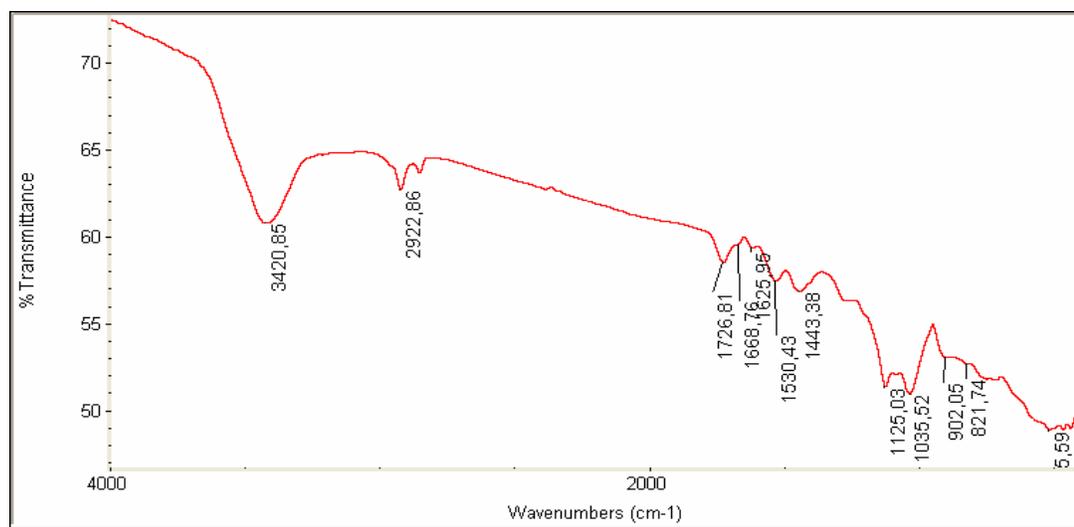


Figure 3.2.7 FTIR spectrum of ODME-co-PPy

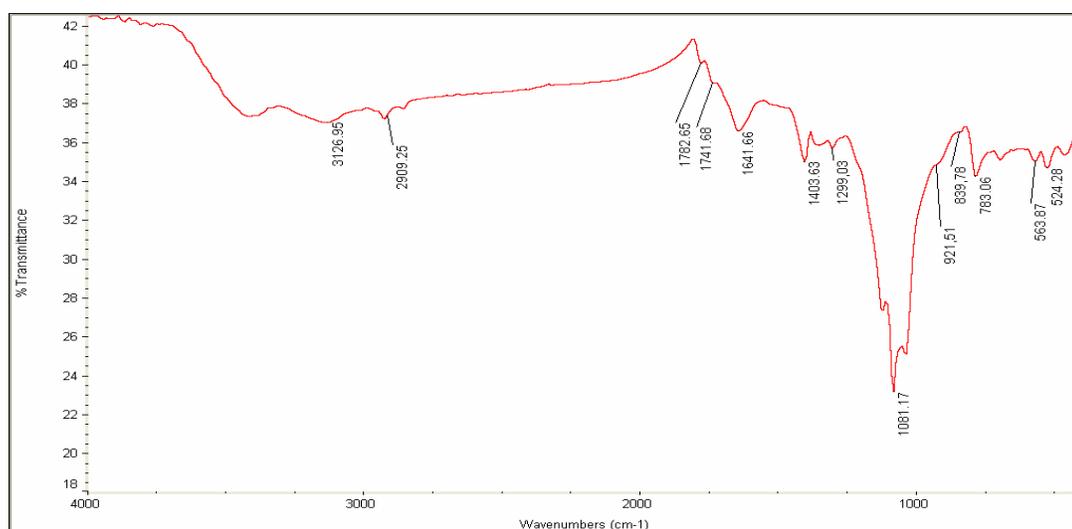


Figure 3.2.8 FTIR spectrum of ODME-co-PTh

The IR spectrum of ODME-co-PTh reveals the presence of carbonyl stretching at 1741 cm^{-1} , and the peak at 1083 cm^{-1} can be attributed to dopant anion (Figure 3.2.8). A new peak emerged at 839 cm^{-1} , C-H $_{\beta}$ stretching indicating that the polymerization proceeds through 2-5 positions of the thiophene rings. The peak at 1641 cm^{-1} can be attributed to the presence of conjugation.

3.2.4 Conductivities of the films

Conductivities of ODME-co-PPy and ODME-co-PTh can be seen in the table below.

Table 3.2 Conductivities of ODME-co-PPy and ODME-co-PTh

	Conductivities S/cm
ODME-co-PPy (in ACN)	18.9
ODME-co-PTh	9×10^{-3}

Compared to pristine polypyrrole and thiophene, they are one or two orders of magnitude low. This is expected since the presence of monomers destroys the conjugation in both pure PPy and PTh, which may be another indication of copolymerization. As it was seen in the CV's that the copolymer with thiophene is more promising, the situation is supported by the conductivity measurements as well.

3.2.5. Thermal analysis for ODME

DSC thermogram of ODME showed an endotherm at 98 °C which can be attributed to the monomer's melting point.

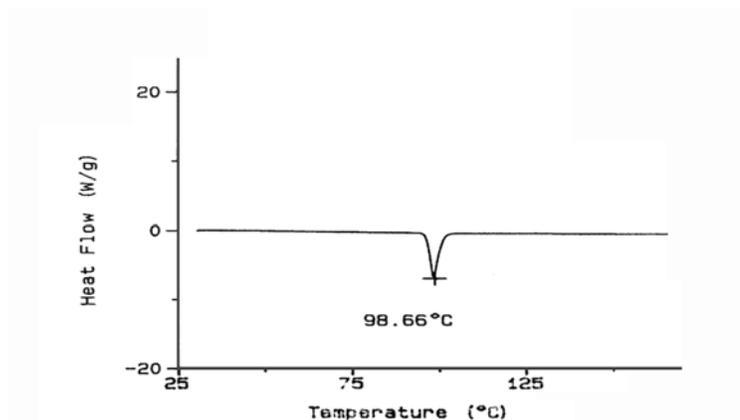


Figure 3.2.9 DSC thermogram of ODME

The sharp weight loss on the TGA curve is a gas evolution due to the decomposition of the monomer. 11% of the monomer remained after the process

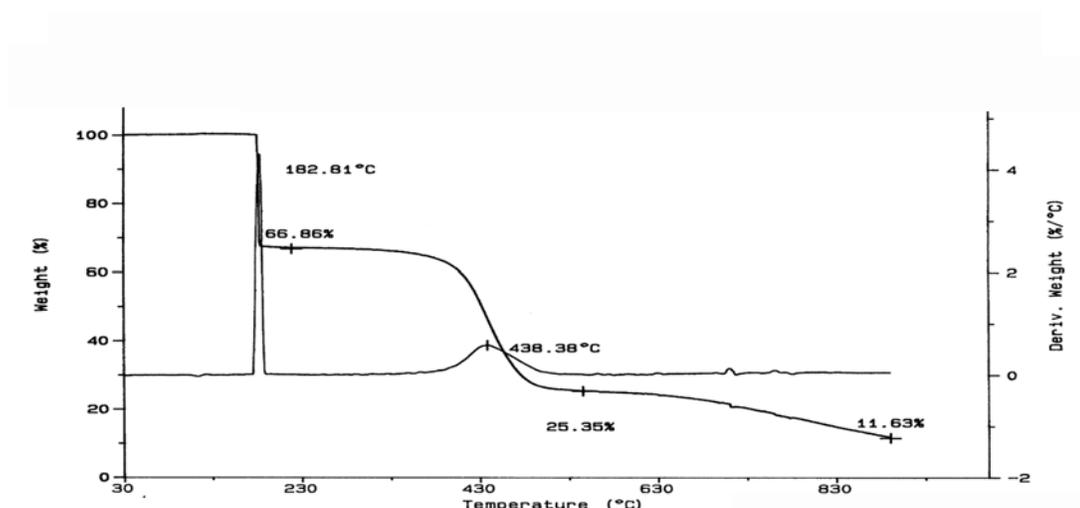


Figure 3.2.10 TGA thermogram of ODME

DSC thermogram of ODME-co-PPy revealed an endotherm at 91 °C, which can be attributed to solvent removal.

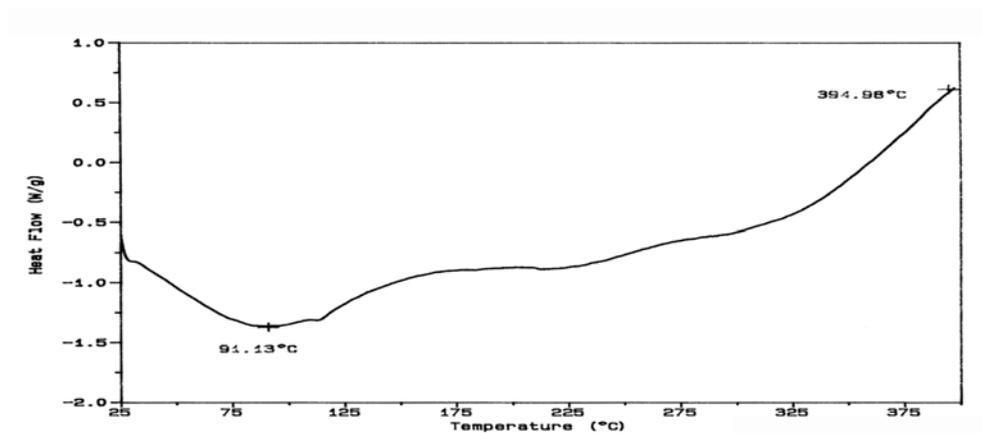


Figure 3.2.11 DSC thermogram of ODME-co-PPy

The slight concave curve around 225 °C may be the dopant removal from the matrix. This behavior is supported by the TGA thermogram as well. The weight loss at a maximum of 66 °C may be attributed to solvent removal. The onset of the weight loss is around 40°C, and continues up to ~130°C, similar to the DSC curve, and the dopant removal can be seen as well.

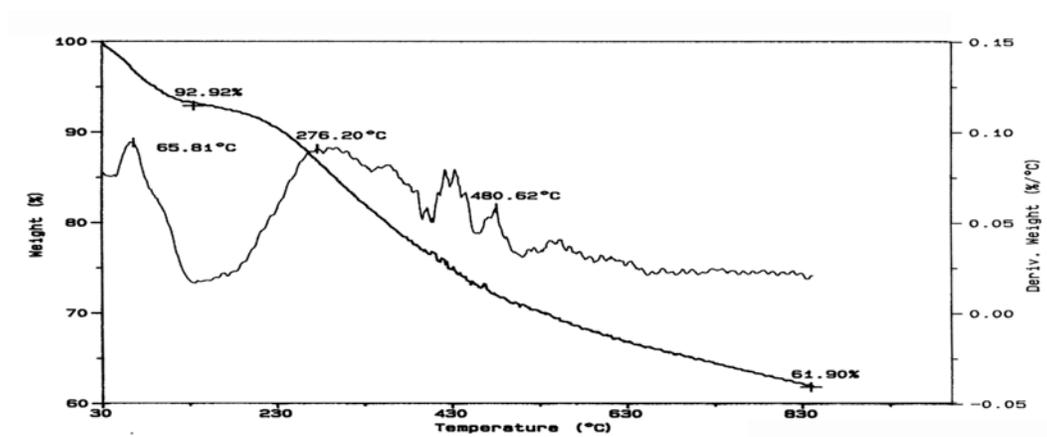
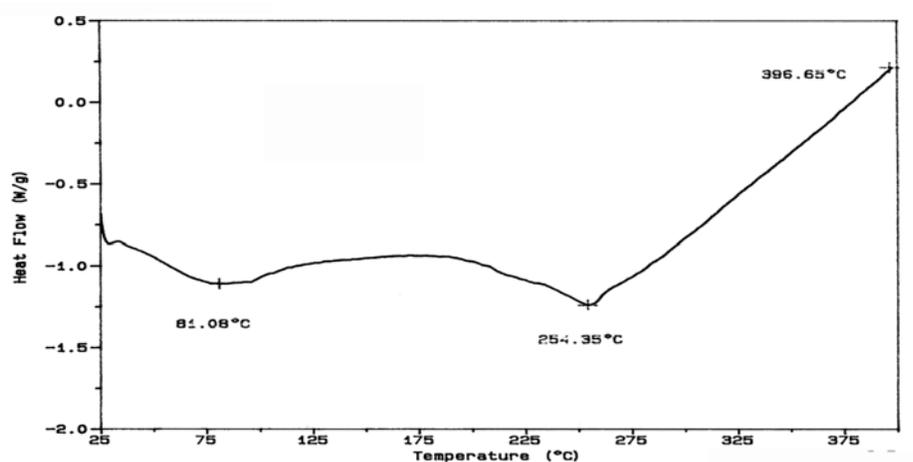


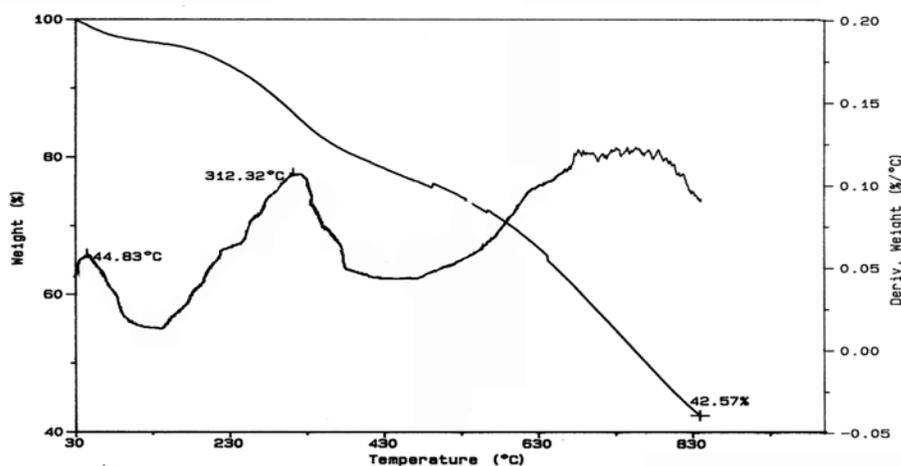
Figure 3.2.12 TGA thermogram of ODME-co-PPy

The polymer is seen to be resistant to heat, since 62% is remained after the process. The copolymer is more resistant to heat when compared to PPy, since pure PPy has a char residue of 52%.

Two endotherms observed in the DSC thermogram of ODME-co-PTh .81°C, with an onset around 30 °C , being the solvent, and 254 °C being the dopant removal.



(a)



(b)

Figure 3.2.13 (a) DSC thermogram of ODME-co-PTh
(b) TGA thermogram of ODME-co-PTh

In the TGA thermogram, the weight loss at 44 °C up to ~125 °C supports the solvent removal, while the one at 312 °C can be attributed to the dopant removal, since its onset is around 150 °C. 42% of the polymer is remained after heat treatment.

3.2.6 Morphologies of the films

SEM photographs reveal a wrinkled electrode side of the ODME-co-PPy film, which is good, since it is different than smooth PPy. When solution sides are concerned, the pattern that ODME-co-PPy possesses is clearly distinguishable than cauliflower structure of PPy (Figures 3.2.14a and b)

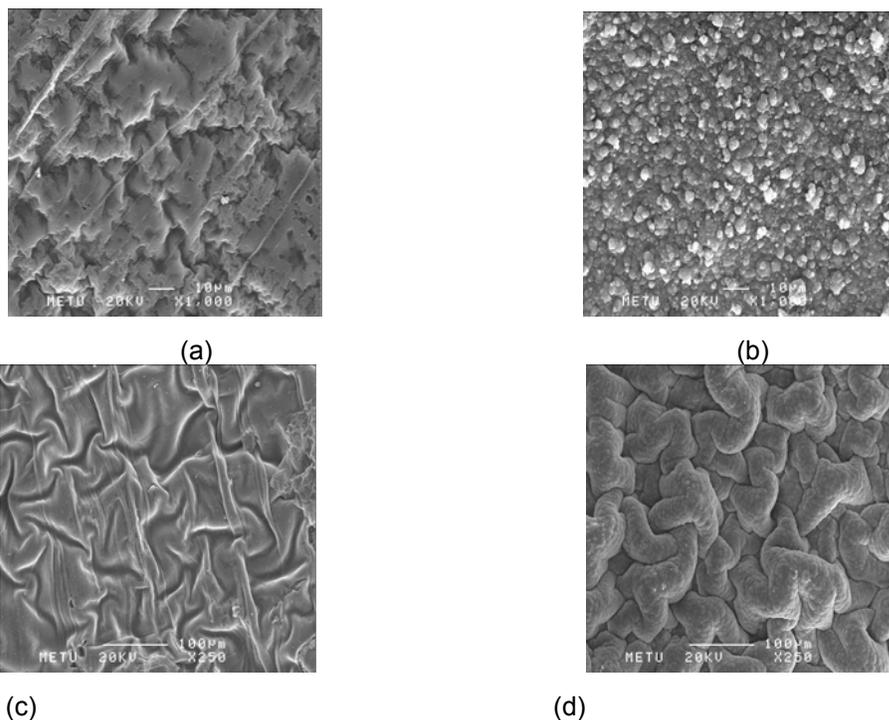


Figure 3.2.14 (a) electrode side of ODME-co-PPy (b) solution side of ODME-co-PPy, (c) electrode side of ODME-co-PTh, (d) Solution side of ODME-co-PTh

When solution side of the ODME-co-PTh films are investigated, worm-like structures are observed, revealing a significant difference of morphology compared to the cauliflower structure of the pure PTh.

The difference is also obvious when the electrode sides are concerned. Star-shaped wrinkles are the indication of difference while pure PTh is smooth on the electrode surface (Figure 3.2.14c and d).

3.2.7 Spectroelectrochemistry

In-situ electrochemical copolymerization of ODME and PTh was examined by copolymerization of the two under +1.4 V constant potential, in BFEE. At every 10 second time intervals, UV-Vis spectrum of the copolymer was taken. The intensities of peaks at 475 nm and 727 nm gradually increased, revealing the formation of the charge carriers of a typical p-type conducting polymer (Figure 3.2.15)

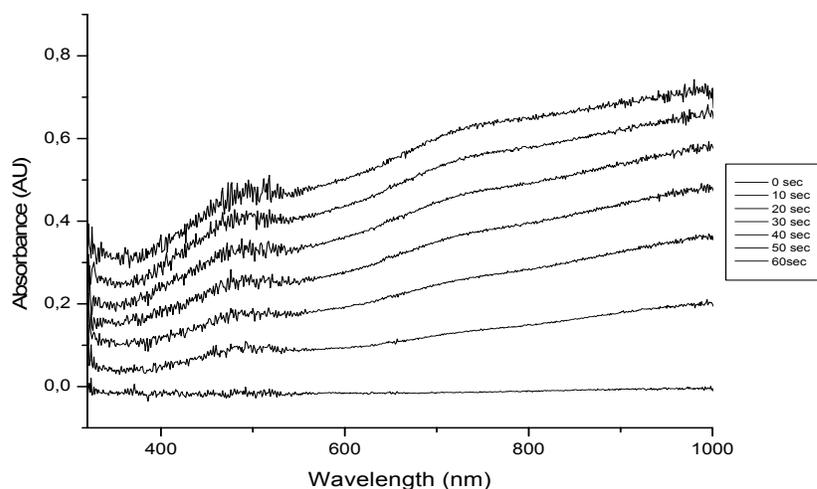


Figure 3.2.15 Spectrum of in situ polymerization of ODME-co-PTh

The copolymer was deposited onto ITO electrode via CV, by cycling between $-0,5V$ and $+1,7V$. The spectroelectrochemical spectrum of ODME-co-PTh can be seen in Figure 3.2.16.

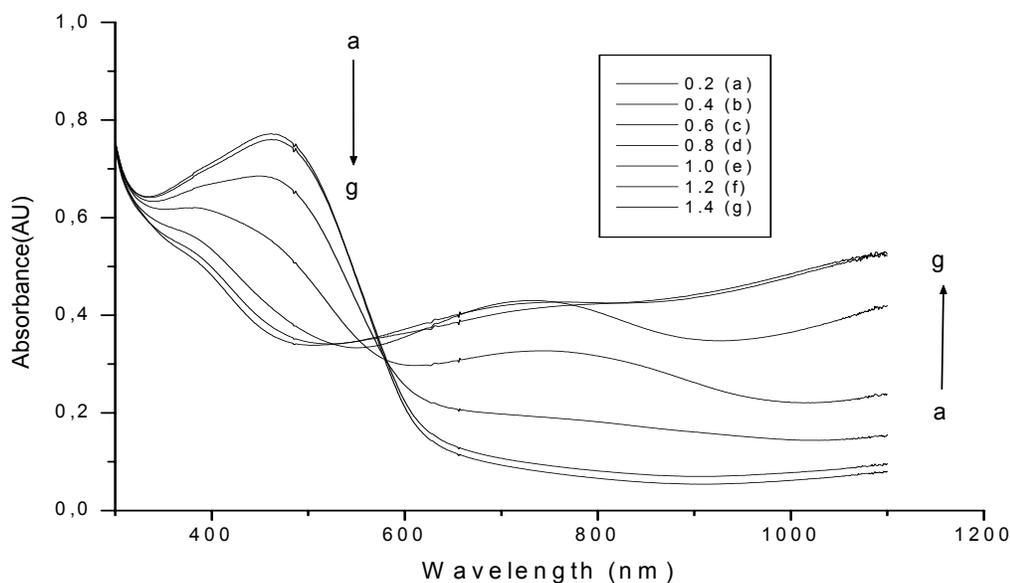


Figure.3.2.16 Spectroelectrochemistry of ODME-co-PTh

The absorption band at 460 nm evolved as a result of the $\pi \rightarrow \pi^*$ transitions and the color of the copolymer at neutral state is pale red. The band gap of ODME-co-PTh estimated at the edge of the $\pi \rightarrow \pi^*$ transition is found to be 1.93 eV. When the applied voltage gradually increased, upon doping, polaron and bipolaron transitions emerged while $\pi \rightarrow \pi^*$ transitions were ceased. Low energy transitions that revealing the polaron charge carrier bands can be seen at 720 nm. Examining the character of spectrum for higher wavelengths, formation of bipolarons can be predicted.

These lower transitions lead to the production of a second color, grayish-green.

3.2.8 Colorimetry Analyses

L*a*b values of the film were measured at the fully reduced and fully oxidized states and the data is given in Table

Table3.3. Electrochemical, electronic and electrochromic properties of PTh and ODME-co-PTh.

	Epa*	Epc*	λ_{max} (nm)	L	a	b	Color (red)	Color (ox)	Eg (eV)
PTh	0.63	0.58	495	(ox) 57 (red) 51	(ox)-7 (red) 52	(ox)-2 (red) 46	bright red	Pale blue	1.92
ODME/PTh		+1.85	460	(ox) 43 (red) 42	(ox) -3 (red) 35	(ox) 8 (red) 36	pale red	Gray-green	1.93

Volts vs. Ag/Ag⁺

(ox) oxidized state, (red) reduced state

Below, the extreme states, that is, fully oxidized and fully reduced states of PCL-co-PTh, with the corresponding colors can be seen.

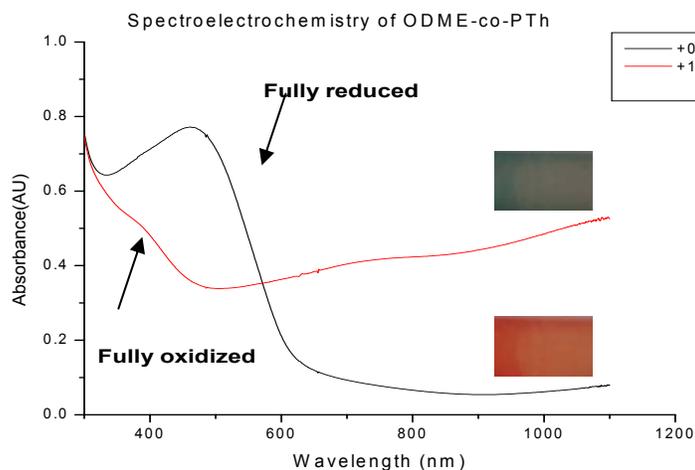


Figure 3.2.17 Extreme states of ODME-co-PTh

ODME-co-PTh copolymer was grayish-green at its fully oxidized state, pale red at its reduced state. The band gap value is close to PTh, but, L*a*b values are different. This variation in color may point to the formation of a new copolymer.

3.2.9 Electrochromic switching

Electrochromic switching behavior of the film was monitored by recording absorption spectra while stepping the potential between -0.5 V and +1.7 V, for a switching time of 5 seconds. Beginning from the first step, the contrast of ODME-co-PTh decreased. The contrast of ODME-co-PTh for the first step was measured as 22% but it ceased after third step. Switching time was found to be 1.1 seconds.

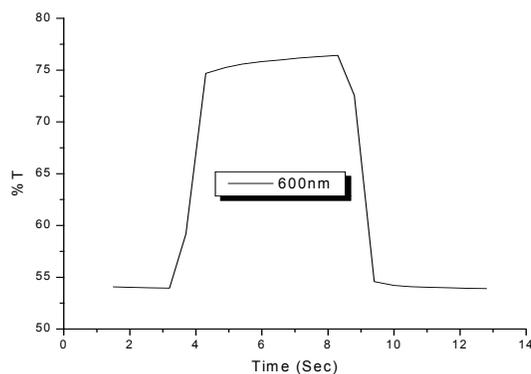


Figure 3.2.18 Switching of ODME-co-PTh

3.3 Characterization of Device Applications

Having observed reversible, distinguishable color changes upon oxidation and reduction for both of our copolymers, we have decided to employ them in device applications. Both PCL-co-PTh and ODME-co-PTh were used as anodically coloring materials, since they have reasonable band gap values which should be <3.0 eV for a material to be used as anodically coloring polymer [42].

The cathodically coloring polymer was poly(3,4-ethylenedioxythiophene), (PEDOT). Neutral PEDOT exhibits an electronic band gap (E_g) defined as the onset for the π to π^* absorbance, of approximately 1.7 eV and has a strong peak at 2.2 eV causing the films to be deep blue and absorbing. Thin films of the unsubstituted PEDOT polymer are transmissive blue-gray in their oxidized state, and a highly absorbing blue-violet in their reduced state, suggesting its use as a cathodically coloring electrochromic material [43].

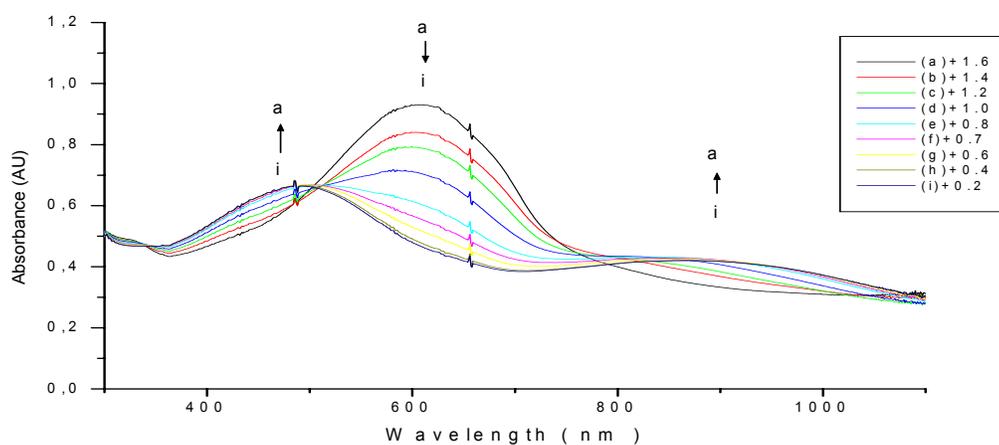
After the discovery of electrochromic materials and the concept of electrochromic devices, a need of a new phase of electrolyte has emerged. Many types of gel electrolytes have been prepared [51, 52]

In our devices, PMMA based conducting gel electrolyte was used. Highly volatile ACN is used because of the ease of evaporation through a gelly medium. When the excess ACN is evaporated, the gel electrolyte seals itself and the device construction stays as it is

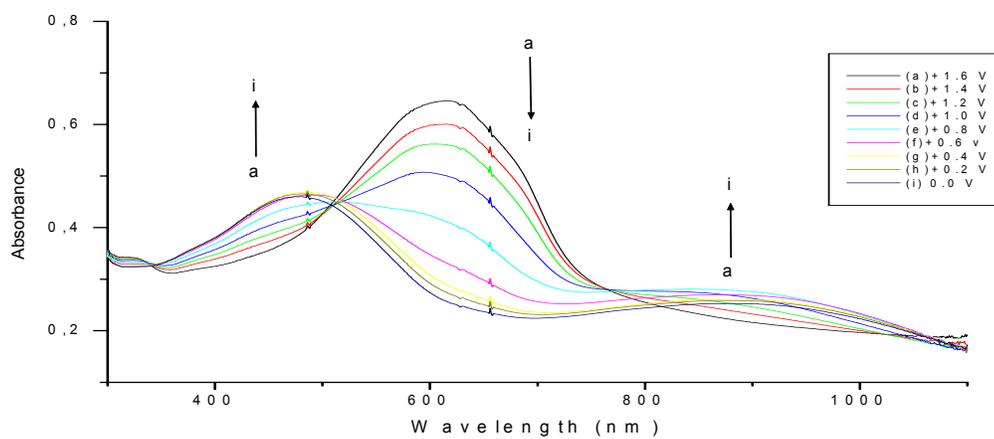
3.3.1 Spectroelectrochemistry

Spectral changes that occur during potential changes can be seen below for PCL-co-PTh/PEDOT device. Potential was gradually increased from +0.2V to +1.6V. At +0.2 V, the dominant wavelength is 475 nm, due to the π - π^* transition of anodically coloring electrochromic materials, since PEDOT layer

is in its oxidized state, revealing transparent sky blue color. When potential is increased, that is, copolymer layers start to oxidize, the maximum wavelength shifts to 610nm, revealing the dominance of $\pi-\pi^*$ transitions of PEDOT this time. In this situation, the copolymer exhibits gray-blue color, since it is in oxidized state.



(a)



(b)

Figure 3.3.1 Spectroelectrochemistry of (a) PCL-co-PTh/PEDOT device
(b) ODME-co-PTh/PEDOT device

The same behavior is also observed for ODME-co-PTh/PEDOT device. The maximum observed at 480 nm, gradually shifted to 625 nm. At the same time $\pi \rightarrow \pi^*$ transitions of copolymers are ceased, another absorption peak evolved at around $\sim 900\text{nm}$, corresponding to the formation of their charge carriers

3.3.2 Switching

Electrochromic switching studies were carried out to monitor absorbance changes with time during repeated potential stepping between reduced and oxidized states to obtain an insight into changes in optical contrast. For this purpose, double potential step chronoamperometry was performed. Potential was stepped between -0.5 V and $+1.7\text{ V}$, with a residence time of 5 seconds. That is, for 5 seconds, -0.5 V potential is applied, for the following 5 seconds, $+1.6\text{ V}$ potential is applied in a continuous sequence.

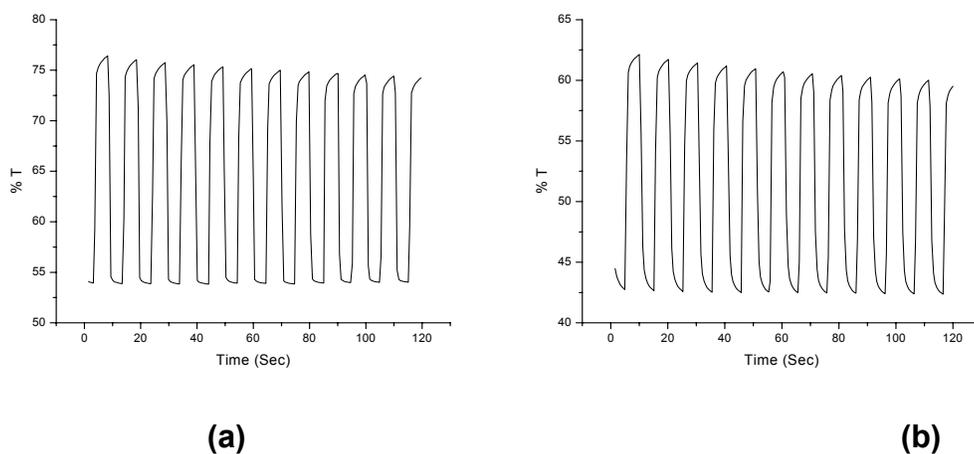


Figure 3.3.2 Switching of (a) ODME-co-PTh/PEDOT device
(b) PCL-co-PTh/PEDOT device

The spectral behavior of the device is monitored for 120 seconds time, at a wavelength of 600 nm. This wavelength is selected in the light of spectroelectrochemistry results. That is the wavelength at which the highest %T is seen.

As indicated here, PCL-co-PTh/PEDOT device has switching time of 1.1 seconds, meaning, 1.1 seconds is required to change from one state to another. This is a reasonable value, but the transmittance drops with continuous cycles. Transmittance is 20% at first cycle, while it drops to 16 % at 10th cycle.

ODME-co-PTh/PEDOT device shows 1.2 seconds of switching time and better stability for numerous cycles when compared to PCL-co-PTh/PEDOT device. % T of ODME-co-PTh/PEDOT device is 22% at the first cycle, and 20% at the 10th cycle. When the switching behavior of ODME-co-PTh copolymer is considered, its switching behavior in the device can be considered as a quite good improvement. The reason for this improvement can be the controlled doping-undoping of the film, since the charge balance is provided by matching the redox sites.

3.3.3 Stability

Stability is examined by sweeping the potential between 0V and +1.7V for 500 cycles, with a scan rate of 500mV/sec.

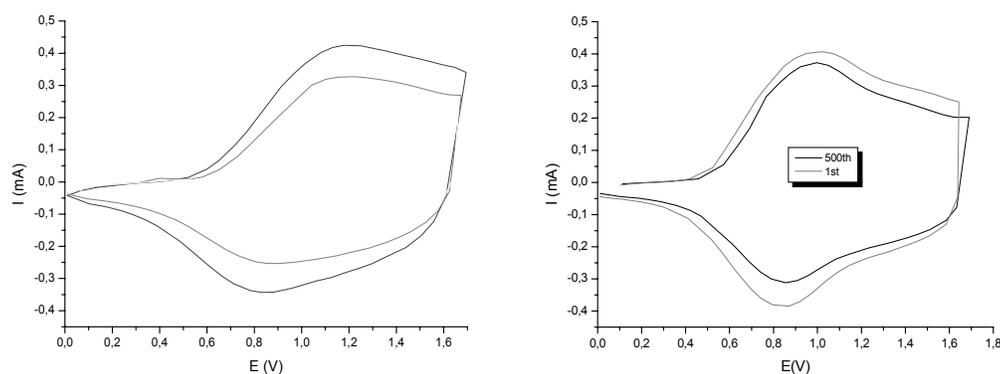


Figure 3.3.3. Stability of (a) PCL-co-PTh/PEDOT device
(b) ODME-co-PTh/PEDOT device

CV is used for this process. Stability data of the ODME-co-PTh/PEDOT device and PTh/PEDOT device can be seen in the figure given above. Upon numerous cycles, PCL-co-PTh/PEDOT device lost 9.5 % of its stability when ODME-co-PTh/PEDOT device lost 8.8 % of its activity. These results support the switching data since the behaviors are similar.

3.3.4 Open Circuit Stability (Memory)

This experiment is done to see the color persistence in the electrochromic device in other words, the ability to retain its color without

applying voltage. The experiment was performed by applying 0 and +1.6V for 1 second's time, as pulses in 200 sec intervals

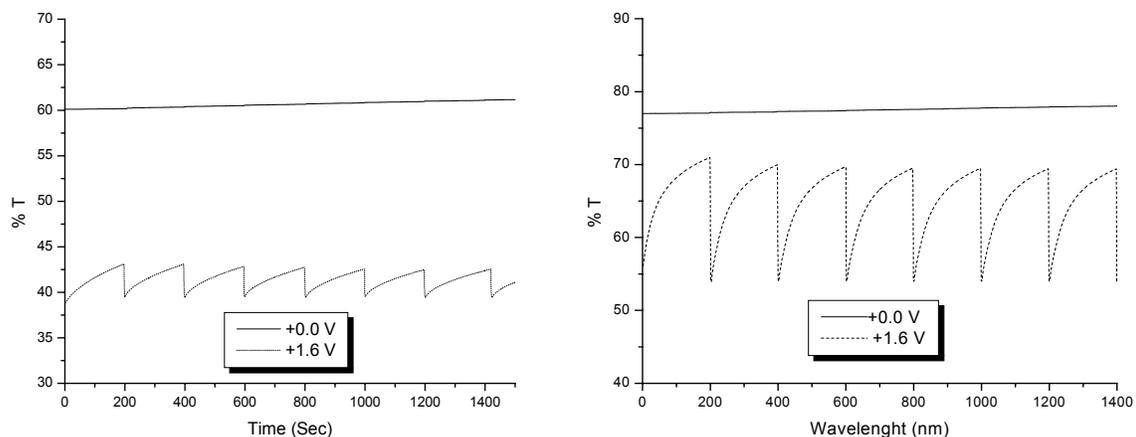


Figure 3.3.4 Open Circuit Stability (Memory)

Optical spectrum for both states was monitored continuously at 610nm. When PCL-co-PTh/PEDOT device is in its reduced state and exhibiting red-brown color, it is quite stable. There is no %T difference between the impulses which implies that the color is retained. However, in its oxidized state, the blue color is not persistent.

While %Transmittance = 42.5%, in the moment of impulse, it decreases to 38% after 200 sec. Still, it is more stable when compared to ODME-co-PTh/PEDOT device. Although its reduced state is reasonably stable, it exhibits about 30% loss of transmission in its oxidized state.

3.3.5 Colorimetry

The colorimetry data of the devices are given below. The Lab values were measured in their fully oxidized state: at 1.6V, and fully reduced state, at -0.5 V.

Table 3.4 Colorimetry data

	L	a	b	Color (red)	Color (ox)
<i>PCL-co-PTh/PEDOT</i>	(ox) 25 (red) 35	(ox)-4 (red) 8	(ox)-19 (red) 26	cinnamon	dark blue
<i>ODME-co-PTh/PEDOT</i>	(ox) 49 (red) 50	(ox) -4 (red) 11	(ox) -5 (red) 26	reddish-brown	pale blue

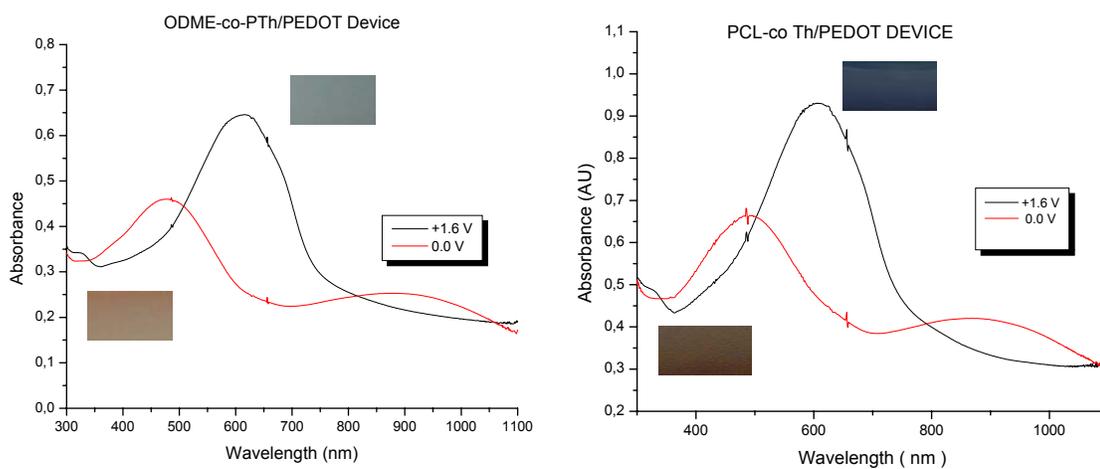


Figure 3.3.5 Extreme states of devices

CHAPTER IV

CONCLUSIONS

Poly- ϵ -caprolactone and oxalic acid-dithiophen-3-yl methyl ester was successfully synthesized. Their copolymerization in ACN/TBAFB solvent/electrolyte couple, with both thiophene and pyrrole were achieved. Their redox behavior were investigated via cyclic voltammetry. For both PCL and ODME, their CV's significantly differ from that of PTh or PPy. FTIR results showed that, the characteristic peaks belonging to precursor materials in addition to Py and Th were seen. The proof of copolymerization was evident in terms of FTIR results. They possess reasonable conductivity values which are lying in the conductivity and semi-conductivity range. the formation of copolymers were also proved by the surface morphologies of the films. The thermal behavior revealed the formation of thermally stable copolymers. Their spectroelectrochemistry results showed that, both PCL and ODME can switch between their fully oxidized and fully reduced states. They both show distinctive colors, changing as a result of the electronic transitions and this change is reversible. These properties enable them to be used in device construction.

Electrochromic devices were constructed by employing the copolymers as anodically coloring materials, while PEDOT was used as cathodically coloring material. Dual-type devices exhibited reversible color change between the two states, reasonable stabilities, and good optical memory in their reduced state. Since devices change color between red and blue, these devices can be used as display devices.

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