43048

DEVELOPMENT OF SOLUBLE π - CONJUGATED POLYMERS AND EVALUATION OF THEIR ELECTROLUMINESCENCE PROPERTIES

A thesis submitted
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

By

Jatindranath Maiti

Registration No. 052 of 2004

Department of Chemical Sciences
Tezpur University
Napaam, Tezpur - 784028
Assam, India

August, 2009

Dedicated to my
Maa, Baba,
Jeythu and Jeythima
With love and gratitude

Development of soluble π - conjugated polymers and evaluation of their electroluminescence properties

ABSTRACT

The present thesis deals with synthesis, characterization and evaluation of thermal, electrochemical, photoluminescence and electroluminescence properties of a few new ester substituted polythiophenes. A considerable effort has been devoted to the synthesis of polymers with special emphasis on the solubility of π- conjugated polymers. The thesis also provides an account of fluorescence quenching and sensor application of ester substituted polythiophenes. The contents of the thesis have been compiled into five chapters.

Chapterl deals with the general introduction of π- conjugated polymers and their application in light emitting diode. A brief review on substitute polythiophenes with special emphasis on solubility, band gap and color tuning, fluorescence efficiency, electrochemical behavior and electroluminescence properties has been described in this chapter. This chapter also describes the scopes and objectives along with the plan and methodology of the present investigation.

Chapter 2 describes the synthesis and characterization of monomers and polymers and their thermal properties. We have synthesized the following 3-ester substituted thiophene.

i) Hexyl 2-(thiophene-3-yl) acetate (HTA)
ii) Octyl 2-(thiophene-3-yl) acetate (OTA)
iii) Decyl 2-(thiophene-3-yl) acetate (DTA)
iv) Dodecyl 2-(thiophene-3-yl) acetate (DDTA)
v) 3-pentadecylphenyl 2-(thiophene-3-yl) acetate (PDPTA)
vi) 3-pentadecylcyclohexyl 2-(thiophene-3-yl) acetate (PDCHTA)
vii) Quinoline -8-yl 2-(thiophene-3-yl) acetate (QTA)

The monomers were synthesized by esterification reaction of 3-thiophene acetic acid and corresponding alcohols and characterized by ^{1}H NMR, FTIR and UV-Vis analysis. The polymerization was accomplished by oxidative coupling in the presence of $FeCl_3$. The synthesized polymers were characterized by ^1H NMR, FTIR, UV-Vis, XRD and GPC analysis. The polymers were found to be soluble in THF and $CHCl_3$. Thermal properties of the polymers were studied by TGA and DSC technique. Polymers have found good thermal stability.

In **Chapter 3,** electrochemical, photo and electroluminescence properties of synthesized polymers have been discussed. The oxidation and reduction potential of polymers were assessed in cyclic voltammetry method. Redox stability of polymers was tested by cyclic voltammetry upto 10 cycles. Furthermore, band gap of polymers was measured by electrochemically and compared with optical method. Photoluminescence properties of polymers in solution and solid state were investigated. The relative quantum yield of polymers with respect to Rhodamine B dye was measured. The electroluminescence properties of polymers were studied by fabricating LED device. The device configuration was ITO / PEDOT: PSS /Polymer/ LiF / Al.

Chapter 4 includes the fluorescence quenching and application of polymers as chemical sensor. The behaviour of photoluminescence property was studied in presence of acids, metals ions, nucleotides and protein (l-proline). The polymers showed both fluorescence quenching in the presence of acids, copper, cadmium and lead metal ions and enhancement in presence of analytes such as aluminium and zinc metals ions, nucleotides and protein (l-proline). The detection limit of HCl acid, copper, lead and cadmium ions has been evaluated by optical quenching method.

Chapter 5, the last chapter of the thesis includes the concluding remarks, highlights of the findings and future scopes of the present investigation. A series of ester substituted polythiophenes has been developed by $FeCl_3$ oxidative coupling polymerization technique, resulting in soluble and high thermal stable polymers. A correlation of structure - property has been drawn with respect to their optical properties. Finally these polymers have been utilized in light emitting diode and in chemical sensors.

DECLARATION BY THE CANDIDATE

The thesis entitled "***Development of soluble π- conjugated polymers and evaluation of their electroluminescence properties***" is being submitted to the Tezpur University in partial fulfilment for the award of the degree of Doctor of Philosophy in *Chemical Sciences* is a record of bonafide research work accomplished by me under the supervision of Prof. S. K. Dolui.

All helps received from various sources have been duly acknowledged.

No part of this thesis has been submitted elsewhere for award of any other degree.

Jatindranath Maiti

Date: 28/08/2009
Place: Tezpur

Jatindranath Maiti
Department of Chemical Sciences
Tezpur University

TEZPUR UNIVERSITY
(A Central University Established by an Act of Parliament)
NAPAAM, TEZPUR-784 028
DISTRICT : SONITPUR :: ASSAM :: INDIA

Ph : 03712 - 267004
03712 - 267005
Fax : 03712 - 267006
03712 - 267005
e-mail: ~~adm~~ dolui @agnigarh.tezu.ernet.in

CERTIFICATE OF THE SUPERVISOR

This is to certify that the thesis entitled "***Development of soluble π - conjugated polymers and evaluation of their electroluminescence properties***" submitted to the School of *Science and Technology*, Tezpur University in partial fulfilment for the award of the degree of Doctor of Philosophy in *Chemical Sciences* is a record of research work carried out by *Mr. Jatindranath Maiti* under my supervision and guidance.

All help received by him from various sources have been duly acknowledged.

No part of this thesis has been submitted elsewhere for award of any other degree.

Date: 28/08/2009

Place: Tezpur

Prof. S. K. Dolui (Supervisor)
School of Science and Technology
Department of Chemical Sciences

Preface

Conjugated polymers are valuable material for scientists to design electronic devices like light emitting diode (LED) to generate light, photovoltaic cell to generate power, sensor to detect materials The advancement made in this field is so rapid that almost every day a new polymer or a modification of existing polymer is appearing in the journals

Conjugated polymers offer several advantages over inorganic and organic molecules such as flexibility, relative ease of processing by common techniques (spin and blade coating, ink – jet printing), or the ability to control the wavelength of emission by changing the molecular structure of the emitting material.

A large number of different classes of conjugated polymers have been developed such as poly(N-vinylcarbazole)s, poly(fluorine)s (PFs), poly(p-phenylene vinylenes) (PPVs), and poly(thiophenes) (PTs) While PPV and its derivatives are still the leading materials for green light –emitting PLEDs, the larger band gap PFs are the blue –light emitting polymers and polythiophenes and its derivatives are remembered for red

The major problem encountered in conjugated polymer is its solubility A considerable effort has been devoted to the synthesis of π- conjugated polymers with special emphasis on the improved solubility The present thesis deals with synthesis, characterization and evaluation of thermal, electrochemical, photoluminescence and electroluminescence properties of few new ester substituted polythiophenes The thesis also provides an account of fluorescence quenching and sensor application of ester substituted polythiophenes The contents of the thesis have been compiled into five chapters Chapter1 deals with the general introduction of π- conjugated polymers and their application in light emitting diode Chapter 2, describes the synthesis and characterization of monomers and polymers and their thermal properties In Chapter 3, electrochemical, photo and electroluminescence properties of synthesized polymers have been discussed Chapter 4 includes the fluorescence quenching and application of polymers in chemical sensor Chapter 5, the last chapter of the thesis includes the concluding remarks, high lights of the findings and future scopes of the present investigation.

We hope that this study contributes a little knowledge to the rapidly advancing field of conjugated polymers and also opens up the possibilities of further research on the subject

This research was carried out in the Department of Chemical Sciences, Tezpur University with financial assistance from the Defence Research and Development Organisation (DRDO) and University Grant Commission (UGC), New Delhi

Jatindranath Maiti

Acknowledgement

First of all, I would like to convey my pranams to my Baba and Jeythima, who passed away when I was doing my Ph D research work The Outcome of this thesis is their blessings from the heaven.

I would like to express my deep sense of profound gratitude and indebtedness to my respected teacher and supervisor, Prof S K Dolui for his inspiring guidance, endless patience, and work of freedom and the opportunity to work in his laboratory It would have not been possible for me to bring out this thesis without his help, fatherly care, and constant encouragement throughout the research work

I am grateful to Dr R K Dutta, Prof N Karak and Prof A Kumar, Tezpur University, for their suggestions and discussions

I am thankful to Dr M N Kamalasanan and Dr (Mrs) R Srivastava, NPL, New Delhi for an adventure in LED device fabrication and testing at NPL, New Delhi I am also thankful to Mr Amit Kumar, Ms Omwati, Ms Rakhi Grover, Ms Gayatri Chouhan, Mr Arunanadan, Ms Priyanka Tyagi, Mr Rahul Kumar, Ms Manisha Bajpai, Mr Arjun Singh, Mr Anzar Gani for their constant support and help in fabricating the LED device

I am grateful to Dr P P Wadgaonkar and Dr A Choubey, NCL, Pune for providing me some organic chemicals My sincere thanks go to Dr N SenSarma and Mr Samiul Islam, IASST, Guwahati, for providing GPC data. I thank Dr Dibyendu Bag, DMSRDE, Kanpur for his help I must thank Dr Igor Perepichka, University of Central Lancashire, UK for his valuable suggestion during my thesis preparation. I am really thankful to Sadhan Sir, Sibdasda, Abhijitda, Swapan, Abuda, Ganeshda, Soumenda, Dipuda, Narayan, Niladri, for their constant help to get the literature

My special thanks go to Mr B Gohain, Dr B Saikia, Mr N Dutta, Mr P Nath, Mr R Borah, Mr S Phukan, Mr P S Barua, Mr S Das, Mr R Boruah, Mr J Borah, Mr H Gogoi, Mr H Das, Mr G B Chhetry for their timely help in many situations

I would like to thank my friends Mr Nilay Kanti Pramanik and Mr Praveen Kumar for their valuable support and help I am thankful to all well wisher especially, Paritoshda, Tapasiba, Nandinidi, Illiusda, Rashmiba, Digantada, Rabiulda, Rajuda, Suvangshuda, Jyotishmoyda, Parashaba, Kausikda, Hiranyada, Manashiba, Nilkamalda, chandanda for their help

I am truly thankful to my lab mates and friends Binod, Anamika, Lakhya, Muhsina, Surajit, Isha and Amar, who have taught and helped me in many aspect of life It has been a great adventure I will remember forever for their friendship and help

I am also thankful to all my friends especially Nirmala, Kalyan, Pubalee, Bulumani, Ajantaba, Lakhinath, Subrata, Suresh, Barnali, Shremayee, Harekrishna, Sivaprasad, Buddha, Uday, Goutam, Mridula, Mandakini, Jeenajyoti, Dhruba Bijoy, Biplab, Ankur, Rashmi, Satya, Upamanyuda, Madhurjya, Subasit, Debasish, Sovan, Soumik, Smritimala, Nabanita, Madhurjya, Sanjeebda, Jyotiprasad, Ranjan, Sudhir, Nabanath, Prasenjitda, Narayan, Dipak, Bimalendu, Kunal, Bidyut for their support and help

I am grateful to Mrs. Sutapa Dolui for her motherly care, kindness and encouragement.

I thank the Defence Research and Development Organisation (DRDO) for funding a project, and University Grant Commission (UGC), New Delhi for awarding me JRF and SRF to complete this research.

I would like to convey my pranams to my grandmother for her blessing, love and affection. I would like to express my respect and gratitude to my Maa, Barodidi, Barodada, Mezodada, Sezodada, Sezoboudi, Chhotodada, Chhotodidi, Chhoto Jamai for their constant encouragement, inspiration and support throughout my studies to fulfil my dream. I am grateful to Moudidi, Chhanchalda, Piudidi and Amitabhda for their constant encouragement and support. My extreme loves go to my nephew Sudin and Aditya and my niece Jhinuk and Rashi for their great source of motivation.

Most of all, I would like to convey my deep regards and profound respect to my Jeythu, Prof. Sukumar Maiti for his advice, unwavering support, constant source of inspiration. It would have not been possible for me to accomplish the research without his mission and vision.

Finally, I thank the authorities of Tezpur University for granting me the permission to do this work.

Looking back at all the hurdles, twists and turns that I have crossed at various stages in my life, I honestly agree it is not only me who did everything to reach this stage. At each difficult moment there has been someone who rescued me.

Jatindranath Maiti

Contents

Abstract i

Preface v

Acknowledgement vi

Table of Contents vii

List of Tables x

List of Figures xi

List of Schemes xiii

Abbreviations xiv

Chapter 1: Introduction

1.1 Conjugated polymers 1

1.2 Synthesis of conjugated polymers 2

1.3 Properties of conjugated polymers 17

1.4 Characterization of luminescenct conjugated polymers 17

1.5 Polythiophene and its derivatives 25

1.6 Objectives and plan of work 32

Reference 35

Chapter 2: Synthesis and characterization of ester substituted polythiophenes

2.1 Introduction 39

2.2 Materials 40

2.3 Instrumentations 40

2.4 Experiment 42

2.5 Results and discussions 47

2.6 Conclusions 84

References 85

Chapter 3: Electrochemical, photoluminescence and electroluminescence properties of ester substituted polythiophenes

3.1 Introduction 87
3.2 Experiment 89
3.3 Results and discussions 92
3.4 Summary of properties in table 122
3.5 Conclusion 123
References 124

Chapter 4: Fluorescence quenching of ester substituted polythiophenes and their application as chemical sensor

4.1 Introduction 127
4.2 Experiment 128
4.3 Results and discussions 128
4.4 Conclusion 141
References 142

Chapter 5: Conclusion and future scope of the present investigation

5.1 Conclusion 144
5.2 Future scope of the present investigation 147
Publication 148

List of Tables

Chapter	Table	Title	
2	2.1	Molecular weight of polymers	64
	2.2	Degree of polymerization and solubility of polymers	67
	2.3	Absorption of monomer and polymers	69
	2.4	Absorption edge and optical band gap of polymers	73
	2.5	Weight loss of polymers at different temperature	75
	2.6	Tg and Tm of polymers	83
3	3.1	Oxidation and reduction potential of polymers	92
	3.2	Onset ox/red potentials and HOMO and LUMO energy levels of polymers	102
	3.3	Electrochemical and optical band gap of polymers	103
	3.4	Absorption, emission and stokes shift of polymers	104
	3.5	Limiting concentration of polymers	109
	3.6	PL emission maxima of polymers in solution and solid	113
	3.7	Relative fluorescence quantum yield of polymers	115
	3.8	Turn on voltage of polymers	118
	3.9	All the properties of polymers	122
4	4.1	K_{sv} and detection limit of PQTA polymer for HCl acid	134
	4.2	K_{sv} and detection limit of PQTA polymer for metal ions (Cu^{+2}, Cd^{+2}, Pb^{+2})	137

List of Figures

Chapter	Figure	Title	
1	1.1	Jablonski diagram for fluorescence	18
	1.2	Photoluminescence process	19
	1.3	A simplified excitonic band structure	22
	1.4	LED structure	23
	1.5	Energy level diagram of LED device	24
	1.6	Possible diad linkages for 3-alkyl thiophene	26
	1.7	Colour tuning in 3- substituted polythiophenes	29
	1.8	A voltagram of an ideal system in forward scan	30
2	2.1-2.7	FTIR spectra of monomers	49
	2.8- 2.14	Proton NMR spectra of monomers	53
	2.15-2.21	FTIR spectra of polymers	57
	2.22-2.28	Proton NMR spectra of polymers	61
	2.29-2.35	GPC curve of polymers	65
	2.36-2.42	UV- Vis Spectra of monomers and polymers	69
	2.43	X-ray diffractograms of polymers	74
	2.44-2.50	TGA curve of polymers	76
	2.51-2.57	DSC curve of polymers	80
3	3.1	Typical 3-electrode electrochemical cell	90
	3.2	Fabrication of electroluminescence device	91
	3.3-3.9	CV of polymers	93
	3.10-3.16	CV (10 cycles) of polymers	97
	3.17	Measurement of onset in CV	101

	3.18-3.24	Absorption, emission and stokes shift of polymers	105
	3.25	Normalized PL spectra of polymers	108
	3.26-3.32	PL intensity of polymers in various concentration	110
	3.33	PL spectra of polymers excited at 350 nm in film	114
	3.34	EL spectra of polymers at 15 V	117
	3.35-3.41	I-V characteristic of polymers	118
4	4.1	Fluorescence quenching of PQTA polymer	129
	4.2-4.8	Fluorescence of polymers in HCl acid	129
	4.9	Normalized PL spectra of PQTA in various acids	133
	4.10	Fluorescence of PQTA in different concentration of hydrochloric acid, excited at 392 nm	135
	4.11	Fluorescence intensity versus different concentration of $NaHCO_3$ in PQTA polymer HCl solution	135
	4.12	SV plot of PQTA polymer in HCl acid	136
	4.13	Fluorescence of PQTA polymer in various metal ions	137
	4.14	SV plot of PQTA polymer in copper metal ions	138
	4.15	SV plot of PQTA polymer in cadmium metal ions	138
	4.16	SV plot of PQTA polymer in lead metal ions	139
	4.17	Fluorescence of PQTA in aluminium and zinc ions	139
	4.18	Fluorescence of PQTA in nucleotides and protein	140

List of Schemes

Chapter	Scheme	Title	
1	1.1	Chain polymerization of acetylene	3
	1.2	Step polymerization synthesis of polythiophene	3
	1.3	Precursor synthesis of PPV	6
	1.4	Mechanism of electrochemical synthesis of PT	8
	1.5	Free radical mechanism of oxidative coupling of PT	10
	1.6	Synthesis of P3AT via $FeCl_3$ oxidative coupling	11
	1.7	Curtis synthesis of P3AT	12
	1.8	Synthesis of poly (9, 9-dialkylfluorene) via Yamamoto coupling	12
	1.9	Metal –catalyzed cross coupling mechanism	13
	1.10	Grignard synthesis of P3AT	13
	1.11	Regio-regular P3AT synthesis	14
	1.12	Reike synthesis of P3ATs and catalyst specificity	15
	1.13	Suzuki coupling	16
	1.14	Stille coupling	16
2	2.1	Synthesis of monomers and polymers	48
3	3.1	EL mechanism	116
	3.2	Energy level diagram of polymers	117

Abbreviations used in the thesis

CP	Conjugated polymer
CV	Cyclic voltammetry
DCE	Dichloroethene
DDTA	Dodecyl 2-(thiophene-3-yl) acetate
DMAc	Dimethyl acetamide
DMAP	Dimethylamino pyridine
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
DP	Degree of polymerization
DSC	Differential scanning calorimetry
DTA	Decyl 2-(thiophene-3-yl) acetate
EL	Electroluminescence
FET	Field effect transistor
FTIR	Fourier transform infrared spectroscopy
GPC	Gel permeation chromatography
HOMO	Highest occupied molecular orbital
HTA	Hexyl 2-(thiophene-3-yl) acetate
ITO	Indium tin oxide
LED	Light emitting diode
LUMO	Lowest unoccupied molecular orbital
MEH- PPV	poly [2-methoxy-5-(2- ethylhexyloxy)-1,4-phenylenevinylene)]
NMR	Nuclear magnetic resonance spectroscopy
OTA	Octyl 2-(thiophene-3-yl) acetate
PA	Polyacetylene
PAT	Polyalkylthiophene
PDCHTA	3-pentadecylcyclohexyl 2-(thiophene-3-yl) acetate

PDDTA	Poly (dodecyl-2-(thiophene-3-yl) acetate)
PDPTA	3-pentadecylphenyl 2-(thiophene-3-yl) acetate
PDTA	Poly (decyl-2-(thiophene-3-yl) acetate)
PEDOT	Poly (ethylene dioxythiophene)
PHTA	Poly (hexyl-2-(thiophene-3-yl) acetate)
PL	Photoluminescence
PLED	Polymer light emitting diode
POTA	Poly (octyl-2-(thiophene-3-yl) acetate)
PPDCHTA	Poly (3-pendecyl cyclohexyl-2-(thiophene-3-yl) acetate)
PPDPTA	Poly (3-pendecylphenyl-2-(thiophene-3-yl) acetate)
PPP	Poly (p-phenylene)
PPV	Poly (phenylenevinylene)
PQTA	Poly (quinoline 8-yl-2-(thiophene-3-yl) acetate)
PSS	Poly (styrene sulfonate)
PT	Polythiophene
QTA	Quinoline -8-yl 2-(thiophene-3-yl) acetate
ROMP	Ring opening metathesis polymerization
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
T_m	Melting temperature
UV	Ultra violet
XRD	X-ray diffraction
ϕ	Quantum yield
λ	Wave length

CHAPTER 1

Introduction

1.1 Conjugated polymers

Today, conjugated polymers (CPs) represent one of the most highly progressive fields of polymer research and mesmerise much importance in light emitting diode, photovoltaic cell and sensors application [1-51]. Along with semiconducting properties, conjugated polymers extend light weight, good strength, flexibility and easy processability. CPs have an alternating sequence of single and double bonds along the polymer backbones. The overlap of π bonding and π* antibonding molecular orbitals forms a continuous system of electron density along the polymer backbone. CPs are not ideal conjugated systems. There is a break in the conjugation length due to twists and kinks, as well as due to the chemical defects. The extent of this overlap (conjugation length) together with the bond alternation determines the HOMO-LUMO band gap. CPs have band gaps in the range of 1 to 4 eV, which makes them ideally suited for applications in optoelectronic devices operating in the visible light range.

The field of conducting polymers was born in 1977 when electrically conductive polymers were discovered i.e. polyacetylene doped with iodine [52]. In recognition of this extraordinary discovery, the scientists Alan J Heeger, Alan MacDiarmid, and Hideki Shirakawa were jointly awarded the Nobel Prize in chemistry in 2000 for "the discovery and development of electrically conductive polymers" . By 1979, Su, Schrieffer, and Heeger had proposed a theoretical model describing conductivity in doped conjugated polymers [53-54], and a collection of new polymers had been synthesized, including the luminescent polymer poly (p-phenylene) (PPP) [55]. Additionally, in 1979 it was discovered that these materials could also be electrochemically doped to achieve a conductive state, and that this process was reversible [56]. In the 1980's and 1990's research focus tended to be on demonstrating the usefulness of semiconducting and conducting polymers in a broad range of applications. Organic field-effect transistors [57], electrochromic devices [58], actuators [59], and several other applications based on conjugated polymers all made their appearance in the late 1980's [60-62]. In 1990, electroluminescence from a light-emitting diode based on the luminescent polymer poly (phenylenevinylene) (PPV) was demonstrated [63]. One year later, a polymer light-emitting diode was fabricated by spin-casting a polymer film from the soluble PPV derivative, poly [2-methoxy-5-(2- ethylhexyloxy)-1,4-phenylenevinylene)] (MEH-PPV) [64]. In the mid-1990's the polymer based photovoltaic cell [65-66] and the polymer based light-emitting electrochemical cell [67-68] were reported. In 2004, the most significant gain comes from the liquid processing capabilities of polymers [69]. This opens up the possibility of making large area, mechanically flexible devices on a wide range of substrates including plastic, paper, or even textiles. In addition, film deposition can be skilled by cheap, efficient processes such as ink-jet printing, screen-printing, and others that will allow roll-to-roll production of technologies such as all-polymer displays. Currently the field of polymer electronic devices has reached the performance and stability necessary to achieve commercial production for a few applications [43-51, 70].

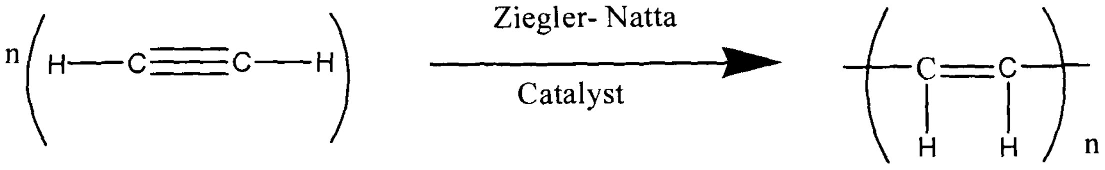
1.2 Synthesis of conjugated polymers

The first challenge in studying conjugated polymers is their synthesis. Conductive polymers may be synthesized by any one of the following techniques [71-83]:

- Chain Polymerization
- Step Polymerization
- Photochemical polymerization
- Metathesis polymerization
- Emulsion polymerization
- Template polymerization
- Solid-state polymerization
- Plasma polymerization
- Inclusion polymerization
- Pyrolysis
- Soluble precursor polymer preparation
- Electrochemical polymerization
- Chemical polymerization

1.2.1 Chain polymerization

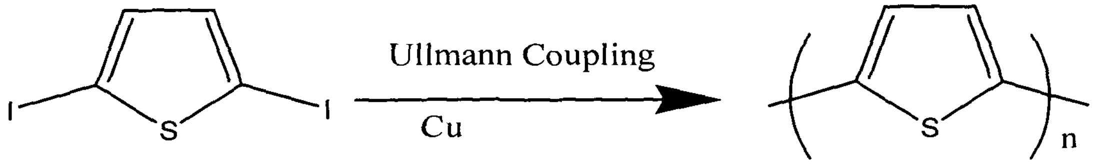
Polyacetylene was prepared by the chain polymerization of acetylene by Ziegler – Natta catalysts [84]. Freestanding films of polyacetylene prepared by the Shirakawa process involves the passage of acetylene gas over the $TiCl_4/Al(C_2H_5)_3$ catalyst solution in *n*-heptane at 0°C, and the polymer is obtained as a film on the surface of the catalyst solution.



Scheme 1.1: Chain polymerization of acetylene

1.2.2 Step polymerization

Step polymerization, unlike chain polymerization, involves either a self – condensation or condensation between two reactants with the elimination of some small molecules [85]. Polythiophene is prepared by Ullmann coupling reaction of 2,5-diiodothiophene with copper [86].



Scheme 1.2: Step polymerization synthesis of polythiophene

1.2.3 Photochemical polymerization

Photochemical polymerization takes place in presence of sunlight. This technique utilises photons to initiate a polymerization reaction in presence of photosensitizers. The mechanism of photopolymerization involves the onset of the one-electron transfer process from a photosenitizer by the oxidizing agent (electron acceptor) under photoirradiation, which initiates polymerization of the monomer. Photochemical synthesis has the advantage of ease in control of polymerization so that a film of any desired thickness can be deposited on any particular area of a suitable substrate. Pyrrole has been photopolymerized using a ruthenium (II) complex as photosensitizer. Under photoirradiation, Ru (II) is oxidised to Ru (III) and the polymerization is initiated by a one –electron transfer oxidation process [87].

1.2.4 Metathesis polymerization

Metathesis polymerization is unique, different from all other polymerizations where all the double bonds in the monomer remain in the polymer. It was the natural outgrowth of Zieglar-Natta polymerization. Here catalysts are similar, and often identical, i.e. a transition metal compound plus usually an organometallic alkylating agent. Metathesis polymerization is further divided into three classes: ring opening metathesis of cyclo-olefins (ROMP); metathesis of alkynes, acyclic or cyclic; and metathesis of diolefines. By far the greatest amount of work has been done on ROMP [72, 88].

1.2.5 Emulsion polymerization

The emulsion polymerization method is employed to obtain the porous host polymer and an imbibitions technique is used to incorporate polyheterocylic polymers in the host polymer. The scope of this work is to study the effects of initial molar ratios of oxidants to monomer and the effect of environmental stability on the conductivity of composites [89].

The host polymer was first imbibed with monomer (pyrrole or 2,2'- bithiophene)ether solution and then partially dried to evaporate ether. Subsequently, the partially dried host polymer was soaked again in excess oxidant ($FeCl_3$) solution for 20 min. The conducting composites were rinsed with water and acetone [90].

1.2.6 Template polymerization

Highly oriented fibrils of conjugated polymers may be synthesized by the template method in which the pores of the porous membrane act as templates for the nascent polymer. Nanoscopic polyacetylene fibrils has been synthesized by polymerizing acetylene within the pores of a filtration membrane impregnated with the solution of a Ziegler-Natta catalyst, $Ti(OBu)_4/AlEt_3$. Template synthesized PA has been found to be preferentially oriented parallel to the fibril axis [91-92].

1.2.7 Solid State Polymerization

Solid state polymerization is carried out in cases where the lattice structures of both the monomer and the polymer have considerable similarity. Except for the polymerization of tetrasulfer tetranitride, S_4N_4, into poly(sulphur nitride), $(SN)_x$, the polydiaceylenes are synthesized by the solid state polymerization of their monomer crystals under ultraviolate(UV) or γ radiation, or even by thermal initiation. In all such cases, nearly defect-free polymer crystals are obtained [93].

1.2.8 Plasma Polymerization

Plasma polymerization is a useful method for obtaining polymers as an ultrathin uniform layer on an appropriate substrate. The process requires low temperature plasma, called 'cold' plasma, which is generated by electric glow discharge. Polymers formed by this polymerization method are amorphous, hard, tough, insoluble in organic solvents, and resistant to high temperatures as a result of their cross-linked and branched structures. The advantage of this method is that it eliminates various steps needed for the conventional coating process. It is used to synthesize ionic conducting thin siloxane polymer films having sulfonate groups [94].

1.2.9 Inclusion Polymerization

Inclusion polymerization occurs within the channel structure made from the crystalline inclusion complexes between a monomer guest and its designated host molecules. Therefore, linear polymers, which have constrained conformations, configurations, and molecular weights, may be produced within the channels available inside the crystal structure, where the propagation step takes place without branching found in conventional homogeneous chain-growth polymerization. The confined reaction proceeds by the general chain-growth mechanism, commonly initiated by radiation. Thus, the high yield of polymer from limited initiation steps is guaranteed [95-96].

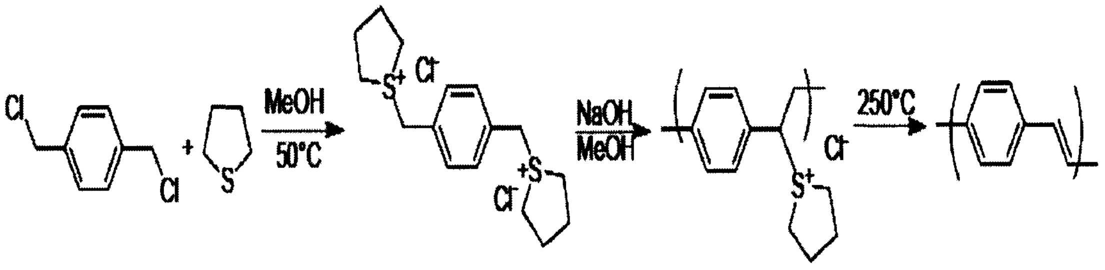
1.2.10 Pyrolysis polymerization

Pyrolysis is probably one of the oldest approaches utilized to synthesize conductive polymers by eliminating heteroatoms from the polymers by heating it to form extended aromatic structures. The product of polymer hydrolysis can be a film, powder or a fibre depending on the form and nature of the standing polymer including the pyrolysis condition [72].

1.2.11 Soluble precursor polymer preparation

The innovative and useful technique of synthesis via precursor polymers, developed to overcome the problem of intractability in conducting polymers, involves the synthesis of a highly soluble precursor polymer that is processed and purified in solution and finally converted to the more tractable conducting polymer.

Polymerization of the 1,4-xylylenebis-(dialkylsulfonium)- dichloride was achieved in the presence of NaOH to form the precursor polymer. With heating, elimination of the tetrahydrothiophene and HCl affords the corresponding PPV polymer [97].



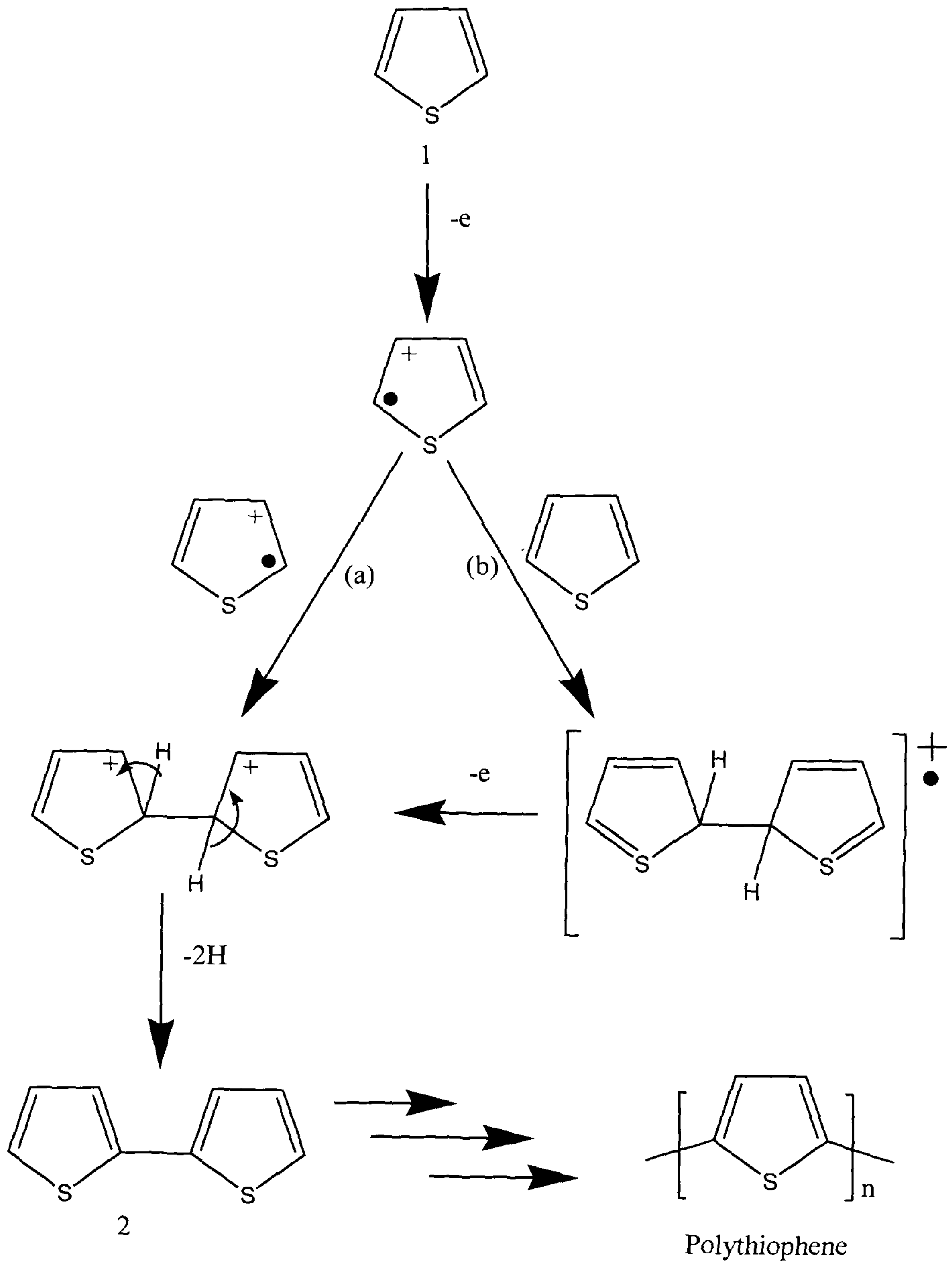
Scheme 1.3: Precursor synthesis of PPV

1.2.12 Electrochemical polymerization

Electrochemical synthesis of conjugated polymers is a novel method in which simultaneous polymerization and doping occur and the polymer is deposited on the electrode surface [71-73]. It is generally accepted that anodic electrochemical polymerization of thiophene and its derivatives proceed via a radical cationic mechanism as shown in Scheme 1.4. In the first step of polymerization, an electron is removed from the monomer to form the corresponding radical cation. Since the electron transfer reaction is much faster than the diffusion of monomer from the bulk solution, a high concentration of radical cation is generated and maintained near the surface of electrode. In the second step, two radical cations undergo a coupling reaction to form a dihydro dimeric dication as shown in reaction (a). Alternatively, the radical cation can react with a neutral monomer through reaction (b) to yield a dimeric radical cation, which then loses an electron to afford the same dication. The dication tends to split off two protons and rearomatizes to yield a neutral dimer. The driving force for this step is the rearomatization. The dimers, possessing a lower oxidizing potential than the monomers, are more easily oxidized to the corresponding radical cations, which then further couple with either a monomeric radical cation or a neutral monomer. This procedure repeats until the polymer becomes insoluble and precipitates on the electrode surface [98-99].

In general, conjugated polymers with high electroactivity are obtained in rigorously deoxygenated, anhydrous aprotic solvents with high dielectric constant and low nucleophilicity, such as acetonitrile, nitrobenzene, benzonitrile, and propylene carbonate. Other experimental variables such as monomer concentration, reaction temperature, applied electrical conditions, supporting electrolytes, electrode materials and configuration also exert significant effects on the structure and electrochemical properties of conducting polymer films. Electrochemical polymerization presents several advantages such as rapidity, absence of catalyst, control of film thickness by the deposition charge, and direct obtainment of the polymer in the oxidized conducting form.

Despite the facile nature of electrochemical polymerization, this method possesses the major limitation of yielding insoluble materials, precluding the analysis of primary structure by traditional analytical techniques. Because of this limitation of electrochemical polymerization, chemical polymerization methods have gained popularity for synthesizing novel soluble conjugated polymers.



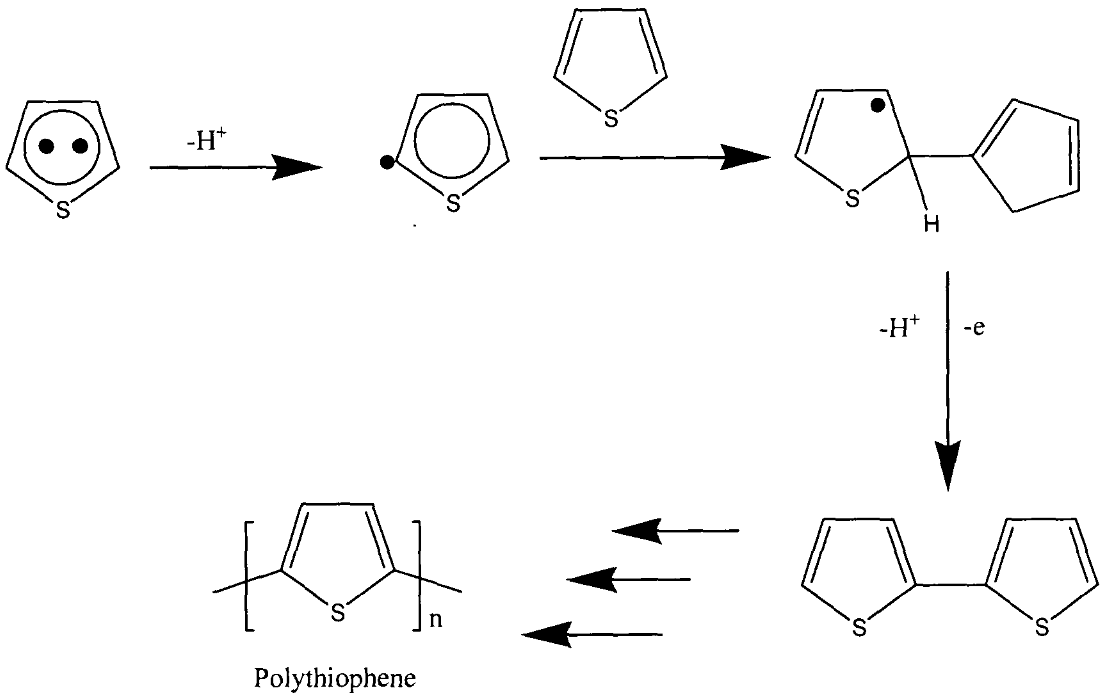
Scheme 1.4: Mechanism of electrochemical synthesis of polythiophene.

1.2.13 Chemical polymerization

One of the shortcomings of electropolymerization is its limitation in large scale preparation and yielding insoluble materials. Therefore, intense efforts in developing methods for chemical preparation of conjugated polymers have been warranted since the early 1980's.

1.2.13.1 Oxidative coupling

Among the chemical polymerization techniques, oxidative coupling symbolizes a straightforward, simple, versatile, without dihalomonomers and least expensive method to synthesize conjugated polymers [71-77]. Sugimoto and co-workers have shown that thiophenes and its derivatives can be polymerized by transition metal halides, such as $FeCl_3$, $MoCl_3$ and $RuCl_3$ [100].This method is generally cited to as the ferric chloride method and is the most widely used method for preparation of polythiophenes and its derivatives. The ferric chloride polymerization is a heterogeneous reaction. The active sites have been found to be iron (III) ions on the crystal surface. Soluble ferric chloride is inert. A plausible mechanism for this polymerization is the radical cation pathway as illustrated in Scheme **1**.4 for electropolymerization of thiophene derivatives. However, Niemi and co-workers have argued that the polymerization might proceed through a free radical mechanism as illustrated by Scheme 1.5 In the free radical mechanism, the first step involves a heterogeneous electron transfer reaction between monomer and crystal iron (III) ion. The monomeric radical cation produced loses a proton to afford the corresponding radical, which reacts with another monomer to form a dimeric radical. This process proceeds until a long chain polymer is formed and precipitates out of the solution.

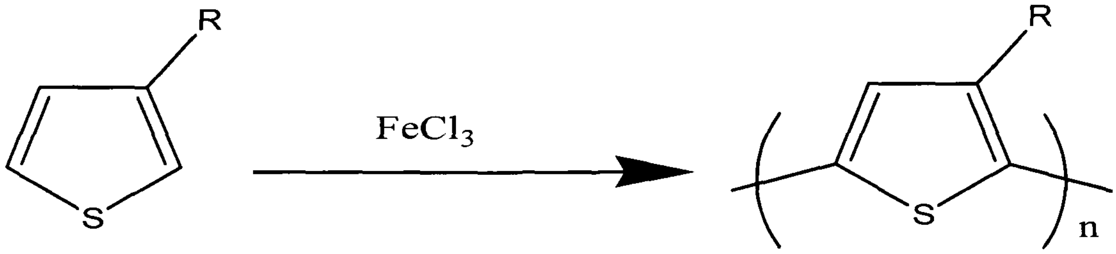


Scheme 1.5: Free radical mechanism of oxidative coupling of polythiophene.

In a typical experiment, a solution of 1 equivalent of monomer is added into a suspension of 4 equivalents of $FeCl_3$ in $CHCl_3$ or other appropriate solvents. The reaction mixture is stirred at room temperature under nitrogen for 2 to24 hours and then poured into methanol to quench the polymerization. The resulting black precipitates are polymers doped with Fe which are subsequently reduced by aqueous ammonia. Highly homogeneous suspensions of the polymers were obtained together with complete monomer conversions and high yields, especially when highly dispersed $FeCl_3$ was precipitated in situ by the addition of a saturated solution of $FeCl_3$ in nitromethane to an excess of a CCl_4 solution of the monomer [101-107].

A tremendous advantage of chemical oxidative polymerizations is that, unlike unsubstituted heterocycles that form insoluble powders, properly substituted heterocyclic and other aromatic monomers form highly soluble polymers. These polymers can be analyzed by traditional analytical techniques to determine their primary structure. The nature of the polymerization conditions also allows for easy scale-up and production of large quantities of polymer.

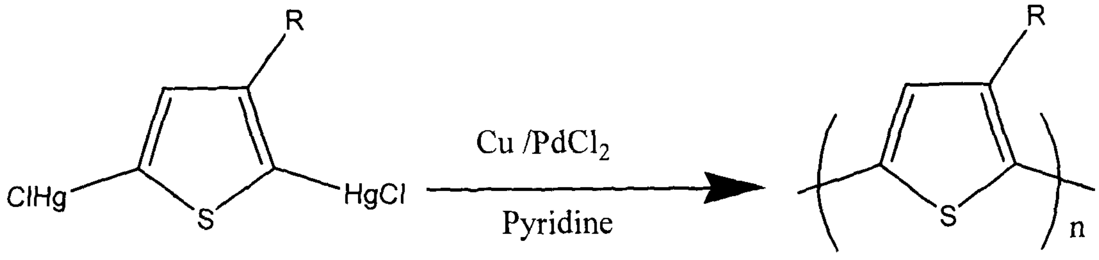
Unfortunately, chemical oxidative polymerizations suffer from several disadvantages that often result in poor quality polymers. As stated earlier, Lewis acid catalyzed polymerizations yield the oxidized polymer, which is thought to be more rigid, resulting in its precipitation from the polymerization medium, limiting the degree of polymerization. Also, the use of strong oxidizing agents can result in the overoxidation and eventual decomposition of the polymers. Unsubstituted heterocycles, like thiophene and pyrrole, present a unique problem for both oxidative polymerization techniques in that several side reactions can take place leading to "coupling defects" along the polymer backbone. It is generally believed that oxidative coupling occurs at sites on the heterocyclic ring where a high spin density resides for the radical cation. For thiophene, pyrrole, and furan, the highest spin densities have been measured at the 2- and 5-positions, also referred to as the α positions. Still, the 3- and 4-positions (referred to as the β positions) have a measurable spin density, meaning that some coupling reactions will occur at these positions. α-β and β-β coupling result in polymers with irregular backbones and poor electronic properties. Main chain imperfections can be eliminated by "blocking" the 3- and 4-positions of the monomer by the attachment of various side groups. In addition, several other electronic properties are dramatically affected by the structural modifications including monomer oxidation potential, electronic and band gap of the resultant polymers. It has been also reported that these defects can be minimized by performing the reactions at lower temperatures or by using vanadium based oxidants. However, the inability to remove completely the oxidant from the final product can still dramatically influence its performance in devices such as FETs and LEDs.



Scheme 1.6: Synthesis of P3AT via $FeCl_3$ oxidative coupling.

1.2.13.2 Curtis demercuration polymerization

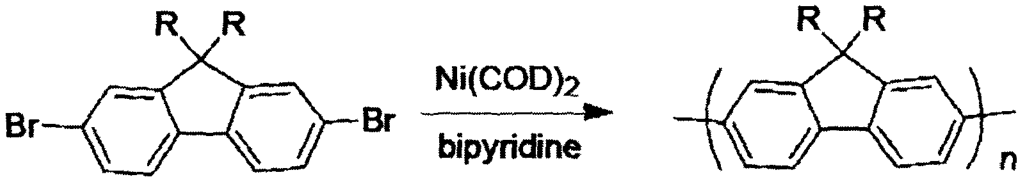
Curtis and co-workers have developed a new preparation method for P3ATs based on the Pd-catalyzed, reductive coupling reaction of 2,5-bis(chloromercurio)-3-alkylthiophenes as shown in Scheme 1.7. The Curtis method ensures only α, α'-coupling between thienylene moieties. The most appealing feature of this method is its tolerance to electrophilic groups, such as carbonyls, esters, and nitriles. This method has also been extended to prepare poly(3-alkylthienyl ketones) [108].



Scheme 1.7: Curtis synthesis of P3AT.

1.2.13.3 Yamamoto coupling

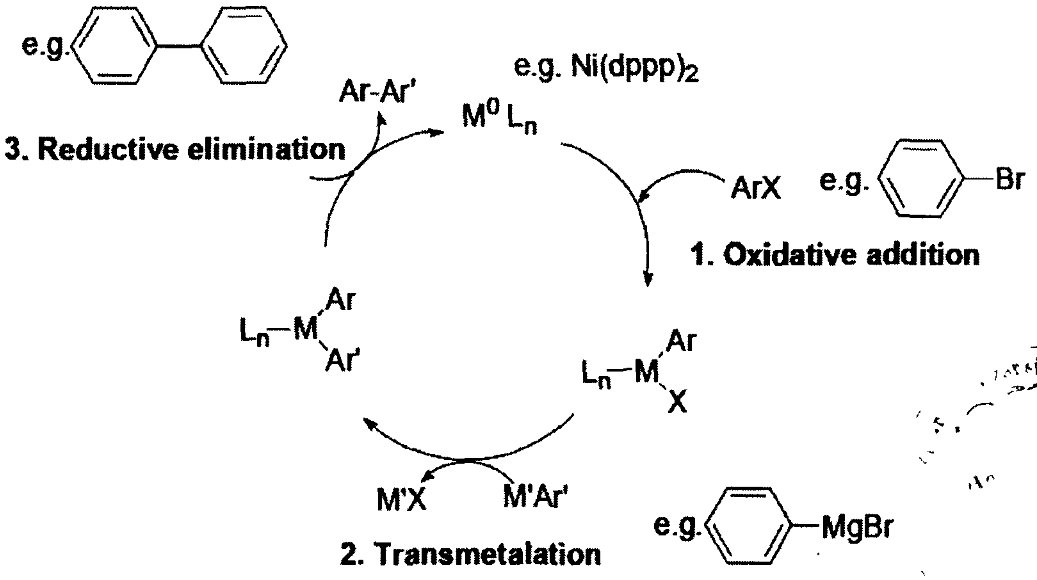
The Yamamoto coupling method is an effective route to synthesize conjugated polymers. This route has been successful in polymerizing several classes of conjugated polymers which includes thiophenefluorene, thiazole and phenylene. The use of a large quantity of $Ni(COD)_2$ (COD= 1, 3- cyclooctadiene) and the instability of nickel complex, however, makes this reaction undesirable[76,109].



Scheme 1.8: Synthesis of poly(9,9-dialkylfluorene) via Yamamoto coupling

1.2.13.4 Metal-catalyzed cross coupling

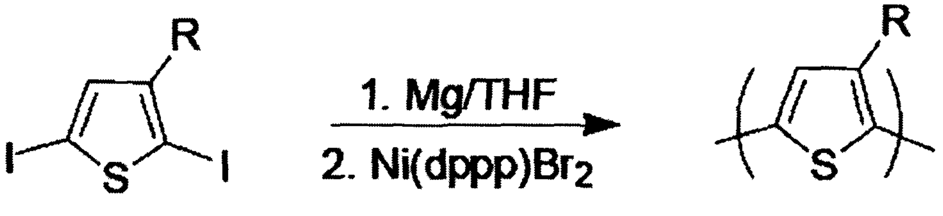
Metal-catalyzed cross coupling has been proven a versatile route to synthesize conjugated polymers. The catalyzed reaction mechanisms are essentially the same regardless of the reaction type, and follows three key steps: (i) oxidative addition of an aryl halide to the metal catalyst, (ii) transmetallation between the aforementioned catalyst complex and the organometallic reagent to form a diorganometallic, (iii) reductive elimination to give an aryl-aryl bond and a regenerated catalyst. The use of this method- with several different catalysts – is discussed in the next subsection.



Scheme 1.9: Metal-catalyzed cross coupling mechanism.

1. 2.13.4.1 Kumada coupling

Kumada cross coupling was first used to prepare soluble and processable poly(3-alkylthiophene)s (when alkyl chains are greater than propyl) by Elsenbaumer and co-workers. In this method, 2,5 – diiodo-3-alkylthiophene was treated with one mole equivalent of magnesium to form the Grignard species. When Ni(dppp)Br_2 (dppp= diphenylphophinopropane) catalyst was introduced, a polymer formed. Since poly(3-alkylthiophene)s are non-centrosymmetric, regioregularity is a factor. PATs may couple as: head-to-head, head-to-tail, and tail-to-tail. These linkages have a pronounced effect on their properties. The PATs synthesized by Elsenbaumar and co-workers were regio-random [110].

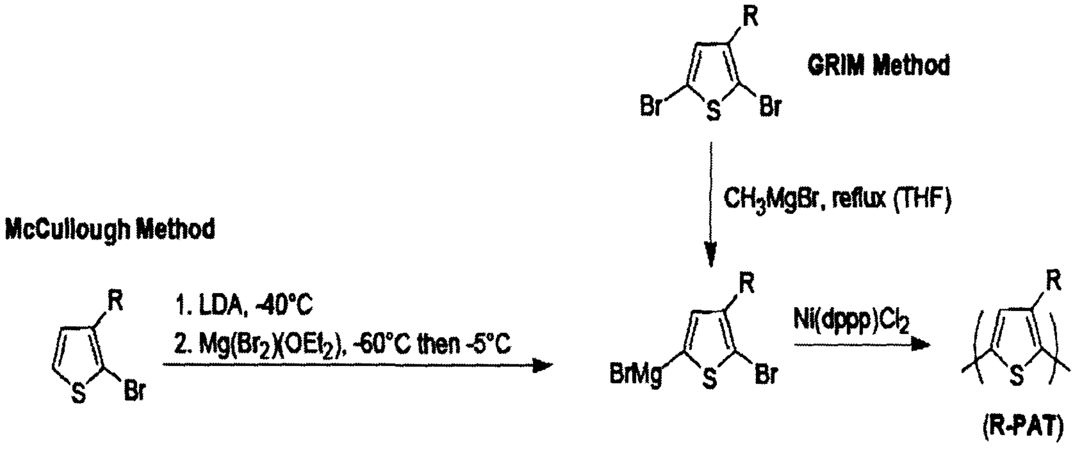


Scheme 1.10: Grignard synthesis of P3AT.

McCullough and co-workers discovered two methods to produce regio-regular (>98% head – to-tail coupling) P3ATs. The McCullough and the Grignard Metathesis (GRIM) methods, these two methods are based on the Kumada cross coupling of 2-bromo-5-(magnesiobromo)-3-alkylthiophene.

1.2.13.4.2 McCullough method

In the McCullough method, high purity 2-bromo-3-alkylthiophene (free from the 2-bromo-4-alkylthiophene isomer) is selectively lithiated at the 5-poition with lithium diisopropylamine (LDA) at low temperatures (-40^{0}C) to afford 2-bromo-3-alkyl-5-lithiothiophene. This organolithium intermediate is converted to a Grignard reagent by reacting with $MgBr_2.Et_2O$ to yield 2-bromo-5-(magnesiobromo)-3-alkylthiophene. With the addition of $Ni(dppp)Cl_2$ catalyst, reaction of the Grignard with 2-bromo-3-alkylthiophene results in regio-regular poly(3-alkylthiophene) [74,111].



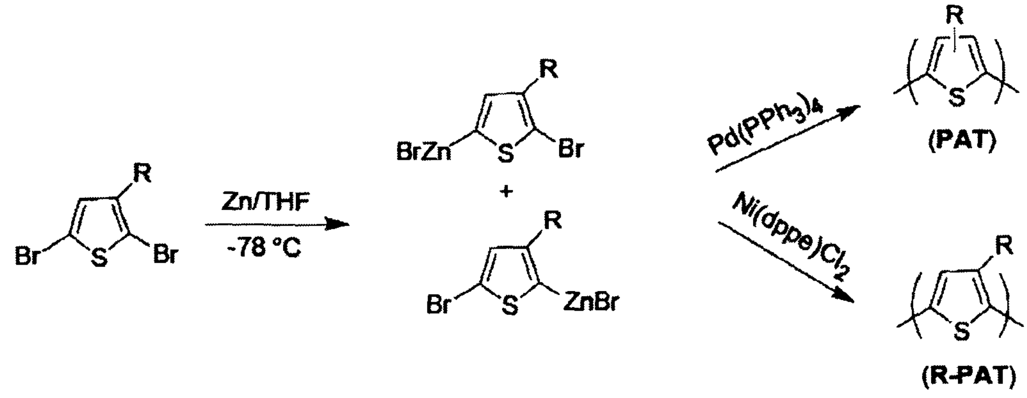
Scheme 1.11: Regio-regular P3AT synthesis.

1.2.13.4.3 Grim method

The Grim method is a facile route to make regio–regular P3ATs. In this method, 2,5-dibromo-3-alkylthiophene monomer is used, rather than 2-bromo-3-alkylthiophene. The former is easier to purify due to the large differences in volatility of the reactants and the side products. The 2-bromo-5-(magnesio-bromo)-3-alkylthiophene is easily formed by reacting 2,5-dibromo-3-alkylthiophene with methyl magnesium bromide, followed by introduction of the nickel catalyst to yield a region-regular poly(3-alkylthiophene) in high yields (60-70%) [74, 112].

1.2.13.5 Reike method

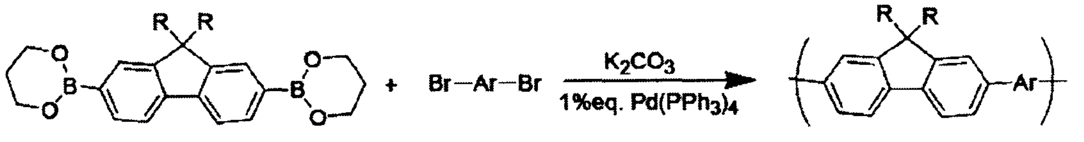
Reike and co-workers discovered a method to produce regio-regular PATs. This method is illustrated in Scheme 1.12. This polymerization method is a one pot reaction in which reactive Reike zinc undergoes a regio-selective oxidative addition on the 5-position of 2,5-dibromo-3-alkylthiophene to form 2- bromo-5-bromozincio-3-alkylthiophene. With the addition of Ni(dppe)Cl_2 (dppe =diphenylphosphinoethane), regio-regular PAT (R-PAT) is formed. Alternatively, with the addition of Pd(PPh_3)$_4$ (PPh_3 = triphenylphosphine), a regio-random polymer is obtained. It is rationalized that the size of the catalyst (both metal and ligands) controls the regio-specificity of the resulting polymer [74,113].



Scheme 1.12: Reike synthesis of P3ATs and catalyst specificity

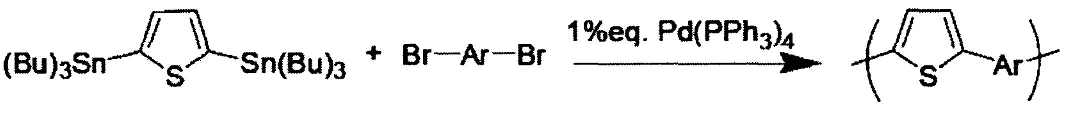
1.2.13.6 Suzuki and Stille polycondensation

Pd-Catalyzed cross coupling is a convenient method for aryl-aryl coupling and provides a route to synthesize a wide variety of conjugated polymers, and copolymers. Two common Pd-catalyzed cross coupling methods are Suzuki and Stille type reactions. The advantages of these methods are water insensitivity, commercial availability of many monomers (and precursors), and the yield of high molecular weight polymers. In Suzuki coupling, a diboronic acid (or ester) is coupled with a dibrominated aryl group in the presence of a base (e.g. K_2CO_3), as illustrated in Scheme1.13. This procedure was first reported in 1989 by Wegner and co-workers, for the synthesis of well-defined processable poly(*p*-phenylene)s. This method is quite versatile, especially for the synthesis of alternating copolymers, and can tolerate a large number of functional groups. Fluorene type polymers are commonly synthesized by this method [114].



Scheme 1.13: Suzuki coupling

Stille coupling is also a versatile, polycondensation reaction to form conjugated polymers. The primary drawback of this method is the use of toxic tin compounds [115].



Scheme 1.14: Stille coupling

Among all the above categories, chemical polymerization is the most useful method for preparing large amounts of conductive polymers. All the classes of conjugated polymers may be synthesized by this technique. However, chemical polymerization method is time – consuming. Most of the chemical polymerization techniques involve the use of costly chemicals except ferric chloride oxidative coupling.

Conjugated polymer synthesis in general differs from other chemical reactions in many ways. The most stringent requirement for polymerization reaction is the high purity of the monomers and chemicals required for the reaction. A trace amount of impurity might even stop polymerization or lead to undesirable products. The reaction conditions (i.e., catalysts, temperature, time of reaction, etc) must be strictly controlled. Isolation and purification of conjugated polymers becomes a problem because a trace amount of an ionic or catalyst impurities present in the polymer will result in a large error in end use application. The presence of moisture and air is highly undesirable in polymerization reactions, particularly in oxidative polymerization. In most of the polymerization processes, the requirement of an inert and dry atmosphere is essential. This may ensured by the passage of dry and pure nitrogen or argon gas through the polymerization chamber.

1.3Properties of conjugated polymers

A large number of different classes of conjugated polymers has been developed, e.g., poly(acetylene)s, poly(p-phenylene)s, poly(pyrrole)s, poly(aniline)s, poly(phenylene vinylenes) (PPVs), poly(carbazole)s, poly(flourene)s (PF)s, poly(thiophene)s (PT)s. The early interest of conjugated polymers was to study their electrical conductivity and their corresponding electronic structure. Highest values reported up to now for the electrical conductivity of doped polymers are 80000 S/cm. [116]. The different path breaking application oriented discovery of conjugated polymers gave the opportunities to analyse their properties. The development of soluble conjugated polymers has led to significant improvement in their properties.

Charge carrier mobility of conjugated polymers was reported as high as 10 $cm^2/V.s.$ [117]. As per our knowledge, excellent on / off ratios in polymer based FETs was found up to 10^7 [118]. Polymers based photovoltaic cell with record power conversion efficiencies up to 5 % were accounted till to date [44].

Recently PLEDs can sustain 400 cd/m^2 of luminance for over 1,98,000 hours for green LEDs and 62,000 hours for blue LEDs [119]. To date, PLED have been demonstrated with emission wavelengths from the ultraviolet to near infrared [51], external quantum efficiency 10% photons/ electrons [120].

For light emitting polymers, PPV and its derivatives are still the leading materials for green light-emitting PLEDs, the larger band gap PFs are the blue –light emitting polymers and polythiophenes and its derivatives are remembered for red and almost all visible light emitting polymer materials [121].

1.4 Characterization of luminescent conjugated polymers

Characterization techniques discussed in the following sections are those used to examine the optical properties of conjugated polymers. These characterization tools are important for understanding the role of the chemical structure on the properties of these materials.

1.4.1 Absorption, photoluminescence and electroluminescence spectroscopy

Generally, the observed transitions in absorption spectroscopy of conjugated polymers are attributed to electronic excitation from π to π^* states and π^* to π states for emission spectroscopy. Upon electronic excitation of the polymer, a number of photo-physical processes, shown in Figure 1.1-1.2, may occur: fluorescence, phosphorescence, or radiationless decay [122]. Fluorescence is observed after singlet relaxation from the first excited state. If intersystem crossing occurs, a triplet excited state is generated whose relaxation will result in phosphorescence. If emission does not occur, then a non-radiative pathway is dominant and the electronic excitation is converted into rotational or vibrational motion within the polymer and its surroundings. The difference between the absorption and emission maxima of the spectra is called the Stokes shift, and it occurs when emission from the lowest vibrational excited state relaxes to various vibrational levels of the electronic ground state.

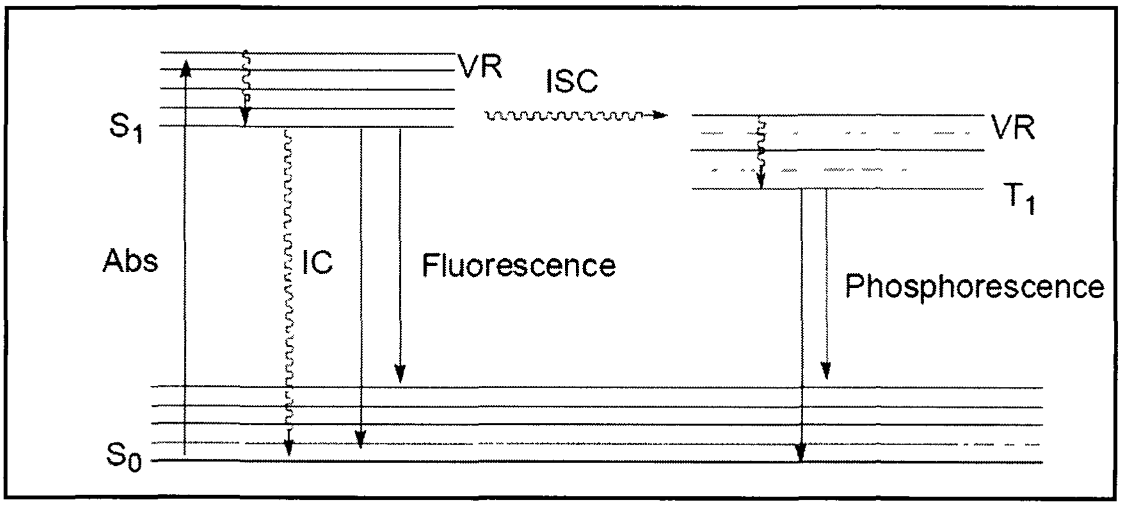


Figure 1.1: Jablonski diagram. Abs = absorption, VR = vibrational relaxation, ISC = intersystem crossing, IC = internal conversion, S_0 = ground state singlet, S_1 = first singlet excited state, T_1 = first triplet excited state

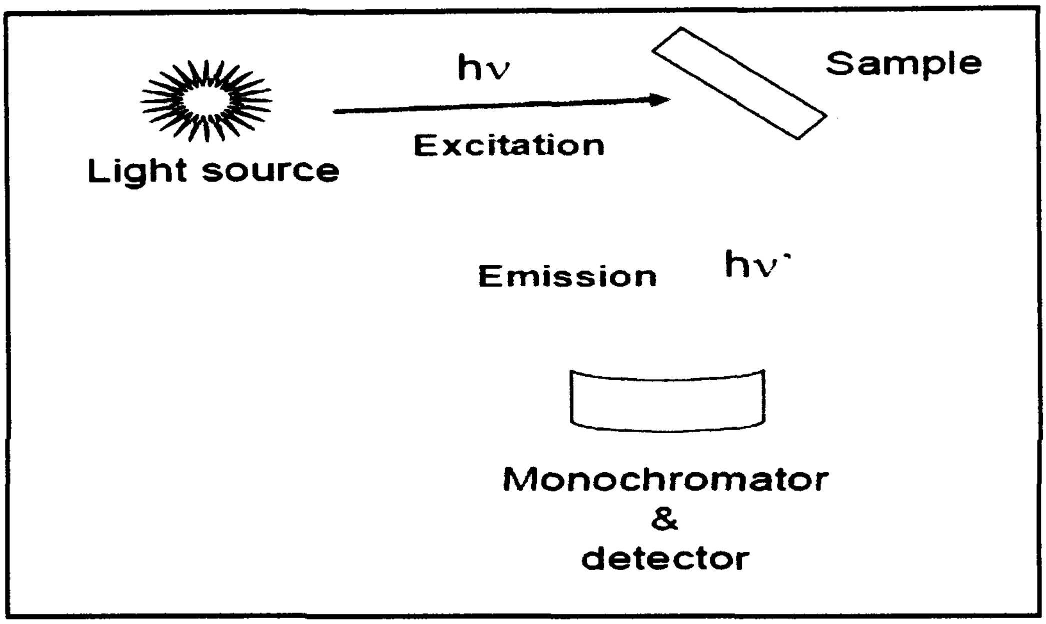


Figure 1.2: Photoluminescence process

Quantitative analysis of the emission efficiency of the polymer is characterized by its quantum yield of luminescence (Φ_{PL}). The Φ_{PL} is the ratio of the number of photons emitted to the number of photons absorbed, as shown in Equation 1.1

$$\phi_{PL} = \frac{\text{Photons}_{EM}}{\text{Photons}_{ABS}} \qquad (1.1)$$

Equation 1.1: Quantum yield of photoluminescence. Photons $_{EM}$ = photons emitted, Photons $_{ABS}$ = photons absorbed.

According to the law of conservation of energy, the maximum Φ_{PL} must be 1. The value of Φ_{PL} is related to the rates of radiative (τ_r) and non-radiative (τ_{nr}) decays, as described in Equation 1.2 [123].

$$\phi_{PL} = \frac{\tau_r}{\tau_r + \tau_{nr}} \qquad (1.2)$$

Equation 1.2: Quantum yield of luminescence with respect to rates of radiative(τ_r) and non-radiative relaxation (τ_{nr}).

As τ_{nr} approaches 0, the quantum yield of luminescence approaches unity. Generally, Φ_{PL} is highest in dilute solutions, where the emitting species are isolated from each other. In most cases, increasing the concentration of the polymer in solution decreases the quantum yield of luminescence due to concentration quenching, which follows the Stern-Volmer relationship [122].

The interchain interactions of the CPs lead to formation of tight aggregates, which results in fluorescence quenching because of π- stacking between main chains of the CPs [124-125]. The quenching efficiency increases with increasing tendency of the polymer to be associated with the quencher in solution. This association can occur either through the formation of a nonluminescent complex between the polymer and the quencher (static quenching) or due to collisions between the photoluminescent macromolecule and the quencher (dynamic quenching). For both mechanisms, the quantitative measure of the luminescence quenching efficiency is given by the Stern-Volmer constant K_{SV} defined by equation (1.3) [126].

$$\phi^{o}/\phi = 1 + K_{sv}[quencher] \qquad (1.3)$$

Equation 1.3: Stern-Volmer relation.

Where ϕ^{o} is the intensity of fluorescence in the absence of the quencher and ϕ is the intensity of fluorescence in the presence of the quencher and [quencher] is the concentration of quencher. The equation reveals that ϕ^{o}/ϕ increases in direct proportion to the concentration of the quenching moiety, and the constant K_{sv} defines the efficiency of quenching. When all the other variables are held constant, higher the K_{sv}, lower is the concentration of quencher.

The quantum yield of luminescence can be determined either by secondary or primary methods. In the secondary method, the quantum yield is related to that of a known standard as shown in equation 1.4 [127].

$$\phi_s = \phi_r \left(\frac{A_r}{A_s} \times \frac{I_s}{I_r} \right) \qquad (1.4)$$

Equation 1.4: Secondary method for quantum yield of luminescence calculation.

In this equation, Φ_s represents quantum yield of a sample in solution and Φ_r represents known quantum yield reference sample of in solution. A_s and A_r are the absorbance of the sample and reference solution respectively at the excitation wavelength, Ir and Is are the corresponding relative integrated fluorescence intensities. In order to obtain reliable results, it is important to match as closely as possible the optical absorption properties of the sample with those of the references. Typical standards are 9,10-diphenylanthracene in cyclohexane (Φ_{PL} = 0.90), quinine sulfate in 1 N H_2SO_4 (Φ_{PL} = 0.546), Rhodamine 101 in ethanol (Φ_{PL} = 1) and Rhodamine B in water (Φ_{PL} = 0.31). This method assumes that the emission from the sample is isotropic (equal in all directions), as is the case in dilute solutions. Measuring the Φ_{PL} of an anisotropic sample, such as a film, is quite difficult since its emission intensity has an angular dependence.

In the primary method, measurement of the Φ_{PL} does not rely on standards, but rather on quantifying the number of photons absorbed and emitted in the sample with an integrating sphere [128-129]. An integrating sphere is a hollow sphere which has its inner surface coated with a reflective material. The sphere allows one to accurately measure the luminescent efficiency of films by collecting light in all directions. That is, the large index of refraction of polymeric semiconductor films could result in substantial wave guiding of the polymer's luminescence, which leads to anisotropic distribution of the emission.

The quantum yield of luminescent polymer largely depends on effective conjugation length of conjugated polymers. The solution quantum yield of luminescence increases with increasing conjugation length, indicating that the rate of non-radiative decay decreases with conjugation length. This increase in Φ_{PL} with higher conjugation lengths can be explained by: (a) an increased structural stability of an unspecified origin [130] or (b) the lack of singlet fission (process where two triplet excitons are produced from the fission of one singlet excited state) [131].

In the solid state, the absorption and emission wavelength maxima increase (red shift), with respect to their corresponding solution values, while the Φ_{PL} decreases pronouncedly. This red shift in the solid state is attributed to strong π-π intermolecular interactions due to aggregate formation, and/or excimer formation [132-133]. Aggregate states are identified as interchain species that occur in the ground state. Upon aggregation, both the ground and excited state wave functions are delocalized, resulting in a shift in both the absorption and emission maxima with respect to the isolated species in solution. An excimer is a photoexcited emissive intermolecular singlet excited state complex which is delocalized over two molecular units [133]. This excimer cannot be directly excited since the ground state of the dimer is dissociative. These aggregate and excimer states are induced by strong intermolecular interactions between two or more molecules. The interaction between the wave functions of the molecules results in the formation of two or more new states, as depicted in Figure 1.3. As a consequence, the absorption spectrum of an aggregate may blue-shift and/or red-shift, depending on the orientation of the molecular packing: parallel, head-to-tail or oblique [132]. An optical transition is allowed only for a non-zero transition moment. Therefore, a blue-shift in the absorption spectrum is observed for a parallel orientation, while a red-shift is observed for a head-to-tail orientation. For an oblique orientation, both orientations have non-zero transition moments, which results in band splitting. The emission spectra of these aggregate or excimer states are red shifted compared to their isolated molecules, due to fast internal conversion. For parallel aggregates, the emission is optically forbidden and therefore leads to a strong decrease in the quantum yield of luminescence. In conjugated polythiophene, the absorption maximum in the film state red shifts (indicating a head-to-tail orientation) and a decrease in the quantum yield of luminescence are observed with respect to their solution state properties. The red-shift in the absorption is explained by the planarization of the polymer backbone, which preponderates the aggregation, while the decrease in the quantum yield of luminescence is observed due to the aggregation phenomenon.

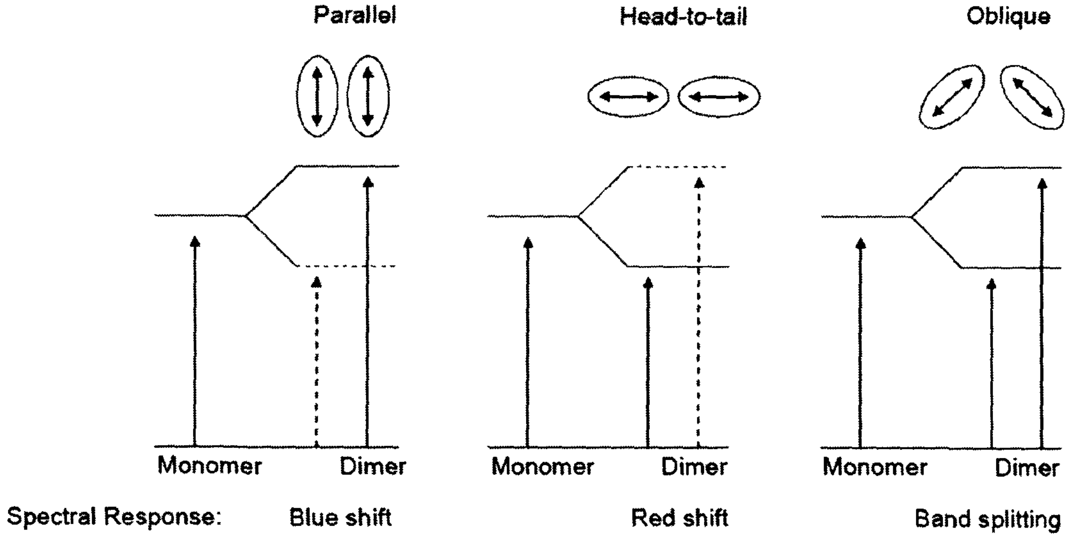


Figure 1.3: A simplified excitonic band structure of isolated (monomer) and aggregated (dimer) phases with their corresponding spectral shifts

Light-emitting diodes (LEDs) produce light under electric field called electroluminescence. Electroluminescence (EL) is a creation of light by electrical excitation in fluorescent materials [9-12]. Fluorescent materials may be inorganic, organic or polymeric in nature. Inorganic and organic materials have to be deposited as thin film by relatively expensive techniques of sublimation or vapour deposition, which are not well suited to fabrication of large area devices. Also organic materials are intrinsic p-type conductor and therefore are better suited to transport positive charges, electrons and holes usually recombine in the immediate vicinity of the cathode. As a consequence, the lifetime and efficiencies of the corresponding diodes are limited. For application in light emitting diodes (LEDs), fluorescent polymers offer several advantages compared with their inorganic and organic counterparts such a large synthetic flexibility, relative ease of processing by cheap technologies (spin and blade coating, ink – jet printing), or the ability to control the wavelength of emission by changing the molecular structure of the emitting material [6, 51]. A schematic diagram of a simple LED and its corresponding energy level is depicted in Figure 1.4 -1.5.

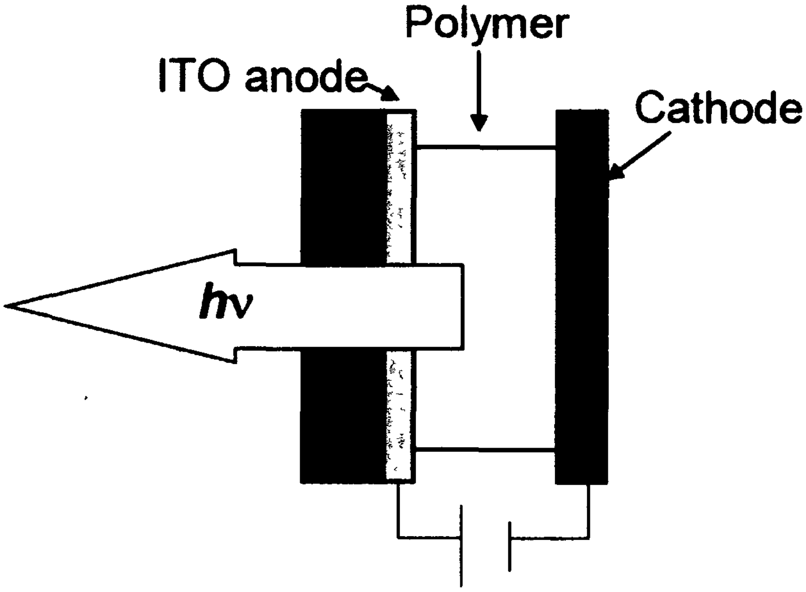


Figure 1.4: LED structure

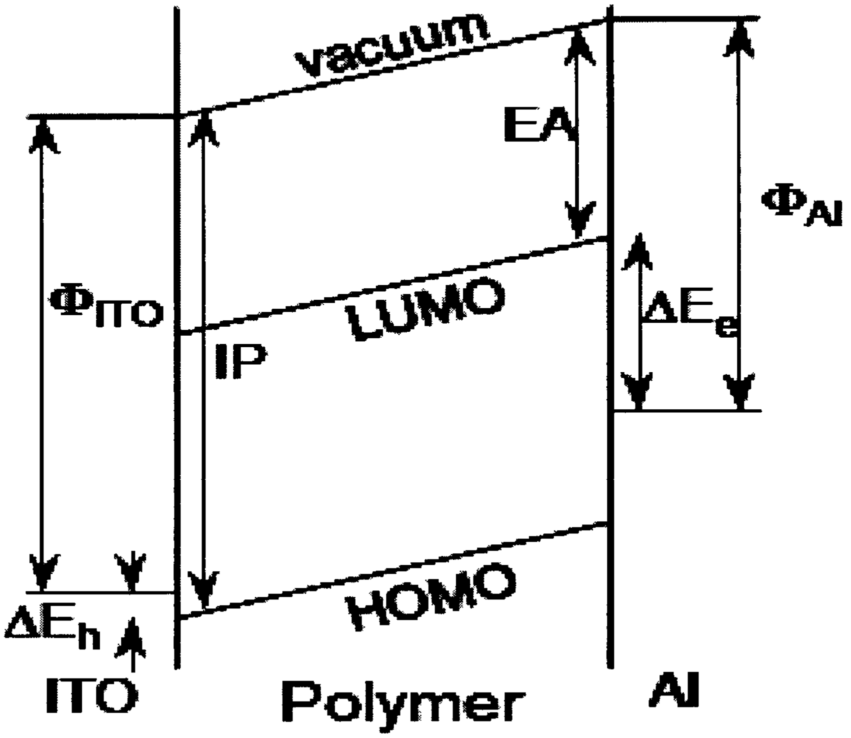


Figure 1.5: Energy level diagram of LED device.

The process requires injection of electrons from one electrode (cathode) and holes from the other, the capture of oppositely charged carriers (so called recombination), and the radiative decay of the excited electron – holes state (exciton) produced by this recombination process. So in the presence of an electric field the charge carriers move through the active layer and are non-radiatively discharched when they reach the oppositely charged electrode. However, if a hole and an electron encounter one another while drifting through the polymer layer, excited singlet and triplet states, so called excitons, are formed. The Singlet state may relax by emission of radiation (fluorescence). Since one of the electrodes needs to be semitransparent in order to observe light emission from the organic layer, usually an indium tin oxide (ITO) coated glass substrate is used as the anode. Electropositive metals with low work function such as Al, Ca, Mg, or In are used as cathodes in order to guarantee efficient electron injection. The internal EL quantum efficiency [15, 35] η_{int} of an LED (the ratio of the number of photons emitted per electrons injected) can be calculated from the measured external EL quantum efficiency η_{ext} using Equation (1.5) [15]. Due to refraction, all photons emitted cannot be perceived by an external observer. External efficiencies η_{ext} are accordingly diminished by the factor of $2n^2$ (n = refractive index of the polymer layer) with respect to η_{int}.

$$\eta_{int} = 2n^2\, \eta_{ext} \qquad (1.5)$$

Power efficiency η_{pow}, the ratio of output light power to input electric power, can be determined from η_{ext} using the known values of the applied voltage U and the average energy of the emitted photons E_p (Equation 1.6) [15].

$$\eta_{pow} = \eta_{ext}E_pU^{-1} \qquad (1.6)$$

Luminous efficiencies η_{lum} are determined by multiplication of η_{pow} by the eye sensitivity curve S as defined by the Commission International de L'Eclairage (CIE). This function pays regard to the fact that the human eye possesses distinct sensitivities with respect to different colours (Equation 1.7) [15].

$$\eta_{lum} = \eta_{pow} \times S \qquad (1.7)$$

Finally, the brightness (cd m^{-2}) of a PLED is also used to estimate the device efficiency.

1.5 Polythiophene and its derivatives

Polythiophenes [15, 35,73-74, 121,134-136] are very unique among other polyconjugated systems for four principal reasons:

i) Versatile synthetic approaches, both chemical and electrochemical path are accessible as compared to other conjugated polymer.

ii) Due to the electron – rich character of the thiophene ring, polythiophenes can be easily and reversibly oxidized by chemical or electrochemical means to form p- doped, usually highly conducting materials.

iii). Their functionalization is relatively easy as compared to polypyrrole, polyacetylene, poly(*p*-phenylene), and other conjugated polymers.

iv). The attachment of substituents as side groups has relatively little impact on electronic and electrochemical properties of the conjugated polythiophene backbone. Thus, by synthesizing 3- and/or 4-substituted polythiophenes, one can produce new materials which combine physical properties of the polyconjugated backbone with specific properties of a given substituent. Such an approach to polythiophene chemistry has been very popular due to their solubility, environmental stability, fusibility, and the tuneability of color from UV to IR by changing the substitutents.

While 3-substitution efficiently improves the solubility and processability of the PTs, polymerization of 3- substituted thiophenes can result in three different types of coupling of the thiophene rings along the polymer main chain, i.e., head-to-tail(HT), head-to-head(HH), and tail-to-tail(TT). Generally, both oxidative polymerization and metal- catalyzed polycondensation afford all three possible types of isomers (Figure 1.6), i.e., HH, HT, and TT, although this process is not completely random and electronic and steric factors have an influence, so that HT coupling is somewhat preferred.

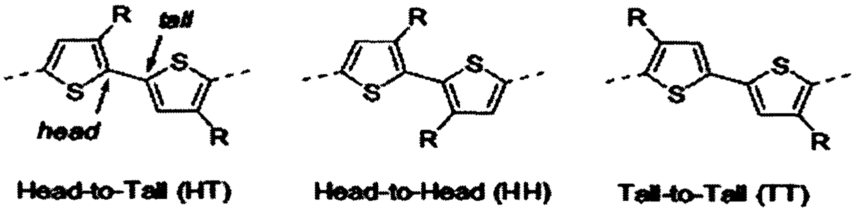


Figure 1.6: Possible diad linkages for 3-alkyl thiophene.

1.5.1 Solubility

From the beginning of their history in 1883, polythiophenes have been found as intractable and insoluble due to their rigid backbone. It was an important goal in basic research as in application-oriented material science to develop techniques by which they could be processed.

A number of general techniques have been developed for improving the solubility of the polythiophenes. These include the following

i) Copolymerization
ii) Chain flexibility incorporation
iii) Polymer blending
iv) Chain substitution

All of these approaches increase the solubility at the cost of desired luminescence of the polymers.

1.5.1.1 Copolymerization

The rigidity of the conjugated chain may be reduced and thereby its solubility improved by copolymerization technique. Block copolymerization of 3- methyl thiophene and methyl methacrylate produces polymers soluble in THF [137]. Poly (3-octylthiophene–co-N-(3-thenyl)-4-amino-2-nitrophenol) develops polymer highly soluble in solvents such as THF, chlorinated solvents, dioxane, toluene, etc [138]. Block copolymers containing thiophene units of several lengths alternating with aliphatic spacers and polyesters have been found to be highly soluble polymers [121,136].

1.5.1.2 Chain flexibility incorporation

Chain flexibility can be improved by incorporation of flexible centres or flexible linkages like sulphur, nitrogen, phosphorous etc in the side chain. Polymers of 3-(ethylmercapto)- and 3,4-bis(ethylmercapto)thiophenes are soluble in common organic solvents such as methylene chloride, chloroform, and THF [139].

1.5.1.3 Polymer blending

Blending of rigid conducting polymers with processable polymers is reported to have improved solubility. The success of blends depends on the mutual adhesion or compatibility of the polymers. For example, a blend of polyurethane and urethane substituted polythiophene in the β-position has improved the solubility of the resulting polymer [140].

1.5.1.4 Chain substitution

Appropriate chain substitution leads to enhanced solubility due to reduction of close packing of the chains in the crystal lattice [74, 141]. Substitution of a long alkyl chain in the 3-position in thiophene molecules gives rise to a soluble polythiophene. The introduction of alkyl groups longer than butyl to the 3-position of the thiophene unit yields the materials soluble in common organic solvents. Replacement of a long alkyl sulfonate group in the 3-position of the thiophene molecule leads to a water soluble polythiophene. Alkoxy side groups on polythiophenes backbone increase the solubility of the polymer. Short alkoxy chains on polythiophenes led to insoluble materials but long chain alkoxy substituents led to large increase in solubility. Polythiophene derivatives with fluoroalkyl, ether, hydroxyl, carboxylic acid, amide, urethane groups in side chain have improved the solubility. The presence of bulky phenyl, cyclohexyl substituents in polythiophene makes it soluble in typical organic solvents [142-157].

1.5.2 Optical properties

The mean conjugation length of the conjugated polymer is related to the maximum wavelength of both absorption and emission spectra. The first electronic transition of undoped PT lies between 300 and 500 nm. As the number of thiophenes increase, both the absorption and emission wavelengths increase due to larger conjugation lengths.

1.5.2.1 Band gap and colour tuning

As the colour of the emitted light depends on the band gap of the π-π* transition which is a function of polymeric structure, modifications of the above will affect the band gap and consequently the emitted colour. Usually, PTs emit orange-red light, consistent with their band gap of ca. 2 eV [121]. The PT emission colour directly depends on the effective conjugation length determined by the twist angle between the thiophene units. Theory predicts a large change in the band gap of PT depending on the torsion angle between thiophene units. The difference in the band gap of fully planar and 90° twisted PTs is calculated to be 1.7 eV. Although the emission of the substituted PTs is not predictable due to the interaction of several other factors (steric effects, regioregularity, electronic effects, substituents effects, intermolecular interaction-aggregation, side-chain crystalinity) [134-135]. The full visible region, i.e., from blue to red color can be achieved by controlling the conjugation length in polythiophenes [146]. The conjugation length is modified by adding different substituents on the repeating unit, imposing continuous steric torsions of the main chain [142-157]. The larger substituents give a large dihedral angle between the rings, and short conjugation along the polymer backbone is achieved, resulting in blue shifted emission. In the case of Poly (3-(4-octyl phenyl)thiophene)(I), Poly(2-(3-(4-octylphenyl)thiophene -2-yl)thiophene) (II), Poly(3-cyclohexylthiophene)(III), Poly(3-cyclohexyl-4-methylthiophene)(IV), steric hindrance offers a blue(IV), green (III), orange (II) and red (I) emission (Figure 1.7) [146]. Other approaches to tune the emission colour of polythiophene are the preparation of completely coplanar systems with controlled inclusion of head – to- tail dyads or the preparation of alternating block copolymers.

Band gap of P3ATs with different long alkyl chains length is typically ca 2.0 eV and an emission colour is red. The band gap and emission colour from alkoxy substituted polythiophene are similar to that of the corresponding P3ATs. The perfluoroalkyl substituents in polythiophene emit green colour. Polythiophene with urethane side chains show orange colour emission. Poly(alkyl thiophene-3- carboxylates) exhibits green and red-orange colour emission in solution and film respectively. Poly (3- alkyl ester thiophene)s display also red-orange colour emission.

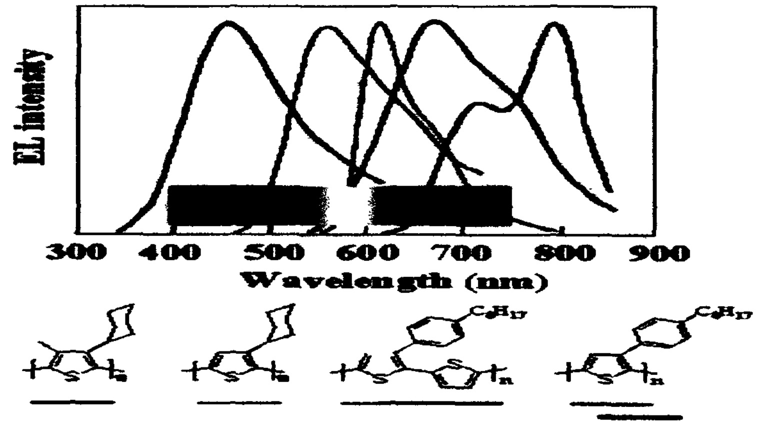


Figure 1.7: Colour tuning in 3- substituted polythiophenes

1.5.2.2 Fluorescence efficiency

Polythiophenes with suitable substituents in the 3-positions have shown different photoluminescence properties. The fluorescence efficiency can be controlled by changing the substitution patterns and the steric interactions of the side-chain substituents on the polythiophene backbone. PTs /dye, PTs blend, and PTs copolymer combination system have proved useful in enhancing the fluorescence intensity by isolating the emitting species. In the case of P3ATs, long alkyl group might enhance the fluorescence efficiency by reducing the ratio of non-radiative processes. Furthermore, modifying the alkyl side chain with sterically encumbered cyclohexyl or aryl groups enhance the solid state emission efficiency by decreasing intermolecular interaction [142-152]. Also the ester-containing polythiophene derivatives show higher fluorescence quantum efficiency than that of alkyl-containing derivatives [153-155].

1.5.3 Electrochemical properties

Electrochemical properties can be studied through cyclic voltammetric method. In cyclic voltammetry (CV), the potential is increased linearly from an initial potential to a peak potential and back to the initial potential again, while the current response is measured. For freely diffusing species, as the potential is increased, easily oxidized species near the electrode surface react, and a current response is measured. When the direction of the scan is reversed, the oxidized species near the electrode surface are reduced, and again a current response is measured.

The current-voltage data taken in a cyclic voltammetry experiment is referred to as a voltammogram. An example of a voltammogram for an ideal system is given in Figure 1.8. In the forward scan, we start the system at point A and start increasing the voltage. The oxidation reaction begins shortly and peaks at point B. Eventually the material becomes completely doped, and the current through the circuit stabilizes. At point C, the voltage peaks and reverses. The doping in the material begins to reverse, resulting in a negative current which peaks at point D. Again this current subsides and stabilizes at point E. The critical parameters of such a voltammogram are *Epc*, *Epa*, *Ipc* and *Ipa* . In this notation, p refers to the fact that we are in the forward, or oxidizing, scan (p doping). The cathodic values are then pc and the anodic values are pa. These values give information about doping potentials and the reversibility of doping in a given material.

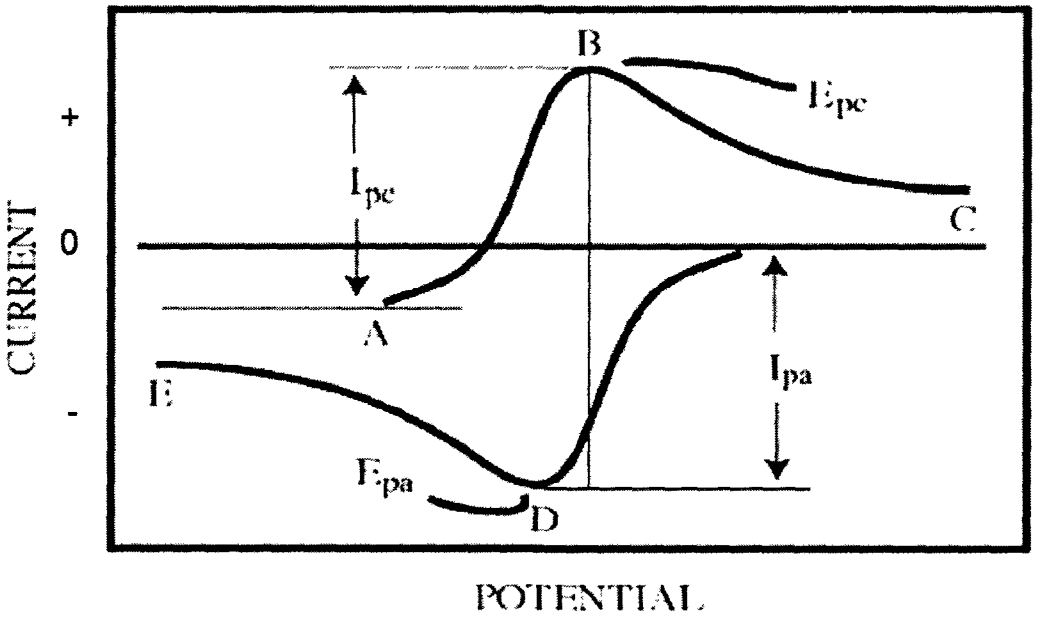


Figure 1.8: A voltagram of an ideal system in forward scan

The electrochemical properties of conjugated polymers offer the information of oxidation and reduction potential, and stability of synthesized polymer. Moreover, it gives the range of electrochemical potential window which is essential for end use application. The oxidation potential is a measure of how much energy is needed to withdraw electrons from the polymer HOMO level and the reduction potential is at the same time a characteristic of the LUMO. Therefore, the onset oxidation and reduction potentials are closely related to the energies of the HOMO and LUMO levels of polymer and thus can provide important information regarding the magnitude of the energy gap.

The polythiophene possesses good electron-donating ability, and consequently, it is more favourable to oxidation rather than to reduction. The oxidation and reduction potential of P3ATs film increases with increasing alkyl side chain length. Introduction of an electron donating group, such as an alkoxy or alkyl thio–group in PT possesses reduced band gaps, low oxidation potentials and a highly stable conducting state. Fluoroalkyl substituents on the polythiophene backbone lead to a higher oxidation potential. Electron withdrawing ester substituents in PTs lower the HOMO and LUMO energies and increase the electron affinity of the polymer [142-157].

1.5.4 Electroluminescence properties

A vapour deposited film of insoluble unsubstituted polythiophene has been reported to be electroluminescent, but no spectral data. P3ATs impart red electroluminescence (EL). The emission intensity becomes larger with increasing chain length, possibly owing to the improved confinement of excitons. Homopolymers based on 3-alkyl-thiophene exhibit good red colour purity, but they tend to have rather low fluorescence quantum yields. The use of charge carrier confinement layers or doping with fluorescent dye materials markedly increases device efficiency. Alkyl side chain substitution by incorporation of ether, ester or urethane functions in PT has been found to cause a colour change to yellow and orange emission. With the increasing steric demand of the substituents in 3-position of polythiophene, emission is shifted stepwise to green and blue [51, 121,134-136, 142-156].

1.6 Objectives and plan of the work

Today, conjugated polymers (CPs) stand for the frontiers of polymer research and magnetize much importance in light emitting diode, photovoltaic cell and sensor applications. Along with semiconducting properties, conjugated polymers tender the classical macromolecules properties, such as light weight, good mechanical behaviour (strength and flexibility) and easy processability which is perfectly suitable for opto-elecronic applications. For application in light emitting diodes (LEDs) and photovoltaic cell, fluorescent polymers offer several advantages compared with their inorganic and organic counterparts such as flexibility, relative ease of processing by common techniques (spin and blade coating, ink – jet printing), or the ability to control the wavelength of emission by changing the molecular structure of the emitting material.

A considerable effort has been devoted to the synthesis of π-conjugated polymers with special emphasis on the improved solubility. The introduction of side chains has proven to be effective for the formation of soluble polymers. Although introduction of side chains on the conjugated backbone not only provide solubility, but also they have a major influence on the characteristics of the polymers, for example, the reduction of the effective conjugation length as a result of the steric interactions of the side chains. Therefore, a balance has to be found between solubility on the one hand and effective π-conjugation on the other.

A large number of different classes of conjugated polymers has been developed such as poly(N- vinylcarbazole)s, poly(fluorine)s (PFs), poly(p-phenylene vinylenes) (PPVs), and poly(thiophenes) (PTs). While PPV and its derivatives are still the leading materials for green light–emitting PLEDs, the larger band gap PFs are the blue–light emitting polymers and polythiophenes and its derivatives are remembered for red and almost all visible light emitting polymer materials.

Polythiophenes and its derivatives are very unique among other polyconjugated systems due to their solubility, band gap, fluorescence efficiency and the tuneability of colour from UV to IR by changing the suitable side group. The length of the alkyl side group affects solubility. The introduction of bulky groups on polythiothiophene causes a steric twisting of the backbone and reduces the conjugation gives blue shifted emission. Phenyl–substituted polythiophenes have been found to be thermally stable and are soluble in typical organic solvents. Alkoxy side groups on polythiophenes backbone reduce the band gap of the polymer. Polythiophene derivatives with fluoroalkyl, ether, hydroxyl, carboxylic acid, amide, urethane groups in side chain have improved the solubility and processability of the conjugated polymers.

The incorporation of strong electron-withdrawing groups such as carboxylates is difficult because these substituents increase the potential for oxidation of the monomer and destabilize the resulting radical cation. The devastating electron withdrawing effect of the oxygen atom in the vicinity of the thiophene can be neutralized by the intercalation of one methylene groups without any loss of polymer electroactivity, balancing the effect of the electron-withdrawing group with an electron-donating group, which are less affected by the withdrawing nature of the substituent.

Now-a-day's electron-withdrawing ester groups on the thiophene ring are of considerable interest, as they might facilitate electron injection, influence electronic properties, promote triplet formation, as well as possibly stabilize the conjugated backbone against oxidation or other unwanted degradative events. The ester containing polythiophene derivatives show higher fluorescence quantum efficiency than that of alkyl containing derivatives. In the present thesis, efforts have been made to synthesize new and soluble ester substituted polythiophene and possible in light emitting diode and chemical sensor application.

Objectives of the present investigation:

- Preparation of 3- ester substituted thiophene monomers.
- Polymerization of monomers by oxidative $FeCl_3$ coupling method.
- To characterize the monomers and polymers by UV-Vis, FTIR, NMR, TGA/DSC, GPC, XRD techniques.
- To investigate the electrochemical, thermal, and photoluminescence properties of synthesized polymers.
- To study the electroluminescence properties of polymers.
- To analyze the chemical sensing properties of polymers.

Plan of the work:

To fulfil the above objectives the following plans of work have been adopted.

- Preparation of 3- ester substituted thiophene monomers.
- Characterization of monomers by UV-Vis, FTIR, ^{1}H NMR.
- Polymerization of monomers by oxidative $FeCl_3$ coupling method.
- Characterization of polymers by UV-Vis, FTIR, ^{1}H NMR, GPC, XRD.
- Study the thermal properties of polymers by TGA/ DSC.
- Investigation the electrochemical behaviour of polymers by cyclic voltametry.
- Study the photoluminescence properties of polymers by fluorescence spectrophotometer.
- Fabrication of LED device using synthesised polymers.
- Testing of device
- Evaluation of electroluminescence properties.

References

1 D. D. C. Bradley, *Synth Met*, *54* **(1993)** 401.
2. D. R. Baigent, N. C. Greenham, J. Gruener, R. N. Marks, R. H. Friend, S. C. Moratti, A. B. Holmes, *Synth Met*, *67* **(1994)** 3.
3. D. Neher, *Adv Mater*, *7* **(1995)** 691.
4. Y. Yang, *MRS Bull*, *June* **(1997)** 31.
5. W. C. Holton, *Solid State Technol*, *40* **(1997)** 163.
6. A. Kraft, A. C. Grimsdale, A. B. Holmes, Angew. Chem. Int. Ed., 37 (1998) 402.
7. J. L. Segura, *Acta Polym*, *49* (1998) 319.
8. A. Greiner, *Polym Adv Technol*, *9* **(1998)** 371.
9. R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dossantos, J. L. Bredas, M. Logdlund & W. R. Salaneck, *Nature, 397* **(1999)** 121.
10. J. Kalinowski, *J Phys D Appl Phys*, *32* **(1999)** R179.
11. M. Grell, D. D C. Bradley, *Adv Mater*, *11* **(1999)** 895.
12. U. Scherf, *J Mater Chem*, *9* **(1999)** 1853.
13. P. S. Heeger, A. J. Heeger, *Proc Nat Aca Sci USA, 96* **(1999)** 12219.
14. M. D. McGehee, A. J. Heeger, *Adv Mater*, *12* **(2000)** 1655.
15. U. Mitschke, P. Bauerle, *J Mater Chem*, *10* **(2000)** 1471.
16. M. T. Bernius, M. Inbasekaran, J. O'Brien, W. Wu, *Adv Mater*, *12* **(2000)** 1737.
17. D. Y. Kim, H. N. Cho, C. Y.Kim, *Prog Polym Sci*, *25* **(2000)** 1089.
18. M. Bernius, M. Inbasekaran, E. Woo, W. Wu, L. Wujk'owski, *J mater Sci Mater Electronics, 11* **(2000)** 111.
19. T. Y. Luh, S. Basu, R. M. Chen, *Current Sci*, *78* **(2000)** 1352.
20. Y. Shirota, *J Mater Chem*, *10* **(2000)** 1.
21. U. H. F. Bunz, *Chem Rev*, *100* **(2000)** 1605.
22. R. H. Friend, *Pure Appl Chem*, *73* **(2001)** 425.
23. L. Dai, B. Winkler, L. Dong, L. Tong, A. W. H. Mau, *Adv Mater*, *13* **(2001)** 915
24. M. Leclerc, *J Polym Sci Part A Polym Chem*, *39* **(2001)** 2867.
25. D. Neher, *Macromol Rapid Commun*, *39* **(2001)** 1365.
26. C. D. Dimitrakopoulos, D. J. Mascaro, *IBM J Res &Dev*, *45* **(2001)** 11
27. A. J. Heeger, *Angew Chem Int Ed*, *40* **(2001)** 2591
28. A. J. Heeger, *Rev Modern Phys*, *73* **(2001)** 681.
29. I. D. Rees, K. L. Robinson, A. B. Holmes, C. R. Towns, R O'Dell, *MRS Bull*, *June* **(2002)** 451.
30. U. Scherf, E. J. W. List, *Adv Mater*, *14* **(2002)** 477.
31. L. S. Hung, C. H. Chen, *Mater Sci Eng R,39* **(2002)** 143.
32. B. J. Schwartz, *Annu Rev Phys Chem*, *54* **(2003)** 141.
33. T. Yamamoto, *Synth Lett*, **(2003)** 425.
34. J. V. Grazulevicius, P. Strohriegl, J. Pielichowski, K. Pielichowski, *Prog Polym Sci*, *29* **(2003)** 1297.
35. L. Akcelrud, *Prog Polym Sci*, *28* **(2003)** 875.
36. A. Misra, L. Kumar, P. Kumar, S. K. Dhawan, M. N. Kamalasanan, S Chandra, *Ind J Pure and Appl Phys*, *42* **(2004)** 793.
37. A. P. Kulkarni, C. J. Tonzola, A. Babel, S. A. Jenekhe, *Chem Mater*, *16* **(2004)** 4556
38. J. L. Bredas, D. Beljonne, V. Coropceanu, J. Cornil, *Chem Rev*, *104* **(2004)** 4971
39. J. Li, C. Ma, J. Tang. C. S. Lee, S. Lee, *Chem Mater*, *17* **(2005)** 615.
40. D. Dini, *Chem Mater*, *17* **(2005)** 1933.

41. G. Hughes, M. R. Bryce, *J Mater Chem*, *15* **(2005)** 94.
42. T. B. Singh, N. S. Sariciftci, *Annu Rev Mater Res*, *36* **(2006)** 199.
43. S. W. Thomas III, G. D. Joly, T. M. Swager, *Chem Rev*, *107* **(2007)** 1339.
44. S. Gunes, H. Neugebauer, N. S. Sariciftci, *Chem Rev*, *107* **(2007)** 1324.
45. X. Yang, T. Loos, *Macromolecules,40* **(2007)** 1353.
46. A. Facchetti, *Materialstoday, 10* **(2007)** 28.
47. J. Kalinoswki, *Opt Mater*, *30* **(2008)** 792.
48. J. F. Lutz, H. G. Borner, *Prog Polym Sci*, *33* **(2008)** 1.
49. M. A. Rahman, P. Kumar, D. S. Park, Y. B. Shim, *Sensor, 8* **(2008)** 118.
50. E. Smela, *MRS Bull*, *33* **(2008)** 197.
51. A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz, and A. B. Holmes, *Chem Rev*, *109* **(2009)** 897.
52. H. Shirakawa, E. J. Louis, A. G. MacDiramid, C. K. Chiang, A. J. Heeger, *J Chem Soc*, *Chem Commun*, **(1977)** 578.
53. W. P. Su, J. R. Shrieffer, A. J. Heeger, *Phys Rev Lett*, *42* **(1979)** 1698.
54. W. P. Su, J. R. Shrieffer, A. J. Heeger, *Phys Rev*, *B22* **(1980)** 2209.
55. D. M. Ivory, G. G. Miller, J. M. Sowa, L. W. Shacklette, R. R. Chance, R. H. Baughman, *J Chem Phys*,*71* **(1979)** 1506.
56. P.J. Nigrey, A. G. MacDiarmid, A. J. Heeger, *JCS Chem Comm*, **(1979)** 594.
57. J. H. Burroughes, C. A. Jones, R. H. Friend.. *Nature*, *335* **(1998)** 137.
58. A. J. Epstein, *MRS Bull*, *22* **(1997)** 16.
59. A. G. MacDiarmid, W. Zhang, *MRS Bulletin.*, *22* **(1997)** 24.
60. H. E. Katz, J. Huang, *Annu Rev Mater Res*, *39* **(2009)** 71.
61. Q. Sun, Y. Li, Q. Pei, *J Display Technol*, *3* **(2007)** 211.
62. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Maokay, R. H. Friend, P. L. Burns, A. B. Holmes, *Nature, 347* **(1990)** 539.
63. D. Braun, A. J. Heeger, *Appl Phys Lett*, *58* **(1991)** 1982.
64. G. Yu, K. Pakbaz, A. J.Heeger, *Appl Phys Lett*, *64* **(1994)** 3422.
65. G. Yu, C. Zhang, A. J.Heeger, *Appl Phys Lett*, *64* **(1994)** 1540.
66. C. J. Brabec, N. S. Sariciffci, J. C. Hummelen, *Adv Funct Mater*, *11* **(2001)** 15.
67. Q. Pei, G. Yu, C. Zhang, Y. Yang, A. J. Heeger, *Science, 269* **(1995)** 1086.
68. Q. Pei, Y. Yang, G. Yu, C. Zhang, A. J. Heeger, *J Am Chem Soc*, *118* **(1996)** 3922.
69. S. R. Forrest, *Nature, 428* **(2004)** 911.
70. M. C. Choi, Y. Kim, C. S. Ha, *Prog Polym Sci*, *33* **(2008)** 581.
71. O. Olabisi (Ed.), "Hand book of Thermoplastics", Marcel Dekker, New York, **(1997)**, pp. 837-871.
72. D. Kumar, R. C. Sharma, *Eur Polym J*, *34* **(1998)** 1053.
73. J. Roncali, *Chem Rev*, *92* **(1992)** 711.
74. R. D. McCullough, *Adv Mater*, *10* **(1998)** 93.
75. U. Scherf, *Top Curr Chem*, *201* **(1999)** 163.
76. T. Yamamoto, *Macromol Rapid Commun*, *23* **(2002)** 583.
77. Y. J. Cheng, T. Y. Luh, *J Organomet Chem*, *689* **(2004)** 4137.
78. M. Grigoras, N. C. Antonoaia, *Rev Roum Chim*, *50* **(2005)** 245.
79. N. Toshima, S. Hara, *Prog Polym Sci*, *20* **(1995)** 155.
80. M. J. G. Tejera, E. Sanchez de la Balanca, I. Carrillo, *Synth Met*, *158* **(2008)** 165.
81. I. Osaka, R. D. McCullough, *Account Chem Research, 41* **(2008)** 1202.
82. S. J. Higgins, *Chem Soc Rev*, *26* **(1997)** 247.
83. A. Pelter, I. Jenkins, D. E. Jones, *Tetrahedron, 53* **(1997)** 10357.
84. H. Segawa, T. Shimidzu, M. Honda, *J Chem Soc Chem Commun*, **(1989)** 132.
85. S. Maiti, *Ind J Chem Sci*, *4* **(1990)** 113.

86. J. Hassan, M. Sevignon, C. Gozzi, E. Sculz, M. Lemaive, *Chem Rev*, *100* **(2002)** 1359.
87. S. Annapoorni, N. S. Sundaresan, S. S. Pandey,, B. D. Malhotra, *J Appl Phys*, *74* **(1993)** 2109.
88. M. R. Buchmeiser, *Chem Rev*, *100* **(2000)** 1565.
89. E. Ruckenstein, J. S. Park, *J Appl Polym Sci*, *42* **(1992)** 925.
90. E. Ruckenstein, J. S. Park, *Synth Met*, *44* **(1991)** 293.
91. Z. Cal, C. R Martin, *J Am Chem Soc*, *111* **(1989)** 4138.
92. W. Liang., C R. Martin, *J Am Chem Soc*, *112* **(1990)** 9666.
93. R. H Baughman, *J Polym Sci Polym Phys Ed*, *12* **(1974)** 1515.
94 Z Ogumi, Y Uchimoto, Z Takehara, F R Foulkes, *J Electrochem Soc*, *137* **(1990)** 29
95. M. Thakur, *Macromolecules, 21* **(1988)** 661.
96. Q. Shang, S. Pramanick, B Hudson, *Macromolecules, 23* **(1990)** 1886.
97. C. Zhang, D. Braun, A. J. Heeger, *J Appl Phys*, *73* **(1993)** 5177.
98. S. N. Hoier, S. M. Park, *J Electrochem Soc*, *140* **(1993)** 2454.
99. G. Schopf, G. Kobmehl, *Adv Polym Sci*, *129* **(1996)** 1.
100.R. Sugimoto, S. Takeda, H. B. Gu, K. Yoshino, Chem Express, 1 (1986) 635.
101.M. Lanzi, P. C. Bizzarri, L. Paganin, G. Cesari, Eur. Polym. J., 43 (2007) 72.
102.M. Zagorska, I. K. Bajer, A Pron, P. Raimond, F. Kajzar, A. J. Attias, *Synth Met*, *102* **(1999)** 1141.
103.H. S. Ganapathy, H. S. Hwang, K. T. Lim, *Ind Eng Chem Res*, *45* **(2006)** 3406.
104.M. Nicolas, F. Guittard, S. Geribaldi, *J Polym Sci Part A Polym Chem*, *45* **(2007)** 4707.
105.F. Andreani, P. C. Bizzari, C. D. Casa, E. Salatelli, *Polym Bull*, *27* **(1991)** 117
106 H. S Ganapathy, J S Kim, S H Jin, Y S Gal, K T Lim, *Synth Met*, *156* **(2006)** 70
107 P C Bizzarri, F Andreani, C D Casa, M Lanzi, E Salatelli, *Synth Met*, *75* **(1995)** 141
108.M. D. Curtis, M. D. McClain, *Chem Mater*, *8* **(1996)** 945.
109.T. Yamamoto, T. Uemura, A. Tanimoto, S. Sasaki, *Macromolecules,36* **(2003)** 1047.
110 K. Y. Jen, R. Oboodi, R. L. Elsenbaumer, *Polym Mater Sci Eng*, *53* **(1985)** 79.
111.R. D. McCullough, R. D. Lowe, *J Chem Soc Chem Commun*, **(1992)** 70.
112.R. S. Loewe, P. C. Ewbank, J. Liu, L. Zhai, R. D. McCullough, *Macromolecules, 34* **(2001)** 4324.
113.T. A. Chen, R. D. Reike, *J Am Chem Soc*, *114* **(1992)** 10087.
114.M. Rehahn, A. D. Schluter, G. Wegner, W. J. Feast, *Polymer, 30* **(1989)** 1054.
115.Z. Bao, W. Chan, L. Lu, *Chem Mater*, *5* **(1993)** 2.
116.http://en.wikipedia.org/wiki/Conductive_polymer, (accessed on 26.07.**2009)**
117.C. D. Dimitrakopoulos, P. R. L. Malenfant, *Adv Mater*, *14* **(2002)** 99.
118.B. S. Ong, Y. Wu, P. Liu, S. Gardner, *J Am Chem Soc*, *126* **(2004)** 3378.
119.http://en.wikipedia.org/wiki/PLED (accessed on 26.07.**2009**).
120.X. Gong, J C. Ostrowski, M. R. Robinson, G. C. Bazan, A. J. Heeger, *Adv Mater*, *14* **(2002)** 581.
121.I. F. Perepichka, D. F. Perepichika, H. Meng, F. Wudl, *Adv Mater*, *17* **(2005)** 2281.
122.J. Guillet, "Photophysics and Photochemistry", Cambrige University Press, London, **(1985)**.
123.J. R. Lakowitz, "Principles of Fluorescence Spectroscopy", Kluwer Academic, New York, 2nd edition, **(1999)**.
124.*J.* Kim, Pure *Appl Chem*, *74* **(2002)** 2031.
125.I. G. Scheblykin, A. Yartsev, T. Pullerits, V. Gulbinas, V. Sundstrm, *J Phys Chem B*, *111* **(2007)** 6303.
126.E. L. Cabarcos , S. A. Carter , *Macromolecules, 38* **(2005)** 4409

127.A. P. Davey, S. Elliott, O. O'Connor, W. Blau, *J Chem Soc Chem Commun*, **(1995)** 1433.

128.J. C. deMello, H. F. Wittman, R. H. Friend, *Adv Mater ,9* **(1997)** 230.

129.L. O. Palsson, A. P. Monkman, *Adv Mater ,14* **(2002)** 757.

130.H. Chosrovian. S. Rentsch, D. Grebner, D. U. Dahm, E. Birckner, H. Naarmann, *Synth Met, 60* **(1993)** 23.

131.D. Beljonne, J. Cornil, R. H. Friend, R. A. J. Janssen, J. L. Bredas, *J Am Chem Soc ,118* **(1996)** 6453.

132.M. Pope, C. E. Swenberg, "Electronic processes in Organic Crystals",Oxford University Press, New York, 2nd edition, **(1999)**.

133.J. B. Birks, "Photophysics of Aromatic Molecules", Wiley Interscience, London, **(1970)**.

134.H. S. O. Chan, S. C. Ng, *Prog Polym Sci, 23* **(1998)** 1167.

135.N. Somanathan, S. Radhakrishnan, *Int J Mod Phys B, 19* **(2005)** 4645.

136.A. Mishra, C. Q. Ma, P. Bauerle, *Chem Rev, 109* **(2009)** 1141.

137.W. S. Huang, J. M. park, *J Chem Soc Chem Commun*, **(1987)** 856.

138.K. G. Chittibabu, L. Li, M. Kamath, S. K.Tripathy, *Chem Mater ,6* **(1994)** 475.

139.J. P. Ruiz, K. Nayak, D. S. Marynick, J. R. Renolds, *Macromolecules, 22* **(1989)** 1231.

140.M. Liu, R. V. Gregory, *Synth Met, 69* **(1995)** 349.

141.J. P. Aime, F. Bargain, M. Schoot, H. Eckhardt, G. G Miller, R. L. Elsenbaumer, *Phys Rev Lett, 62* **(1989)** 55.

142.X. Hu, L. Xu, *Polymer, 41* **(2000)** 9147.

143.D. Fichou, *J Mater Che, 10* **(2000)** 571.

144.M. Leclerc, K. Faid, Adv. Mater., 9 ***(1997)*** *1087*

145.X. Zhao, X. Hu, L. H. Gan, *Polym Adv Technol, 16* **(2005)** 370.

146.M. R. Anderson, M. Beggren, O. Inganas, G. Gustafsson, *Macromolecules, 28* **(1995)** 7525.

147.M. R.Anderson, O. Thomas, W. Mammo, M. Svensson, M. Theander, O. Inganas, *J Mater Chem, 9* **(1999)** 1933.

148.G. Daoust, M. Leclerc, *Macromolecules, 24* **(1991)** 455.

149.M. Pomerantz, H. Yang, Y. Cheng, *Macromolecules, 28* **(1995)** 5706.

150.M. Pomerantz, Y. Chang. R. K. Kasim, R. L. Elsenbaumer, *J Mater Chem, 9* **(1999)** 2155.

151.M. Lanzi, P. C. Bizzarri, L. Paganin, G. Cesari, *Eur Polym J, 43* **(2007)** 72.

152.A. R. Murphy, J. Liu, C. Luscombe, D. Kavulak, J. M. Frechet, R. J. Kline, M. D. McGehee, *Chem Mater ,17* **(2005)** 4892.

153.T. K. Kang, J. Y. Kim, K. J. Kim, C. Lee, S. B. Rhee, *Synth Met, 69* **(1995)** 377.

154.C. Lee, K. J. Kim, S. B. Rhee, *Synth Met, 69* **(1995)** 295.

155. S Lee, S I. Hong, C Lee, S. B Rhee, T J. Kang, *Mol Cryst Liq Cryst, 295* **(1997)** 19

156.A. Bolognesi, C. Botta, Z. Geng, C. Flores, L. Denti, *Synth Met, 71* **(1995)** 2191.

157. T. Johansson, W. Mammo, M. Seensson, M. A. Andersson, O. Inganas, *J Mater Chem, 13* **(2003)** 1316.

CHAPTER 2

Synthesis and characterization of ester substituted polythiopenes

2.1 Introduction

Conjugated polymers exhibit unique electronic and optical properties due to their π-conjugation and special chemical structure [1-11]. The creative design and development strategies for conjugated polymers have led to new materials and enhanced performance. In determining the physical properties of conjugated polymers, more research has been focused on the structure and function of these materials. The synthesis can help to achieve the magnitude of π overlap along the backbone and enhanced solubility. In light emitting diode (LED) application, 3- substituted polythiophene have stimulated much interest due to their solubility, environmental stability, fusibility, better processibility and tuneability of colour from UV to IR by changing the substituents [12-18].

Substituted polythiophenes have been prepared by electrochemical and chemical polymerization techniques [19-20]. Electrochemical polymerization fails to produce large scale and soluble polymers. Therefore, chemical polymerization methods have attained popularity for synthesizing the large scale and soluble polymers. The chemical polymerization methods include oxidative coupling, Yamamoto coupling, McCullough method, Grignard Metathesis (GRIM) method, Reike method, Suzuki and Stille method [15, 20-24]. $FeCl_3$ oxidative coupling is a straightforward, simple, versatile and the least expensive method among other chemical polymerization techniques. 3-substituted polythiophenes with alkyl, fluoroalkyl, phenyl, alkoxy, ester groups in side chain have been synthesized by $FeCl_3$ oxidative coupling [25-40]. Ester substituted polythiophenes have been prepared using either a $FeCl_3$ suspension in $CHCl_3$ or $FeCl_3$ precipitated in-situ by a solvent / nonsolvent mixture (CH_3NO_2 / CCl_4) [41-54]. The later method gives higher monomer conversions and polymer yields.

A considerable effort has been made to the synthesis of polymers with special emphasis on the improved solubility. Introduction of side chains on conjugated backbone not only provide solubility, but also they have a major influence on the characteristics of polymers. We have combined the alkyl group with the chain length from C_6 to C_{12}, 3-pentadecyl phenyl, 3-pentadecyl cyclohexyl and quinoline moiety as a side chain in polythiophene ester backbone.

The part of this chapter was published in *J. Polym. Mater. 25 (2008) 445*

This chapter describes the synthesis and characterization of monomers and polymers and their thermal properties. We have synthesized the following 3-ester substituted thiophene.

i) Hexyl 2-(thiophene-3-yl) acetate (HTA)
ii) Octyl 2-(thiophene-3-yl) acetate (OTA)
iii) Decyl 2-(thiophene-3-yl) acetate (DTA)
iv) Dodecyl 2-(thiophene-3-yl) acetate (DDTA)
v) 3-pentadecylphenyl 2-(thiophene-3-yl) acetate (PDPTA)
vi) 3-pentadecylcyclohexyl 2-(thiophene-3-yl) acetate (PDCHTA)
vii) Quinoline -8-yl 2-(thiophene-3-yl) acetate (QTA)

The monomers were synthesized by esterification reaction of 3-thiophene acetic acid and corresponding alcohols and characterized by ^{1}H NMR, FTIR and UV-Vis analysis. The polymerization was accomplished by oxidative coupling in the presence of $FeCl_3$. The synthesized polymers were characterized by ^{1}H NMR, FTIR, UV-Vis, XRD and GPC analysis. Thermal properties of polymers were studied by TGA and DSC technique.

2.2 Materials

3- thiophene acetic acid (Aldrich), 1- hexanol (Aldrich), 1- octanol (Aldrich), 1-decanol (Aldrich), 1- dodecanol(Aldrich), 8- hydroxyl quinoline (Fluka), $FeCl_3$ (Aldrich) were used as received. 3- pentadecyl phenol, 3-pentadecylcyclo hexanol and dimethylamino pyridine (DMAP) were recrystallized from ethanol. All the solvent were distilled before use and the reactions were performed under nitrogen atmosphere.

2.3 Instrumentation

2.3.1 UV- Visible spectrophotometer

UV-Visible (UV-Vis) spectrophotometer provides information about structure and stability of the materials in solution. Various kinds of electronic excitation may occur in organic molecules by absorbing the energies available in the UV-Vis region. The spectrophotometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance versus wavelength. The intensity of the absorption is proportional to the number, type and location of colour absorbing structures (chromophores) in the molecule. UV-Visible spectra were recorded on a Shimadzu UV-2550 UV-VIS Spectrophotometer using tetrahydrofuran (THF) solvent.

2.3.2 Fourier transform infrared spectrophotometer (FTIR)

FTIR is a useful method for the characterization of monomer and polymers. It is primarily used for the detection of functional groups, but analysis of spectra in the lower frequency finger print region can give evidence of degree of polymerization and the effect of substituents on the electronic properties of the polymer backbone. FTIR spectra were recorded on a Nicolet, Impact 410 by using KBr pallet.

2.3.3 Nuclear magnetic resonance spectrometer (^{1}H NMR)

NMR spectroscopy is one of the principal techniques used to obtain physical, chemical, electronic and structural information about molecules. Structure of compound can be determined by studying the peaks of NMR spectra. It is a very selective technique, distinguishing among many atoms with in a molecules or collection of molecules of the same type but which differ only in terms of their local chemical environment. In proton NMR spectroscopy, structure of molecules is ascertained with respect to hydrogen nuclei within the molecule of a substance. ^{1}H NMR spectra were obtained on a Bruker AMX 400MHz with deuterated $CHCl_3$ having TMS as internal standard.

2.3.4 Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) is used to determine the relative molecular weight of polymer samples as well as the distribution of molecular weights. Generally, GPC measures the molecular volume and shape function as defined by the intrinsic viscosity of polymer sample. Molecular weights of polymers were measured by gel permeation chromatography (410 Waters differential refractometer) (Water, USA). Flow rate is 1ml /min. Polymers were dissolved in THF solvent. Molecular weights were determined on the basis of polystyrene standards.

2.3.5 X- ray diffraction

X-ray diffraction technique gives the information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. X-ray diffraction technique is based on the elastic scattering of X-rays from structures that have long range order. X-ray diffraction data for the polymer were collected at room temperature on a Rigaku Minislex X-ray diffractometer Cu Kα radiation (λ=0.15418nm) at 30kV and 15mAmp.

2.3.6 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) reveals the thermal characteristics of polymers including degradation temperature, absorbed moisture content the level of oligomer in polymer etc. It determines the weight loss with respect to temperature. Thermogravimetric analysis (TGA) was conducted on a Shimadzu TG 50 thermogravimetric analyzer with a heating rate of 10°C/min under a nitrogen atmosphere. Analysis was performed at 0- 650 °C temperature ranges.

2.3.7 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is used widely for polymers. It evaluates glass transition temperature (T_g), melting temperature (T_m), purity of polymers. The result of a DSC experiment is a curve of heat flux versus temperature or versus time. Differential scanning calorimetry (DSC) of the polymers was accomplished on DSC-60 (Shimadzu) with a heating rate of 10°C/ min under a nitrogen atmosphere. Analysis was performed at 0- 300 °C temperature ranges.

2.4 Experiment

2.4.1 Monomers synthesis

2.4.1.1 Hexyl 2 – (thiophene-3-yl) acetate (HTA)

3-thiophene acetic acid (0.0137 moles) in 20ml dichloroethane (DCE) and thionyl chloride (0.0137 moles) were taken in a round bottom flask and refluxed for 6h. The excess thionyl chloride was removed under vacuum. Then hexanol (0.0137mole) in 15ml DCE and 3ml of pyridine were added to the flask drop wise through an additional funnel and the mixture was refluxed for 6h. After refluxing, the reaction mixture was washed with 1N HCl (3× 50ml), then saturated $NaHCO_3$ (3×50ml), and dried over K_2CO_3. The solvent was removed with a rotary evaporator and crude product was obtained. The crude product was purified by silica gel column chromatography using petroleum ether / ethyl acetate (20:1) mixture as the eluent.

The product was yellow - orange liquid.
Yield: 79%
UV- Vis (THF): λ_{max} 255 nm
FTIR (KBr): υ 3105, 2934, 2861, 1735, 1460, 1257, 1147, 765 cm^{-1}
^1H NMR (400MHz) ($CDCl_3$): δ 7.27, 7.14, 7.04, 4.09, 3.64, 1.63-0.88 ppm

2.4.1.2 Octyl 2 – (thiophene-3-yl) acetate (OTA)

Synthetic procedure of monomer (OTA) is same as monomer (HTA).

The product was yellow- orange liquid.
Yield: 71%
UV- Vis (THF): λ_{max} 254 nm
FTIR (KBr): υ 2925, 2860, 1730, 1460, 1250, 1140, 765 cm^{-1}.
^1H NMR (400MHz) ($CDCl_3$): δ 7.27, 7.14, 7.04, 4.09, 3.64, 1.63-0.88ppm

2.4.1.3 Decyl 2 – (thiophene-3-yl) acetate (DTA)

Synthetic procedure of monomer (DTA) is same as monomer (HTA).

The product was yellow orange liquid.
Yield: 73%
UV- Vis (THF): λ_{max} 254 nm
FTIR (KBr): υ 2923, 2857, 1732, 1459, 1245, 1140, 760 cm^{-1}.
^1H NMR (400MHz) ($CDCl_3$): δ 7.27, 7.14, 7.04, 4.09, 3.64, 1.63-0.88 ppm

2.4.1.4 Dodecyl 2 – (thiophene-3-yl) acetate (DDTA)

Synthetic procedure of monomer (DDTA) is same as monomer (HTA).

The product was orange liquid.

Yield: 69%

UV- Vis (THF): λ_{max} 254 nm

FTIR (KBr): υ 2923, 2856, 1734, 1459, 1261, 1145, 763 cm^{-1}.

^{1}H NMR (400MHz) ($CDCl_3$): δ7.27, 7.14, 7.04, 4.09, 3.64, 1.63-0.88ppm

2.4.1.5 3- pentadecylphenyl 2 – (thiophene-3-yl) acetate (PDPTA)

3-thiophene acetic acid (0.005 moles) in 20ml dichloroethane (DCE) and thionyl chloride (0.005 moles) were taken in a round bottom flask and refluxed for 6h. The excess thionyl chloride was removed under vacuum. Then 3-pentadecyl phenol (0.005mole) and dimethylamino pyridine (DMAP) (0.005moles) in 15ml DCE were added to the flask drop wise through an additional funnel and the mixture was refluxed for 6h. After refluxing, the reaction mixture was washed with 1N HCl (3× 50ml), then saturated $NaHCO_3$ (3×50ml), and dried over K_2CO_3. The solvent was removed with a rotary evaporator and crude product was obtained. The crude product was purified by silica gel column chromatography using petroleum ether / ethyl acetate (20:1) mixture as the eluent.

The product was viscous orange- red liquid.

Yield: 62%

UV- Vis (THF): λ_{max} 272 nm

FTIR (KBr): υ 2919, 2848, 1738, 1469, 1252, 1147, 764 cm^{-1}.

^{1}H NMR (400MHz) ($CDCl_3$): δ 7.27-7.00, 3.65, 2.54, 1.6 -0.88ppm

2.4.1.6 3-pentadecylcyclohexyl 2 – (thiophene-3-yl) acetate (PDCHTA)

Synthetic procedure of monomer (f) was same as (e).

The product was viscous orange- red liquid.

Yield: 64.49%

UV- Vis (THF): λ_{max} 253 nm

FTIR (KBr): υ 2921, 2848, 1731, 1462, 1251, 1142, 756 cm^{-1}.

^{1}H NMR (400MHz) ($CDCl_3$): δ 7.27, 7.15, 7.03, 4.00, 3.67, 1.98-0.88. ppm

2.4.1.7 Quinolin-8-yl 2 – (thiophene-3-yl) acetate (QTA)

Synthetic procedure of monomer (QTA) was same as monomer (HTA).

The product was solid.
Yield: 61%, M.P: 128°C
UV- Vis (THF): λ_{max} 256 nm
FTIR (KBr): υ 3092, 3041, 1755, 1591, 1496, 1467, 1339, 1237, 1138, 805, 755 cm^{-1}.
^{1}HNMR (400MHz)($CDCl_3$): δ 7.43-8.92, 7.25, 7.15, 7.02, 3.65 ppm.

2.4.2 Polymer Synthesis

General procedure of polymerization

The general procedure of synthesizing the polymers is shown in Scheme 2.1. Monomers in 30ml carbon tetrachloride were taken in a three-necked flask equipped with a condenser, a pressure equalizing funnel, and a nitrogen gas inlet tube and stirring was done by a magnetic stirrer. Ferric chloride (four times of monomer) in 10ml nitromethane was added dropwise to a stirred solution of monomer at 0°C with the continuous flow of nitrogen and the reaction was continued for 24 h. The reaction mixture was poured into stirred methanol (500ml) and precipitate was obtained. The precipitate was dried in vacuum. The product was dissolved in THF and reprecipitated in methanol. Thus polymer was purified by reprecipitation method.

2.4.2.1 Poly (hexyl-2-(thiophene-3-yl) acetate) (PHTA)

0.005 mole of hexyl -2(thiophene-3-yl) acetate monomer and 0.02mole of ferric chloride were used for polymerization reaction.

Yield: 66%
UV- Vis (THF): λ_{max} 370nm
FTIR (KBr): υ 2928, 2860, 1735, 1460, 1257, 1173 cm^{-1}.
^{1}H NMR (400MHz) ($CDCl_3$): δ 7.04, 4.09, 3.64, 1.63-0.88ppm

2.4.2.2 Poly (octyl-2-(thiophene-3-yl) acetate) (POTA)

0.0025 mole of octyl -2(thiophene-3-yl) acetate monomer and 0.01 mole of ferric chloride were used for polymerization reaction.

Yield: 63%

UV- Vis (THF): λ_{max}363 nm

FTIR (KBr): υ 2934, 2860, 1730, 1440, 1250, 1180 cm^{-1}.

^1H NMR (400MHz) ($CDCl_3$): δ 7.04, 4.09, 3.64, 1.63-0.88 ppm.

2.4.2.3 Poly (decyl-2-(thiophene-3-yl) acetate) (PDTA)

0.0037 mole of decyl -2(thiophene-3-yl) acetate monomer and 0.015mole of ferric chloride were used for polymerization reaction.

Yield: 62.8%

UV- Vis(THF): λ_{max}363nm

FTIR (KBr): υ 2922, 2852, 1732, 1459, 1245,1141 cm^{-1}.

^1H NMR (400MHz) ($CDCl_3$): δ 7.04, 4.09, 3.64, 1.63-0.88 ppm.

2.4.2.4 Poly (dodecyl-2-(thiophene-3-yl) acetate) (PDDTA)

0.004 mole of dodecyl -2(thiophene-3-yl) acetate monomer and 0.016mole of ferric chloride were used for polymerization reaction.

Yield: 61%

UV- Vis (THF): λ_{max} 359

FTIR (KBr): υ 2924, 2853, 1737, 1459, 1261, 1145 cm^{-1}.

^1H NMR (400MHz) ($CDCl_3$): δ 7.04, 4.09, 3.64, 1.63-0.88 ppm.

2.4.2.5 Poly (3-pendecylphenyl-2-(thiophene-3-yl) acetate) (PPDPTA)

0.0034 mole of 3-pentadecylphenyl -2(thiophene-3-yl) acetate monomer and 0.014 mole of ferric chloride were used for polymerization reaction.

Yield: 56%

UV- Vis (THF): λ_{max} 315nm

FTIR (KBr): υ 2922, 2852, 1740, 1469, 1252, 1152 cm^{-1}.

^{1}H NMR (400MHz) (CDCl$_3$): δ 7.15-7.00, 3.65, 2.54, 1.6 -0.88 ppm.

2.4.2.6 Poly (3-pentadecylcyclohexyl-2-(thiophene-3-yl) acetate) (PPDCHTA)

0.0036 mole 3-pentadecylcyclohexyl -2(thiophene-3-yl) acetate monomer and 0.0143 mole of ferric chloride were used for polymerization reaction.

Yield: 54.7%
UV- Vis (THF): λ_{max} 307 nm
FTIR (KBr): υ 2923, 2854, 1732, 1462, 1251, 1142 cm^{-1}.
^{1}H NMR (400MHz) (CDCl$_3$): δ 7.03, 4.00, 3.67, 1.98-0.88 ppm.

2.4.2.7 Poly (quinoline 8-yl-2-(thiophene-3-yl) acetate) (PQTA)

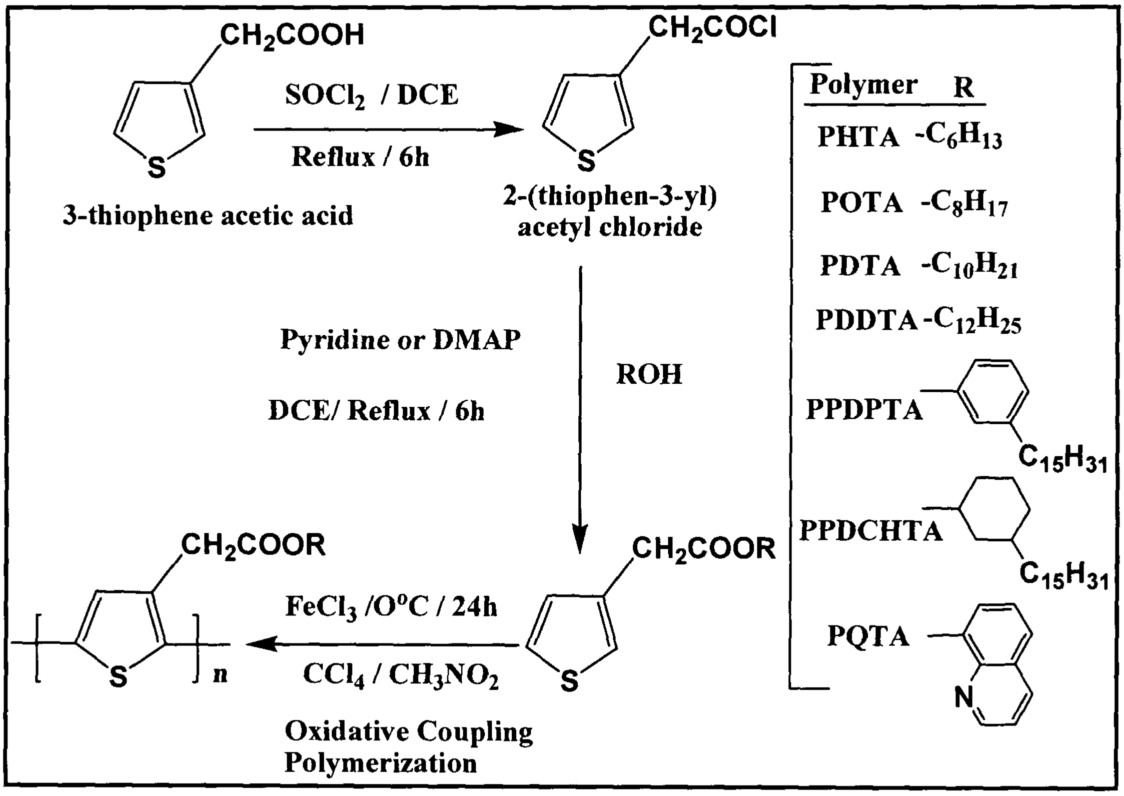
0.011 mole of quinoline 8-yl-2(thiophene-3-yl) acetate monomer and 0.044 mole of ferric chloride were used for polymerization reaction.

Yield: 42.3 %
UV- Vis (THF): λ_{max} 392nm
FTIR (KBr): 3085, 3045, 1731, 1531, 1586, 1464, 1432, 1322, 1222, 1149 cm^{-1}.
^{1}H NMR (400MHz) (CDCl$_3$): δ 7.5-8.7, 6.98, 3.65 ppm.

2.5 Results and discussions

2.5.1 Characterization of monomers

The monomers were prepared by esterification [54-58] of 3-thiophene acetic acid and corresponding alcohols (hexanol, octanol, decanol, dodecanol, 3-pentadecyl pheneol, 3-penta decyl cyclohexanol, and 8- hydroxyl quinoline) (Scheme 2.1). 3-thiophene acetic acid was first converted to 3-thiophenacetyl chloride using thionyl chloride as a chlorinating agent and subsequently reacted with alcohols in the presence of pyridine (for monomers HTA, OTA, DTA, DDTA, QTA) and dimethyl amino pyridine (DMAP) (for monomers PDPTA, PDCHTA) as acid acceptor. The yield of the monomers is 60-80%. The formation of monomers was confirmed by FTIR, ^{1}H NMR spectroscopy. The C$_\beta$-H stretching frequency (Fig2.1 -2.7.) in thiophene ring and alkyl chain on 3000 -2840 cm^{-1} was observed. The formation of ester linkage was confirmed by the presence of >C=O stretching vibration at 1720-1735 cm^{-1} and C-O-C stretching vibrations at 1250-1235 and 1145-1135 cm^{-1}. The C-H bending vibrations of alkyl group appeared at 1460 cm^{-1}. The C-H out of plane bending vibration of thiophene ring on 805-815, 760-750 cm^{-1} was observed.



Scheme 2.1: Synthesis of monomers and polymers

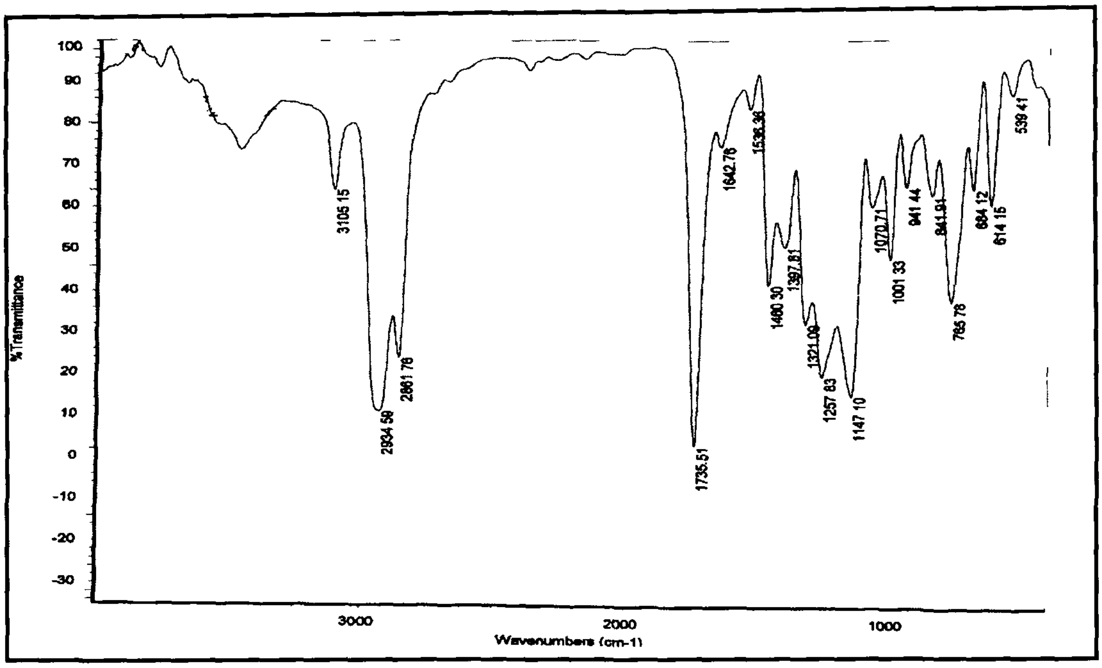


Figure 2.1: FTIR spectra of monomer HTA

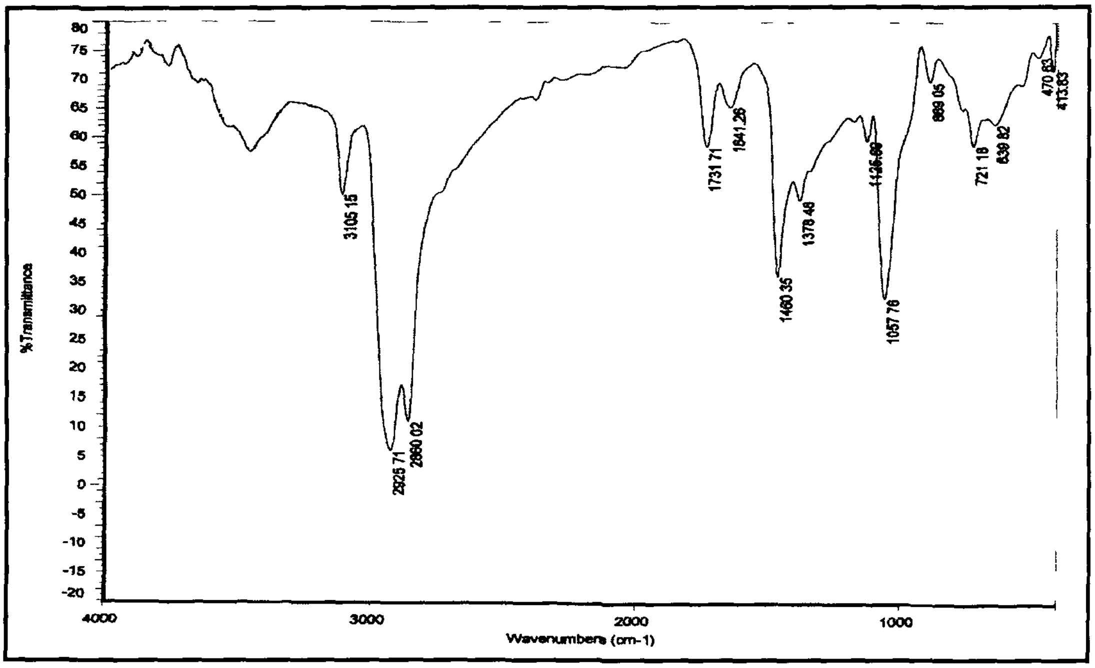


Figure 2.2: FTIR spectra of monomer OTA

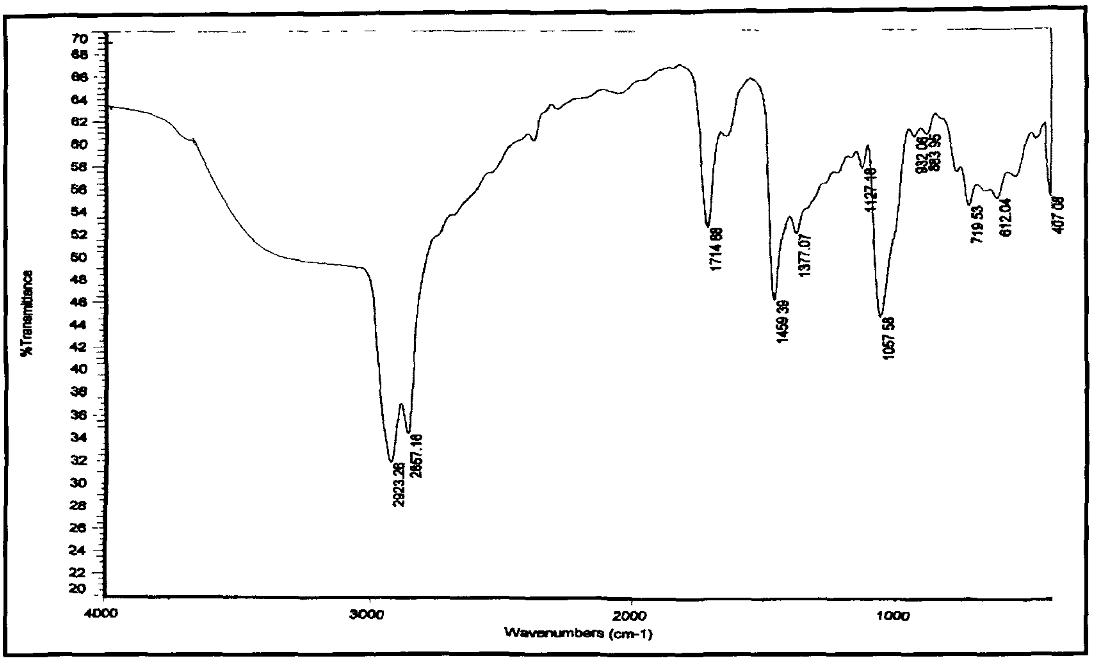


Figure 2.3: FTIR spectra of monomer DTA

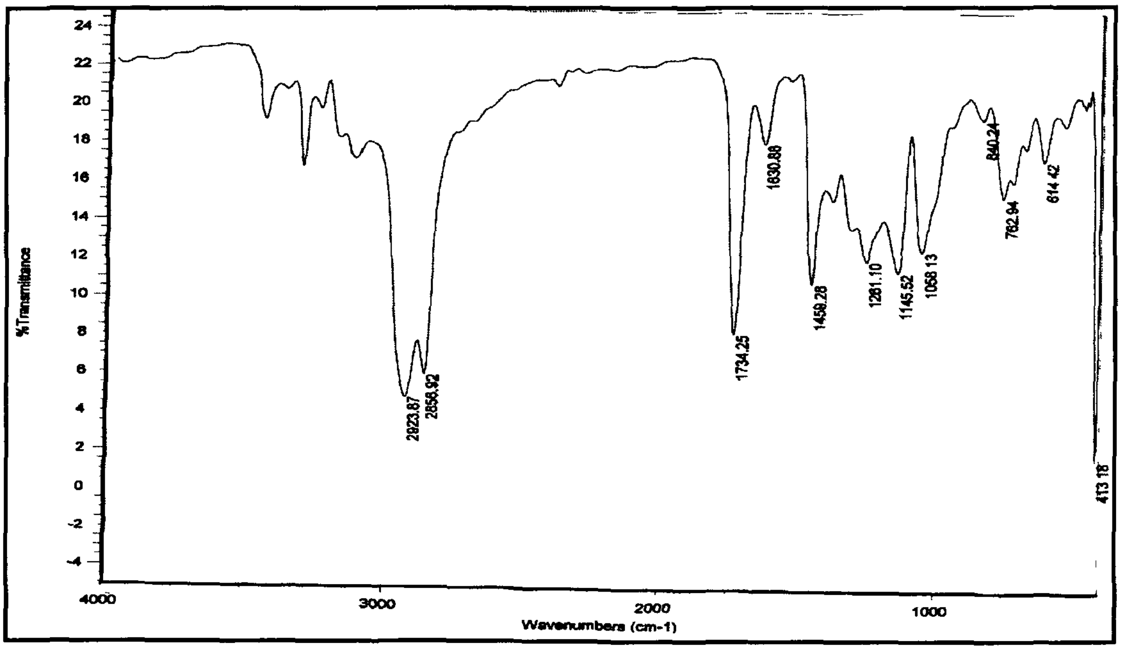


Figure 2.4: FTIR spectra of monomer DDTA

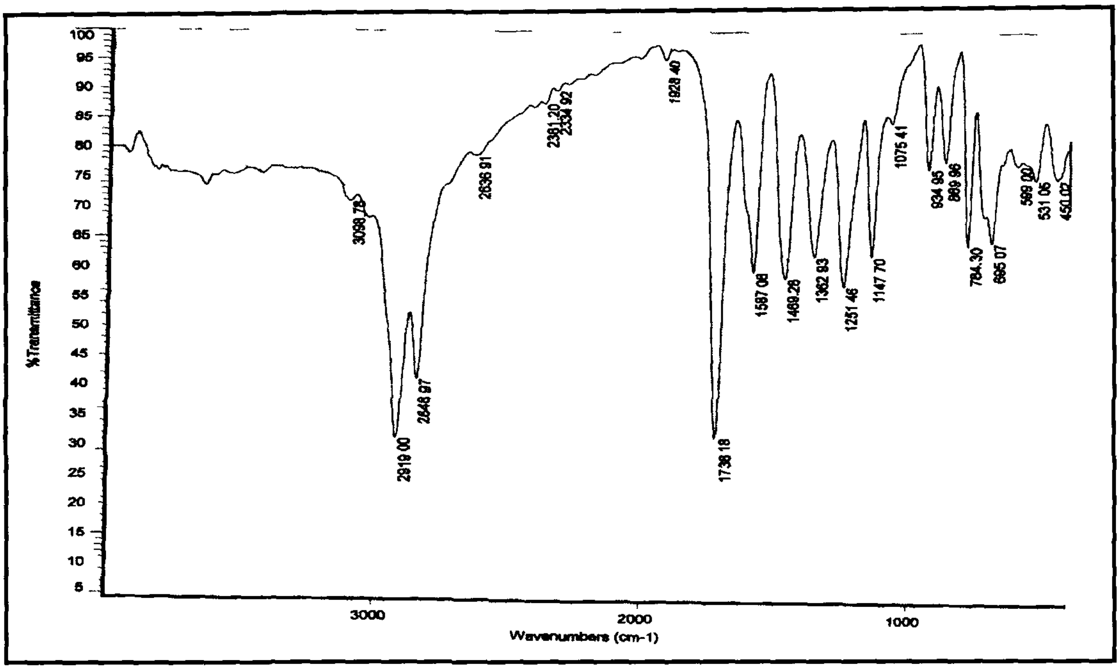


Figure 2.5: FTIR spectra of monomer PDPTA

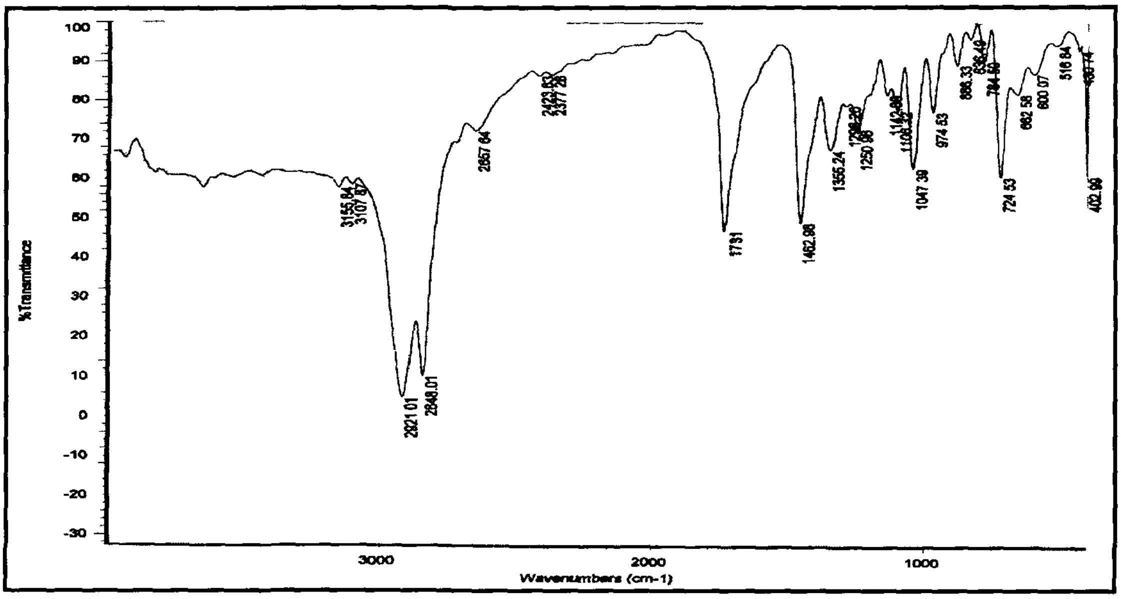


Figure 2.6: FTIR spectra of monomer PDCHTA

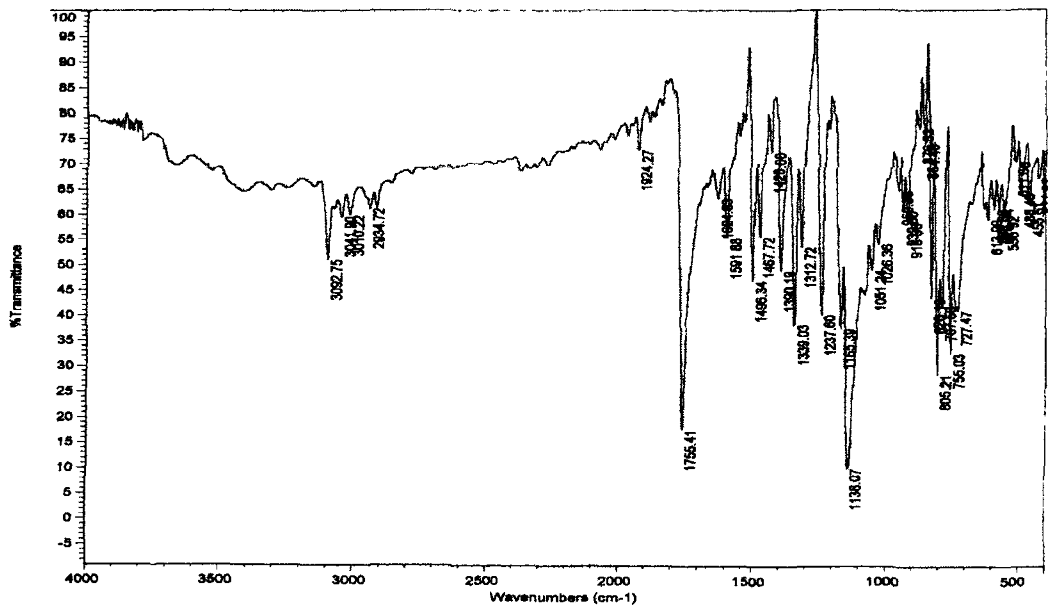


Figure 2.7: FTIR spectra of monomer QTA

In ^{1}H NMR spectra of the monomers, the signals at δ 7.05-7.03, 7.15 – 7.13, 7.27-7.25 ppm are assigned to the protons at 4, 5 and 2 position of the thiophene ring (Figure 2.8 - 2.14.). The signal at δ 3.67 – 3.64 ppm is related to the methylene group protons linked to thiophene ring. The signal at δ 4.00-4.09 ppm is related to methylene group proton linked to oxygen atom. The broad signal at δ1.63-0.88 ppm is associated with alkyl protons. The signals in the range of δ 7.43-8.92 ppm are assigned to the aromatic quinolinyl protons. The broad signal at δ 7.27-7.00 is related to aromatic phenyl protons. The numbers of protons estimated from the integration of peaks are in good agreement with the proposed structure of monomers.

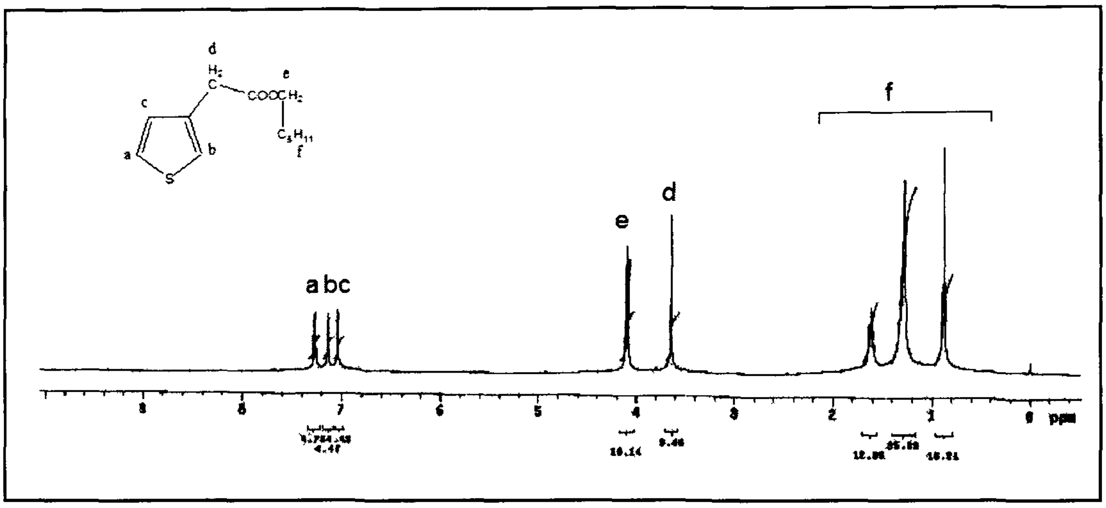


Figure 2.8: Proton NMR spectra of monomer HTA

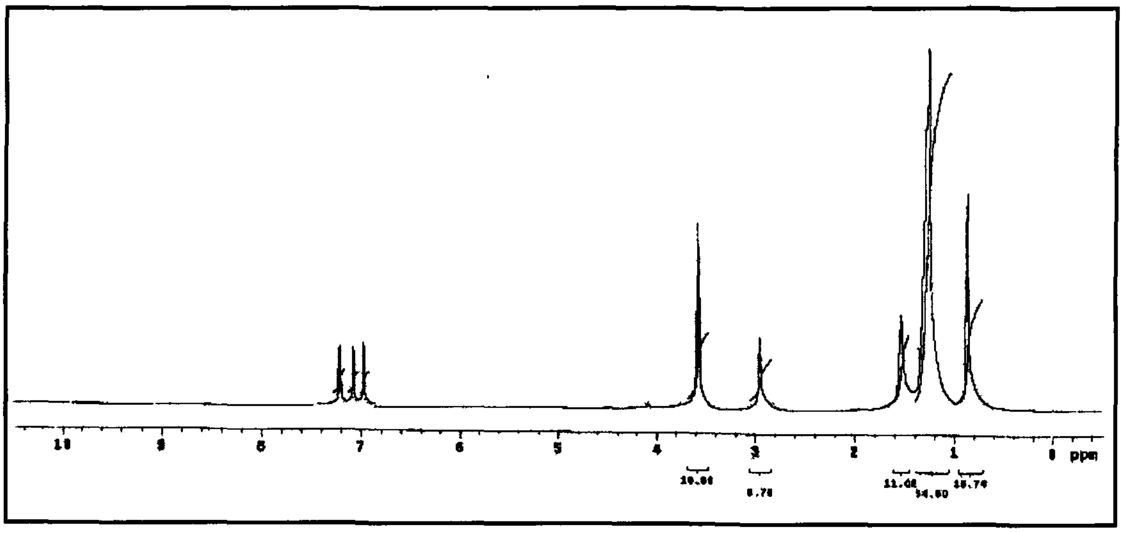


Figure 2.9: Proton NMR spectra of monomer OTA

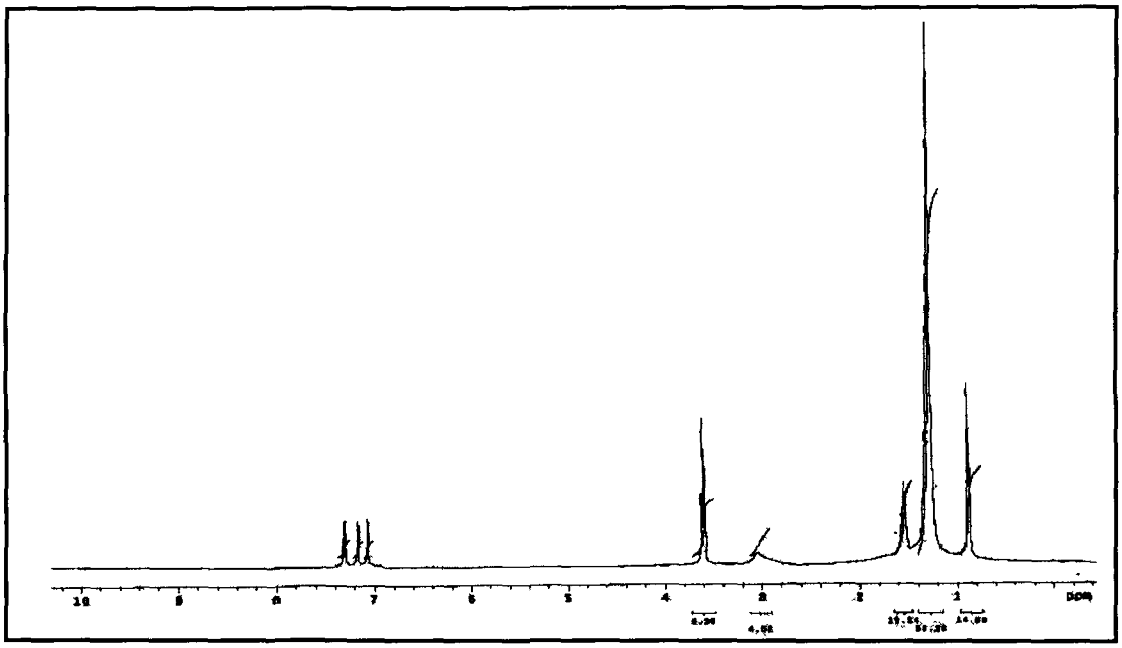


Figure 2.10: Proton NMR spectra of monomer DTA

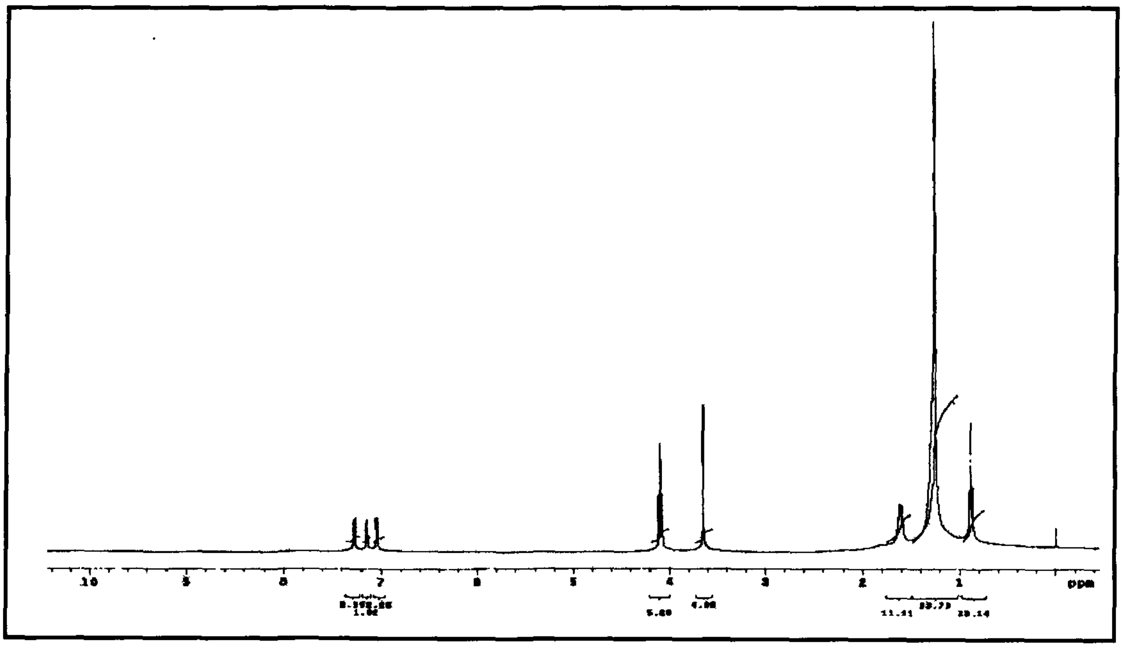


Figure 2.11: Proton NMR spectra of monomer DDTA

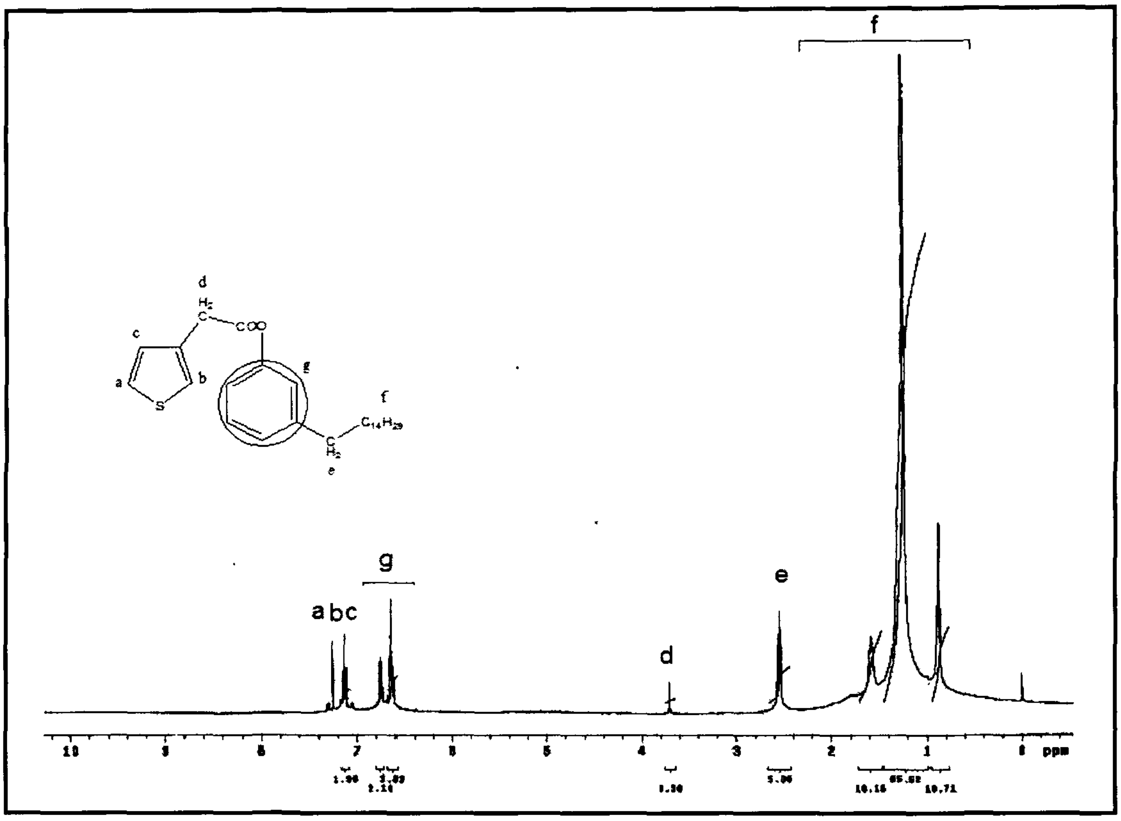


Figure 2.12: Proton NMR spectra of monomer PDPTA

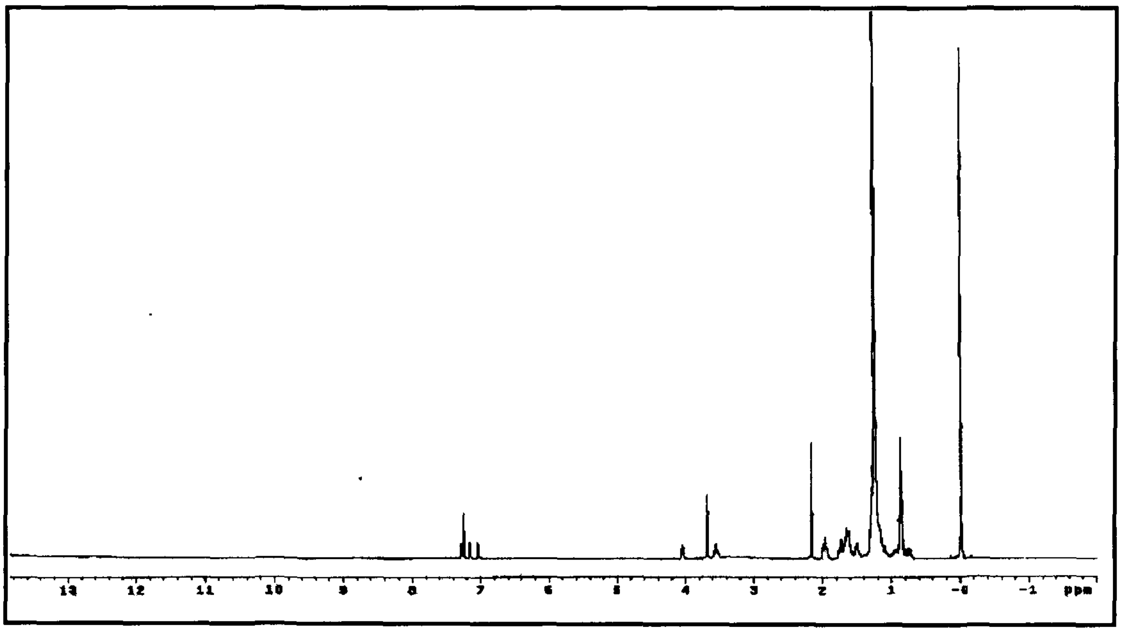


Figure 2.13: Proton NMR spectra of monomer PDCHTA

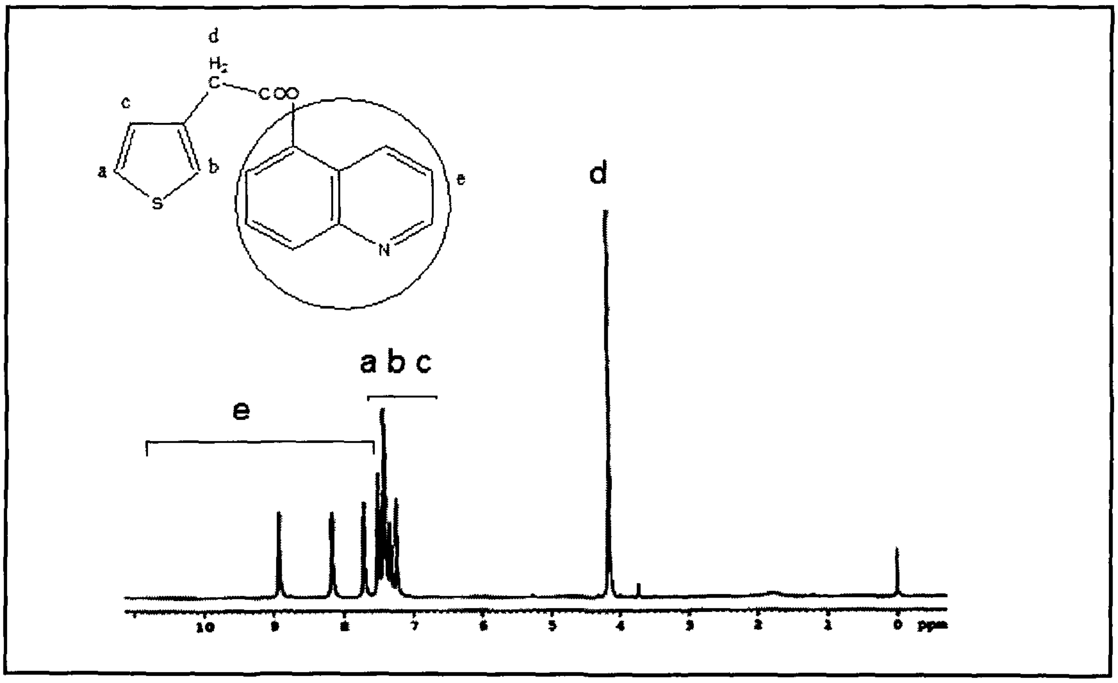


Figure 2.14: Proton NMR spectra of monomer QTA

2.5.2 Characterization of polymers

The polymers were prepared by oxidative polymerization using ferric chloride [41-54]. The polymerization process is slow and yields 42-66% polymer. The polymers showed good solubility in chloroform and THF.

The formation of polymers was further confirmed by FTIR and ^{1}H NMR spectroscopy. In polymers, the C_β-H stretching frequency in thiophene ring and alkyl chain at 3000 - 2800 cm^{-1} were observed (Figure 2.15 - 2.21). The bands at 1720 - 1735, 1250-1235 and 1145-1135 cm^{-1} which is due to the >C=O and C-O-C stretching vibration of ester group. The C-H bending vibrations of alkyl group appeared at 1460 cm^{-1}. The absence of sharp band at 805 - 755cm^{-1} confirms the polymerization, since these absorptions are characteristic of the C-H_α out of plane deformation in mono substituted thiophene ring.

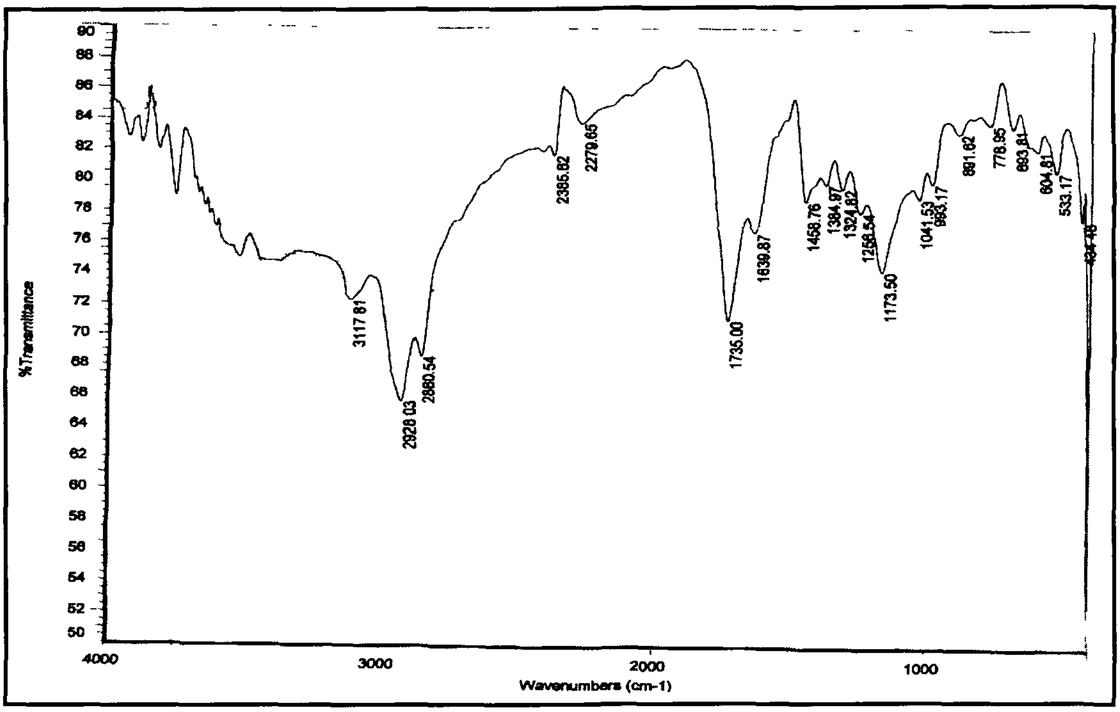


Figure 2.15: FTIR spectra of polymer PHTA

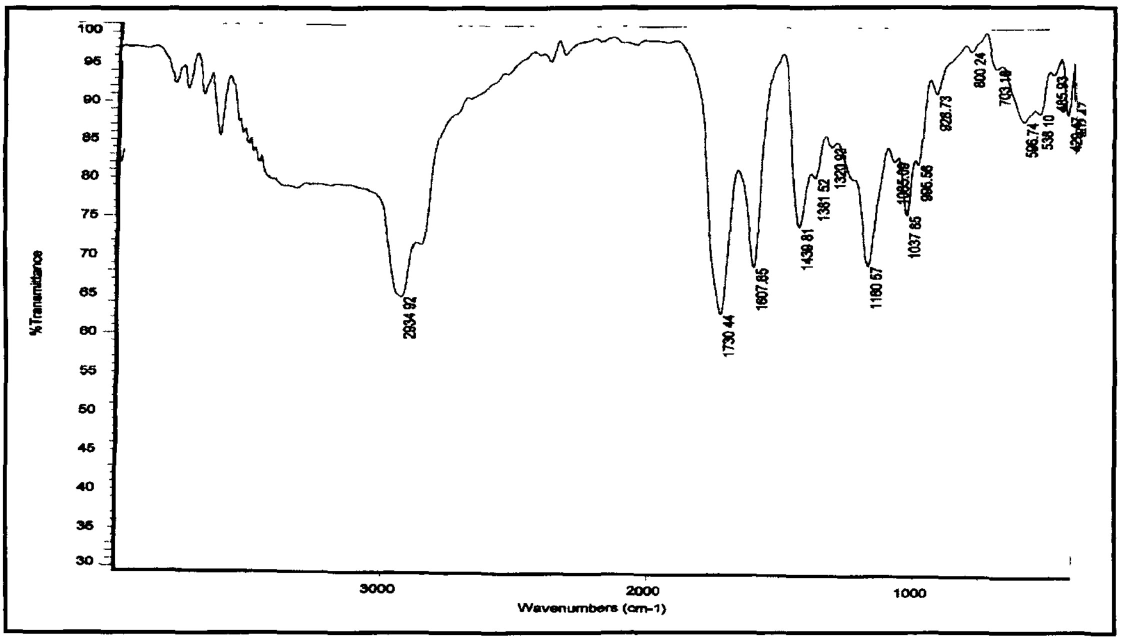


Figure 2.16: FTIR spectra of polymer POTA

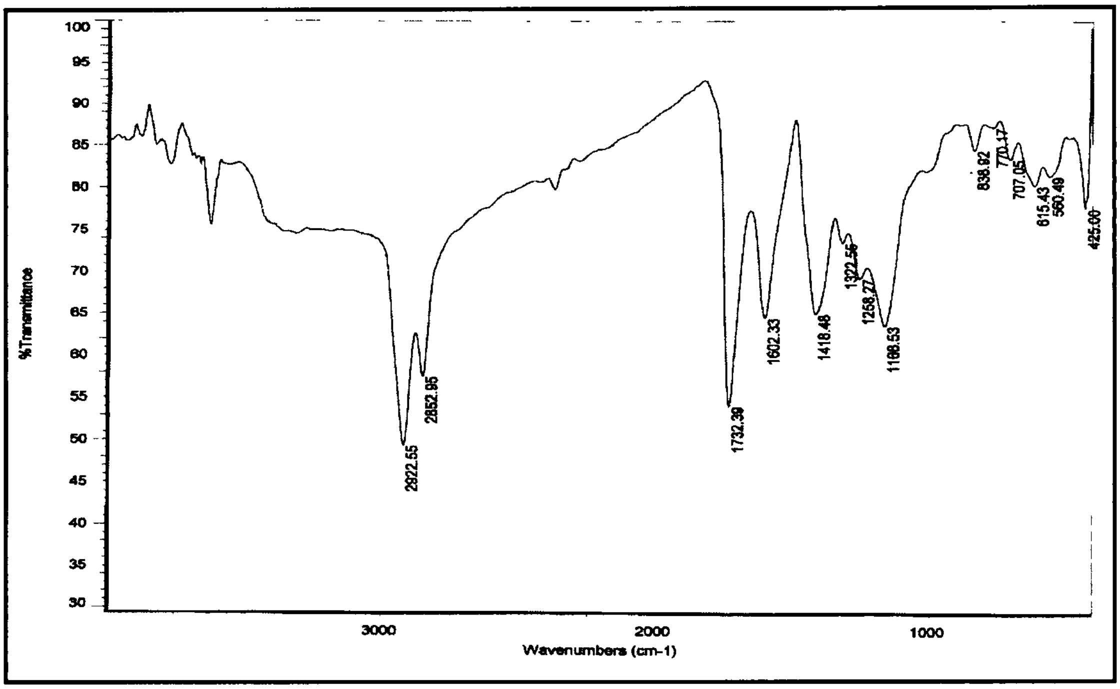


Figure 2.17: FTIR spectra of polymer PDTA

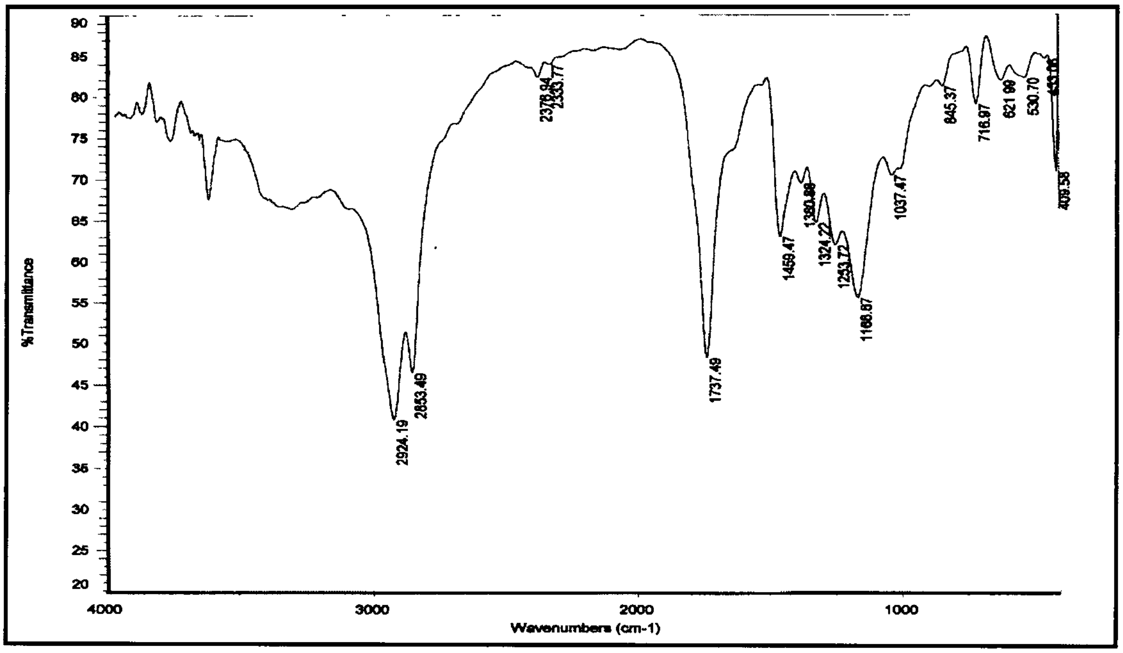


Figure 2.18: FTIR spectra of polymer PDDTA

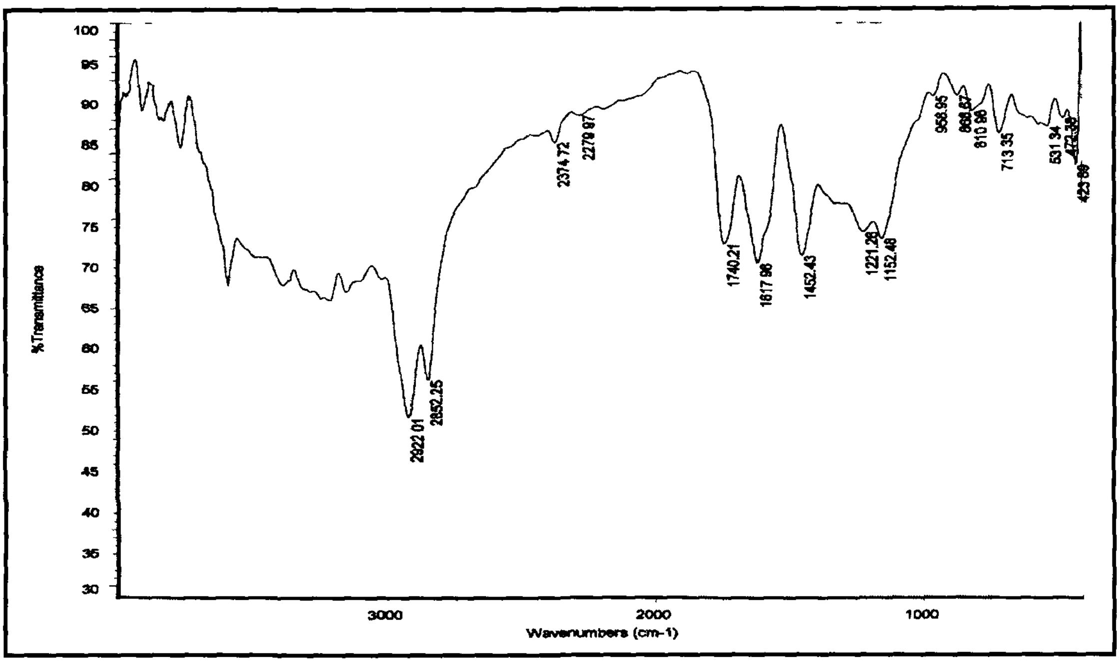


Figure 2.19: FTIR spectra of polymer PPDPTA

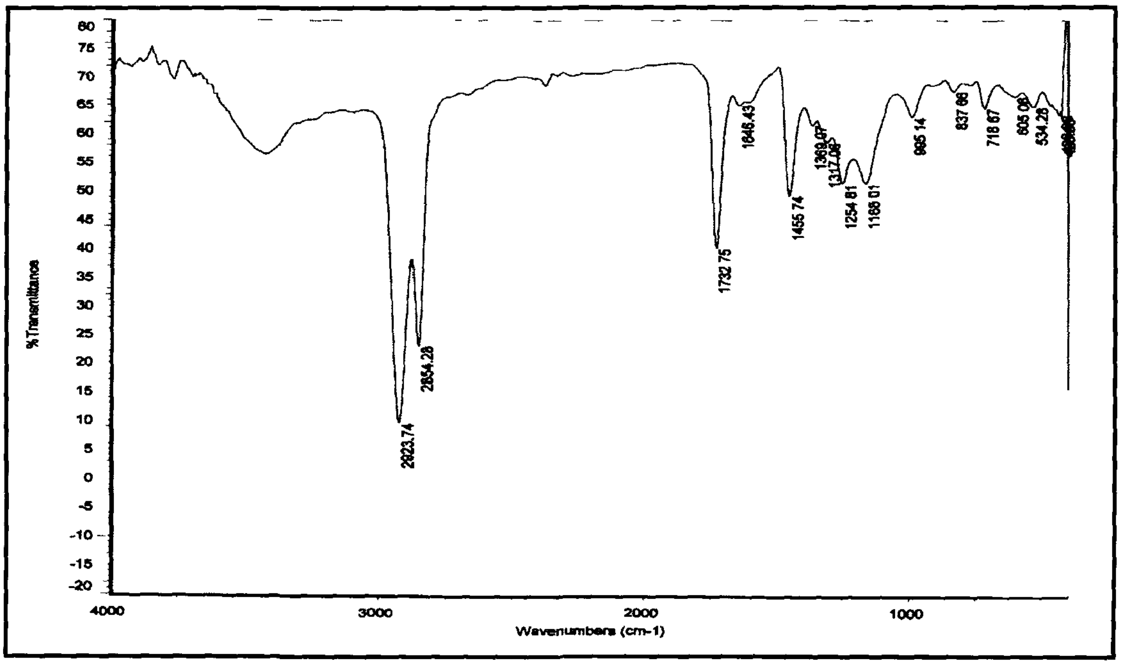


Figure 2.20: FTIR spectra of polymer PPDCHTA

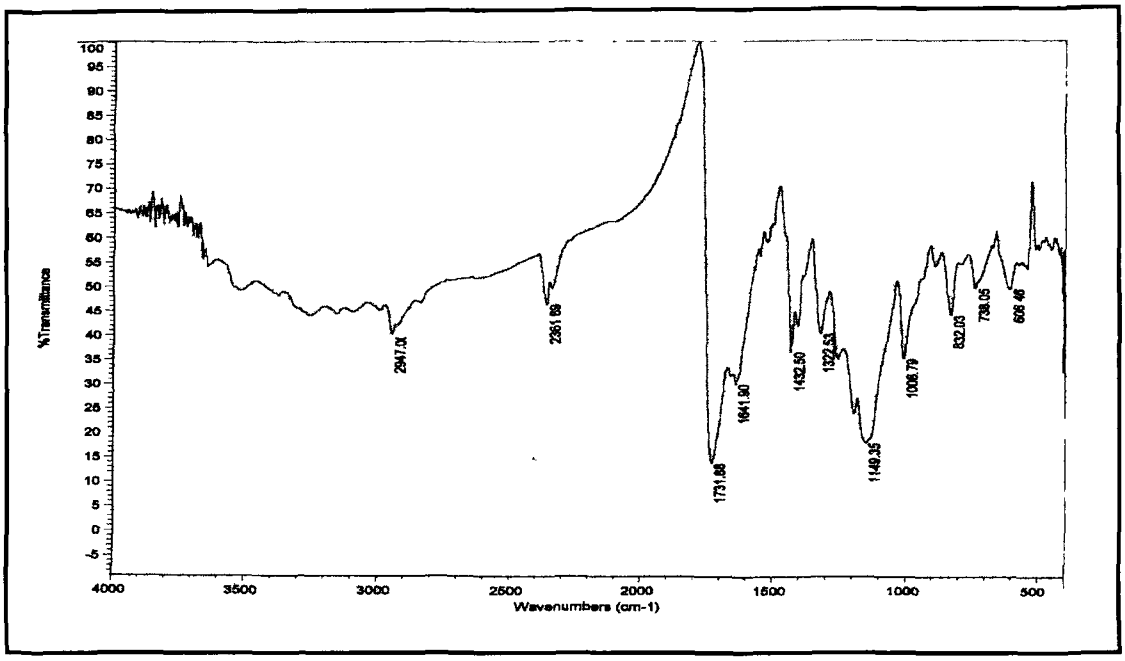


Figure 2.21: FTIR spectra of polymer PQTA

In the ^1H NMR spectra of the polymers, the signals in the range of δ 7.5-8.7 ppm are assigned to the aromatic quinolinyl protons. The signal at δ 7.04-7.00 ppm is assigned to the proton at four position of the thiophene ring (Figure 2.22 - 2.28). The broad signal at δ 7.27-7.00 is related to aromatic phenyl protons. The signal at δ 3.67-3.64 ppm is related to the methylene group protons linked to thiophene ring. The broad signal at δ 1.63-0.88 ppm is associated with alkyl protons. The absence of the signals at δ 7.27 & 7.15 ppm related to the hydrogen at 2 and 5 position of the thiophene ring confirmed the polymerization.

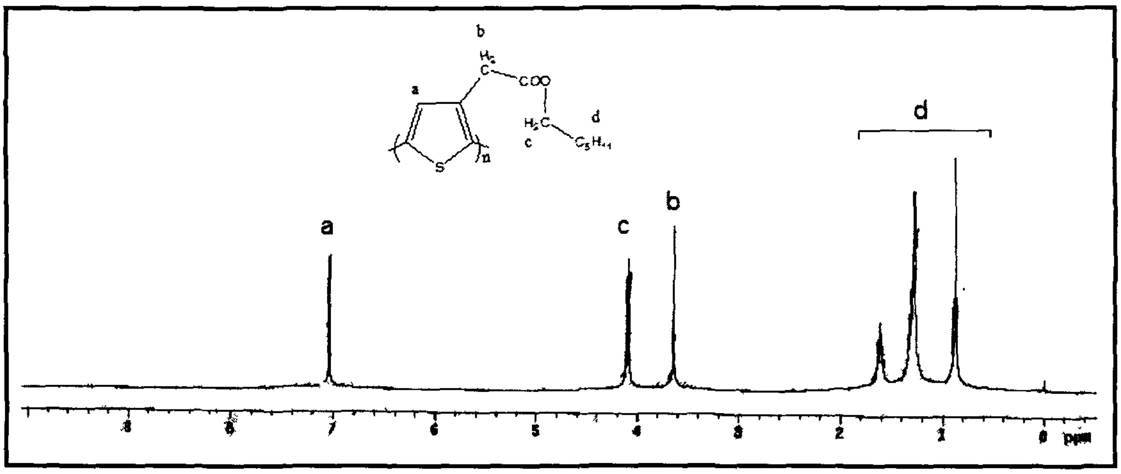


Figure 2.22: Proton NMR spectra of polymer PHTA

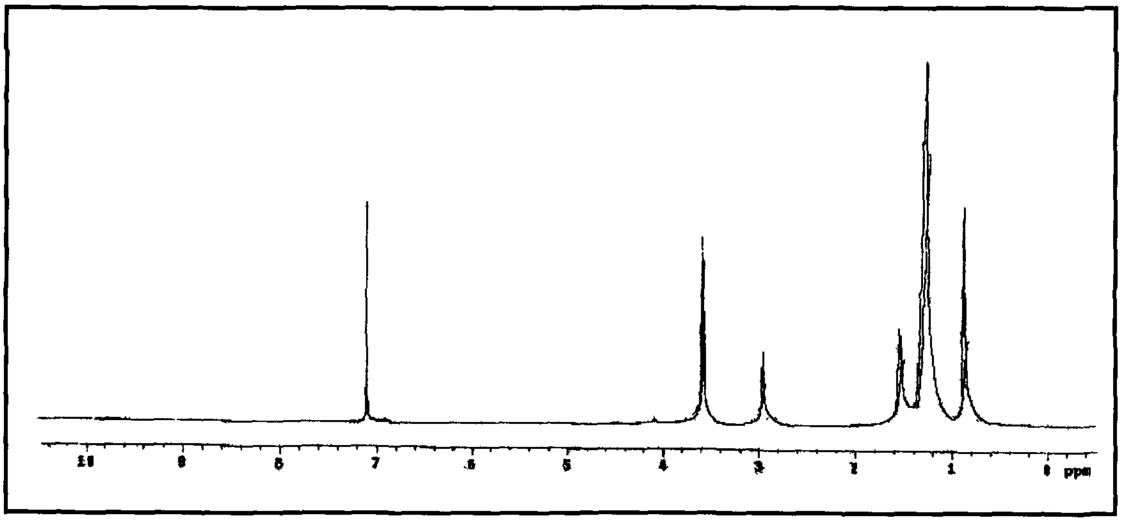


Figure 2.23: Proton NMR spectra of polymer POTA

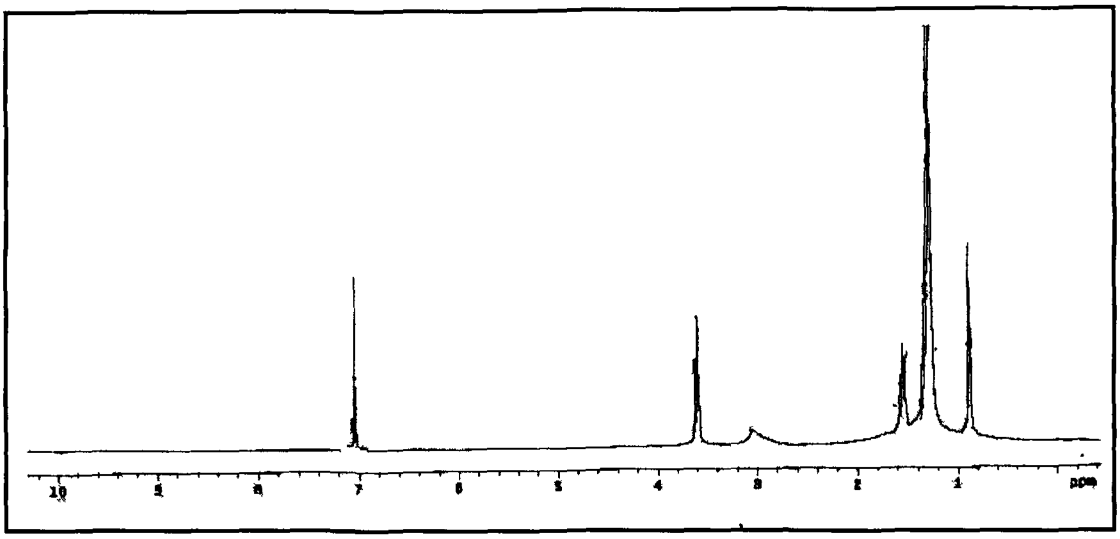


Figure 2.24: Proton NMR spectra of polymer PDTA

Figure 2.25: Proton NMR spectra of polymer PDDTA

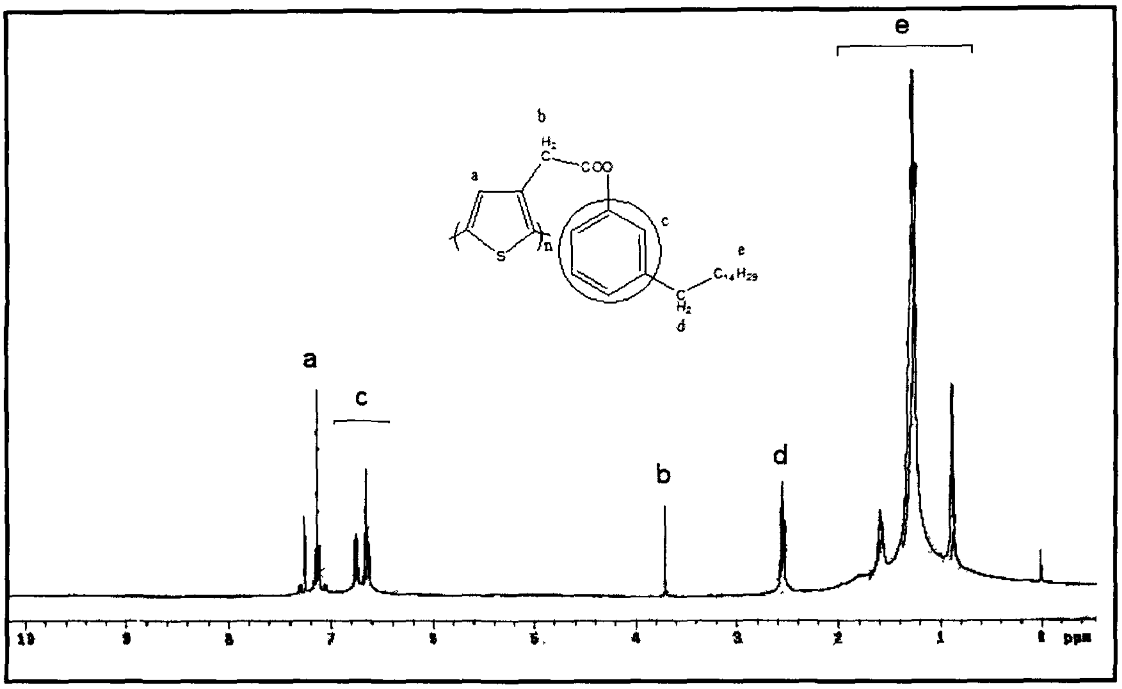


Figure 2.26: Proton NMR spectra of polymer PPDPTA

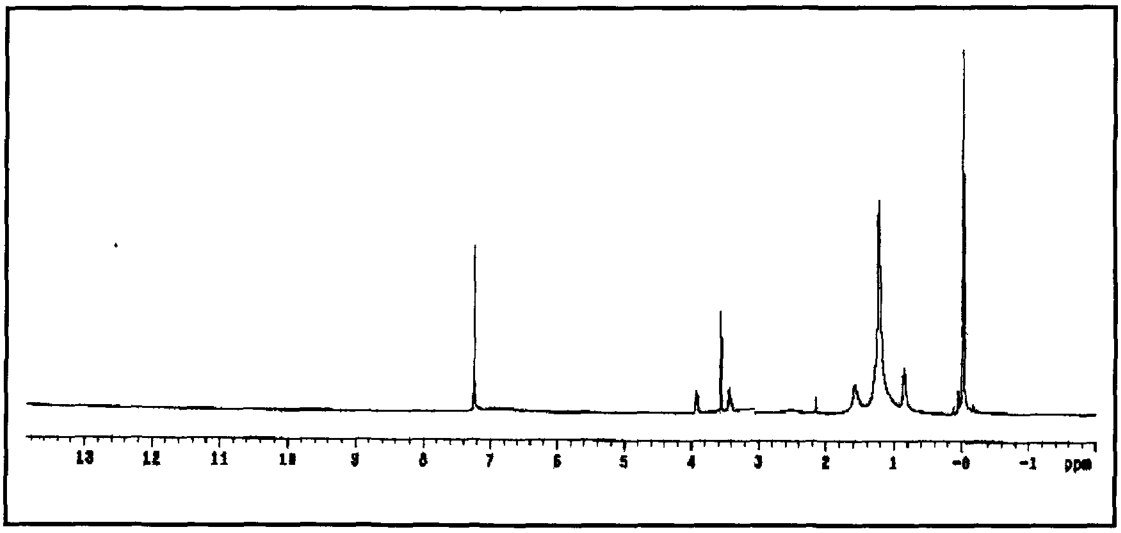


Figure 2.27: Proton NMR spectra of polymer PPDCHTA

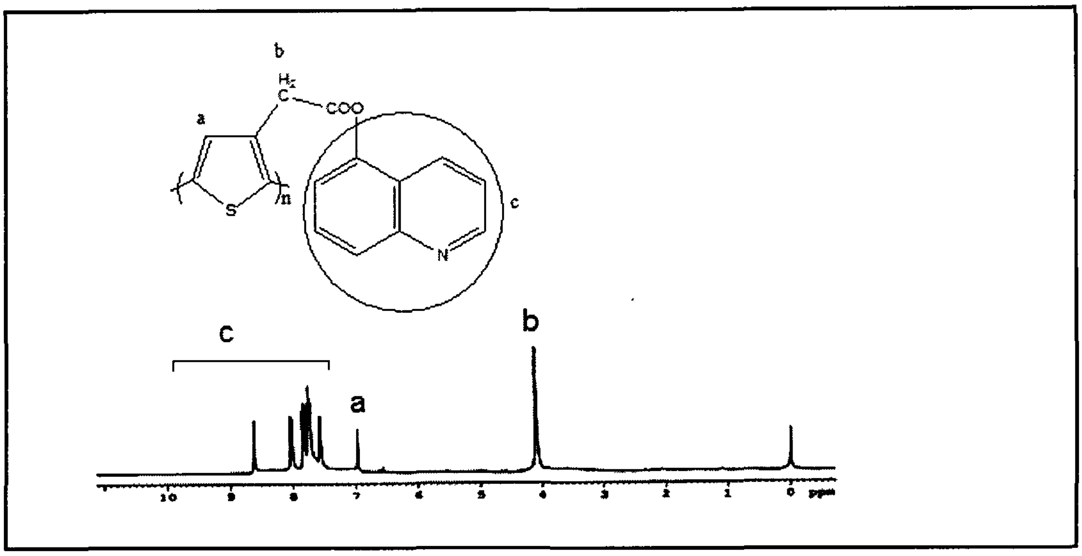


Figure 2.28: Proton NMR spectra of polymer PQTA

2.5.2.1 Molecular weight of polymers

Molecular weight of polymers has been measured by gel permeation chromatography (GPC) in THF solution using polystyrene standard. Molecular weights of the polymers in THF are shown in Table 2.1. GPC curve of the polymers is depicted in Figure 2.29 - 2.35. The number-average molecular weights of the resulting polymers are in the range of 3154–22260 g/mol with polydispersity indexes in the range of 1.67–3.34. The weight average molecular weights of polymers have been found in the range 6097 – 74566 g/mol. The results show that the soluble part of polymers in THF solvent is of low molecular weight.

Table 2.1 Molecular weight of polymers

Polymer	$\bar{M}n$ (g/mol)	$\bar{M}w$ (g/mol)	$\bar{M}w$/ $\bar{M}n$ (PDI)
PHTA	5372	14698	2.73
POTA	3338	6097	1.82
PDTA	3589	13213	2.78
PDDTA	8418	21411	2.54
PPDPTA	6852	11492	1.67
PPDCHTA	3154	6892	2.18
PQTA	22260	74566	3.34

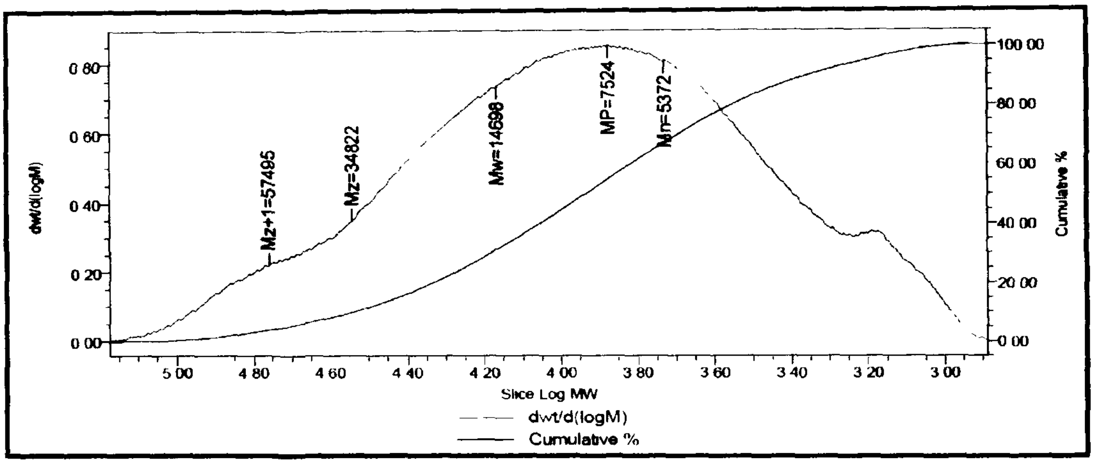


Figure 2.29: GPC curve of polymer PHTA

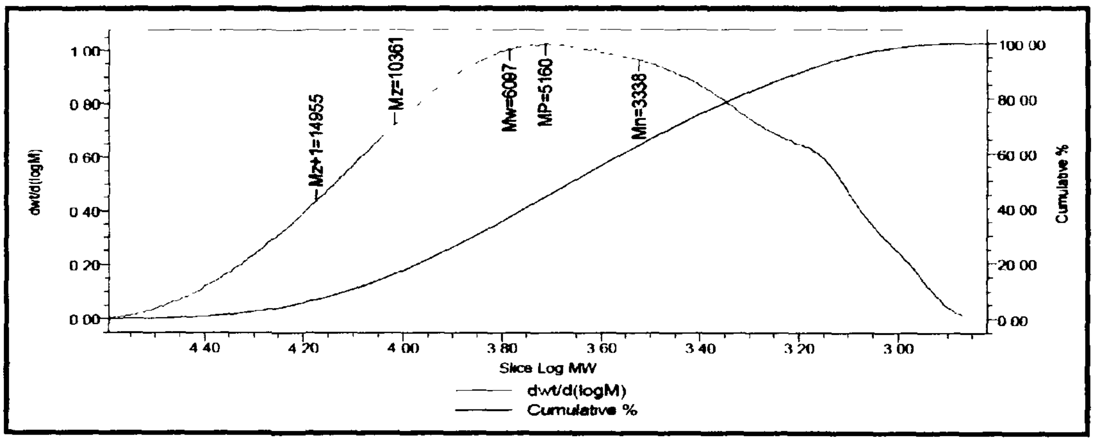


Figure 2.30: GPC curve of polymer POTA

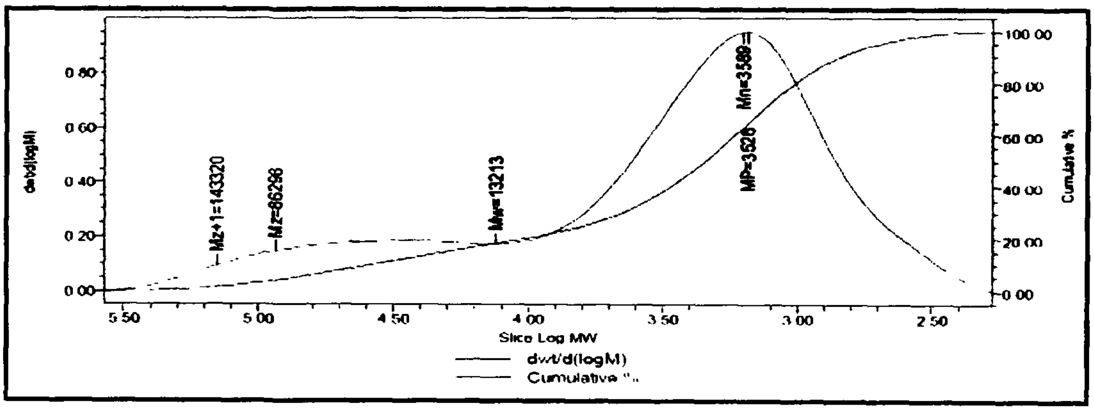


Figure 2.31: GPC curve of polymer PDTA

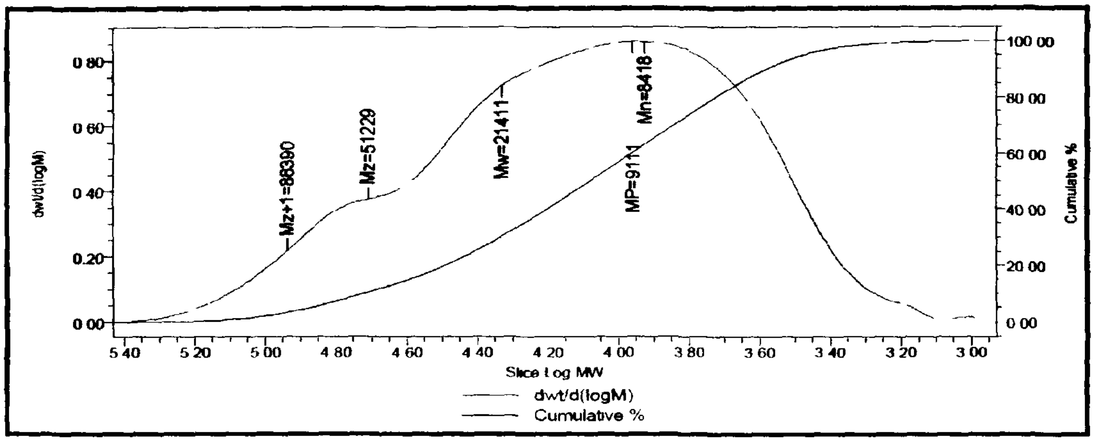


Figure 2.32: GPC curve of polymer PDDTA

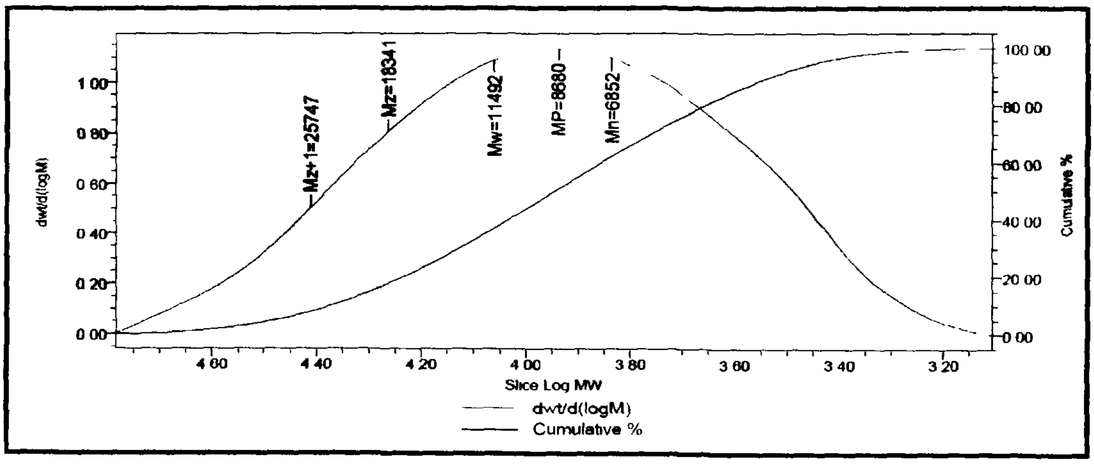


Figure 2.33: GPC curve of polymer PPDPTA

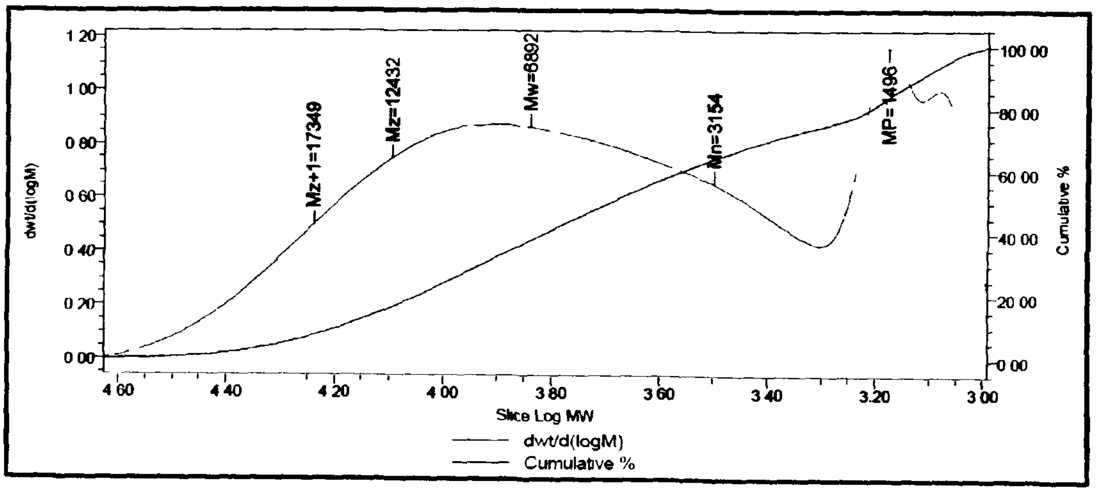


Figure 2.34: GPC curve of polymer PPDCHTA

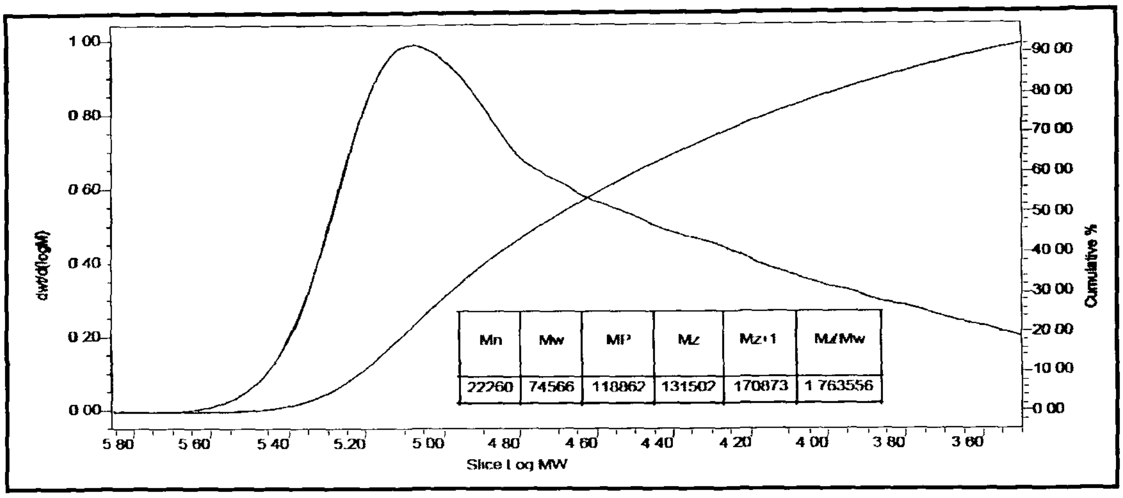


Figure 2.35: GPC curve of polymer PQTA

2.5.2.1.1 Solubility and degree of polymerization of polymers

The solubility is not only an important criterion to assess conjugated polymers for their possible commercial use but equally important also from characterization point of view. The polymers are soluble in $CHCl_3$, THF, DMF, DMAc and DMSO. The solubility and degree of polymerization (DP) of the polymers in THF are shown in Table 2.2. The fraction of polymers soluble in THF is 15-90 %. It is observed that solubility decreases with increasing degree of polymerization. The effective conjugation length as well as delocalization of electron depends on degree of polymerization. The delocalization of electrons requires a conjugated chain structure which in turn brings insolubility to the polymers.

Table 2.2 Degree of polymerization and solubility of polymers

Polymer	$\bar{M}n$ (g/mol)	Molar mass of Monomer unit (g/mol)	Degree of polymerization ($\bar{DP}$)	Fraction of polymer soluble in THF (%)
PHTA	5372	226	24	24
POTA	3338	254	**13**	27
PDTA	3589	282	13	36
PDDTA	8418	310	27	37
PPDPTA	6852	428	16	87
PPDCHTA	3154	434	7	90
PQTA	22260	269	**83**	15

2.5.2.2 UV- Vis spectra

2.5.2.2.1 UV –Vis spectra of monomers and polymers

The UV- Vis spectra of monomers and polymers are shown in Figure 2.36 - 2.42. The maximum absorption (λ_{max}) of monomers and polymer and their shifting are demonstrated in Table 2.3. Polymers possess intensive and broad absorption bands in the UV- Visible region, indicating an extensive π- conjugation in the thienylene backbone. The λ_{max} depends on the effective π- conjugation of the polymer chain and the aggregation state of the polymer. Higher the π- conjugation length, a red shifted λ_{max} is observed. λ_{max} of polymers in THF solution are found to be in the range of 307 to 392 nm. A red shifted λ_{max} in solution is observed for polymer in comparison to their respective monomer. This is due to the π-conjugation of polymer chain. Polymers possessing alkyl side chain with different carbon length ranging from six to twelve have found similar red shifting absorption (105 -115nm) with respect to their monomer. This indicates that alkyl containing polymers have akin π -conjugation length irrespective of their carbon chain length. Polymers containing 3-pentadecyl phenyl and 3- pentadecyl cyclohexyl side chains have experienced 43 and 54 nm red shifting absorption compared with their monomer. This low value of red shifting absorption for polymer PPDTA and PPDCHTA compared to other polymers may be due to the aggregation of polymer side chain [59]. A red shifted λ_{max} is observed for polymer PQTA having qunioline side chain with reference to monomer unit. The red shifting is higher for polymer PQTA than other ester substituted polymers. The results show that π conjugation length is highest for polymer PQTA. This observation is attributed to an increase in coplanarity of the thienylene backbone [60-61].

Table 2.3 Absorption of monomers and polymers

Polymer	Maximum absorption of monomer in THF (nm) (π - π*)	Maximum absorption of polymer in THF (nm) (π - π*)	Red shifting absorption from monomer to polymer (nm)
PHTA	255	370	115
POTA	254	363	109
PDTA	254	363	109
PDDTA	254	359	105
PPDPTA	272	315	43
PPDCHTA	253	307	54
PQTA	256	392	136

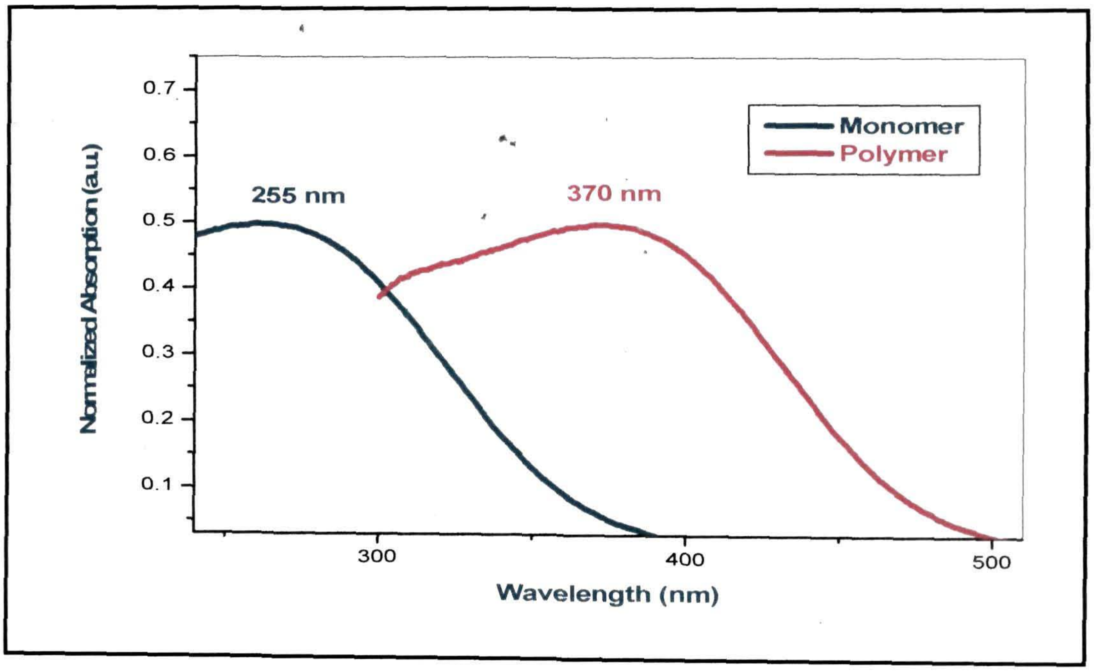


Figure 2.36: UV- Vis Spectra of monomer HTA and polymer PHTA

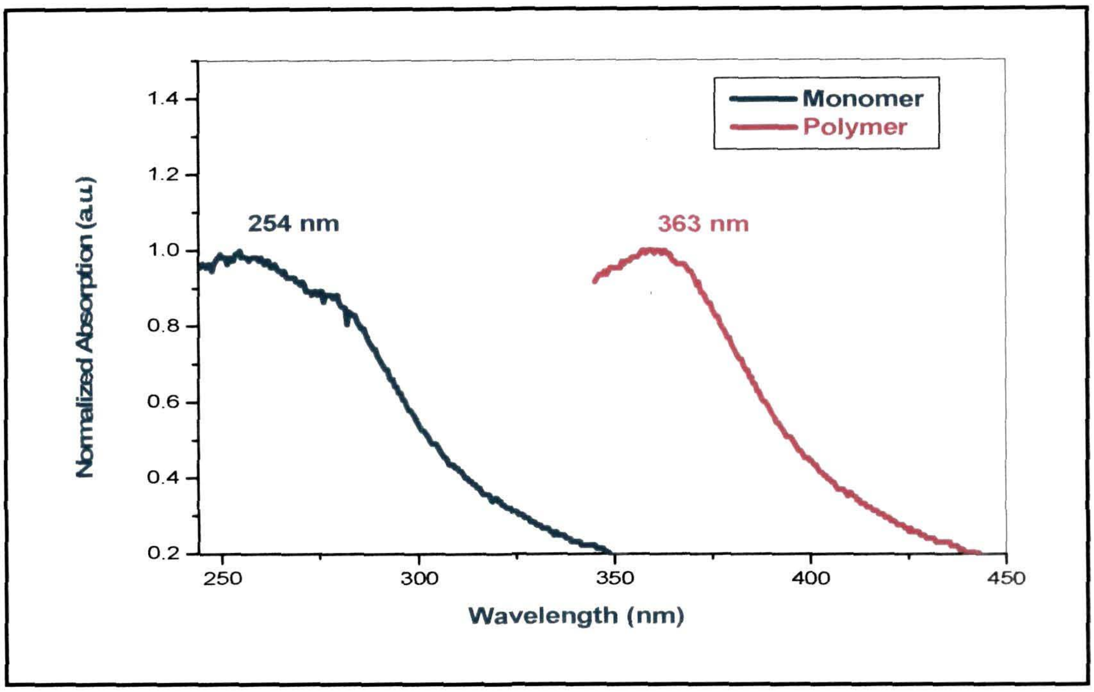


Figure 2.37: UV- Vis Spectra of monomer OTA and polymer POTA

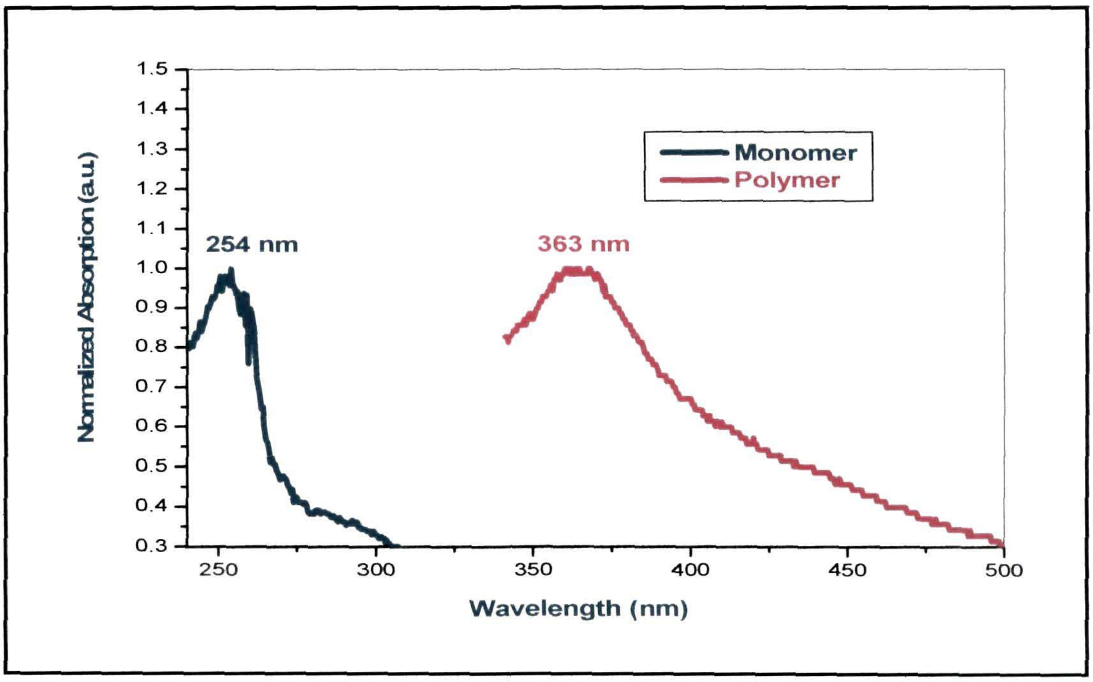


Figure 2.38: UV- Vis Spectra of monomer DTA and polymer PDTA

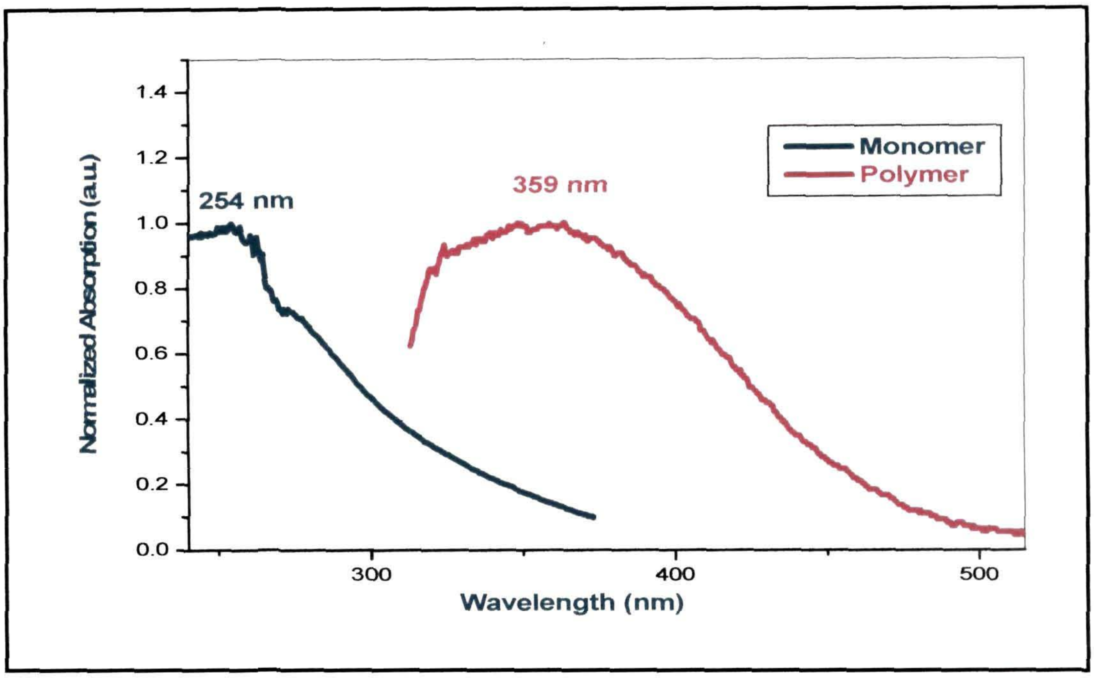


Figure 2.39: UV- Vis Spectra of monomer DDTA and polymer PDDTA

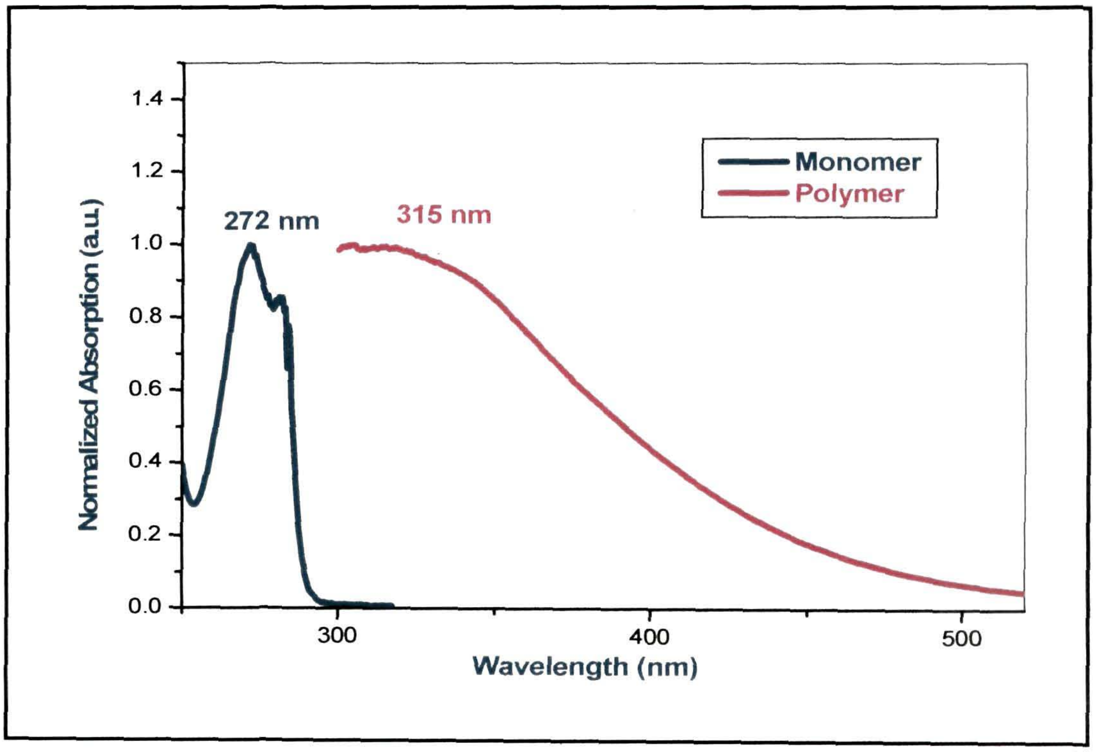


Figure 2.40: UV- Vis Spectra of monomer PDPTA and polymer PPDPTA

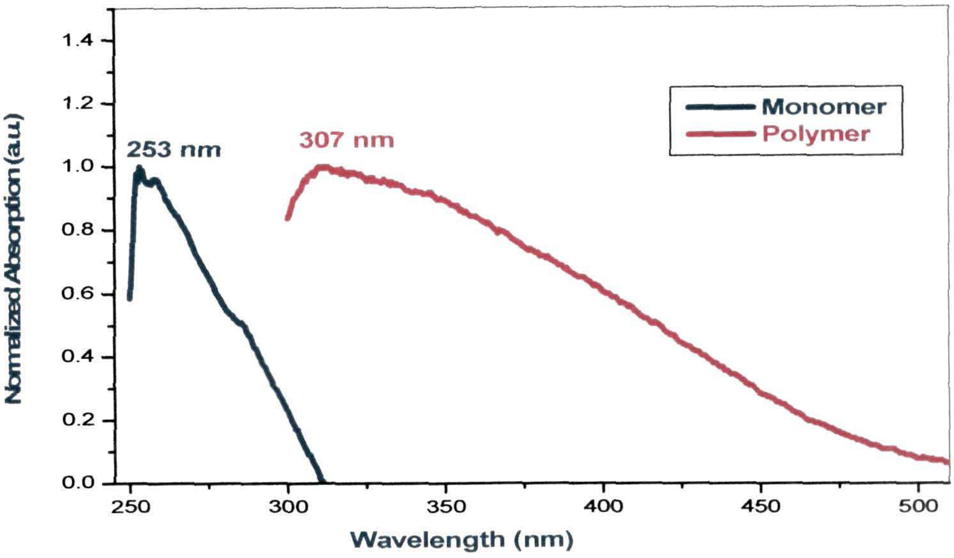


Figure 2.41: UV- Vis Spectra of monomer PDCHTA and polymer PPDCHTA

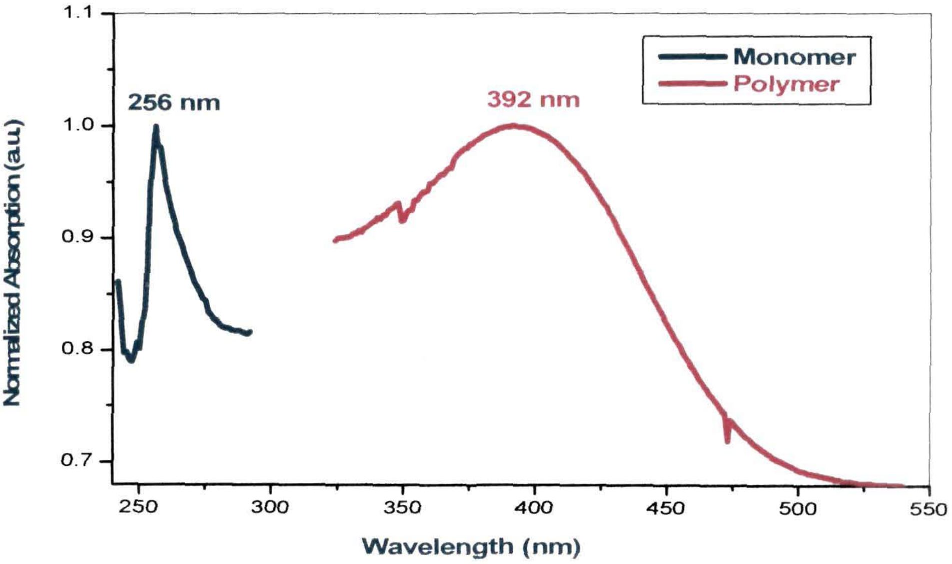


Figure 2.42: UV- Vis Spectra of monomer QTA and polymer PQTA

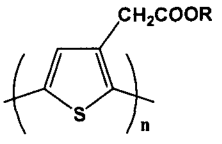
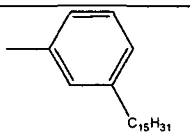
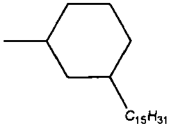
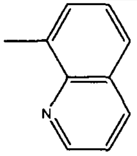
2.5.2.2.2 Optical band gap

Optical absorption in conjugated polymers which are mostly amorphous or semicrystalline may due to the transition of charge carriers, through a forbidden energy gap, called optical band gap. Attempts have been made to determine the optical band gap using the equation 2.2 [62].

$$E_g^{opt}\,(eV) = 12\,40 / \lambda_{edge}\,(nm) \qquad (2.2)$$

Where E_g^{opt} is the optical band gap of polymers and λ_{edge} is the absorption edge. The absorption edge (λ_{edge}) and optical band gap (E_g^{opt}) of polymers are listed in Table2.4. The band gap of polymers is found to be 2.1-2.47 eV. The results show that aromatic containing moieties polymer have higher band gap. We have compared the optical band gap data with electrochemical band gap. Comparison and trend of electrochemical and optical band gap were discussed in next chapter.

Table 2.4 Absorption edge and optical bandgap of polymers

Polymer 	Side chain moiety (R)	Absorption edge of polymer (nm)	Optical band gap (eV)
PHTA	$-C_6H_{13}$	524	2.36
POTA	$-C_8H_{17}$	525	2.36
PDTA	$-C_{10}H_{21}$	540	2.29
PDDTA	$-C_{12}H_{25}$	520	2.38
PPDPTA		506	2.45
PPDCHTA		535	2.31
PQTA		502	2.47

2.5.2.3 XRD analysis

XRD analysis has been performed by preparing the polymer film on the glass substrate. X-ray diffractograms of the polymers are shown in Figure 2.43. XRD analysis reveals a broad peak at 2θ = 20 - 25° with weak intensities for polymers. No diffraction peak is observed for polymers at low angles. Polymers are amorphous in nature. Amorphous morphology prevents light scattering and crystallization-induced degradation [63]. This is generally useful in light emitting diode application.

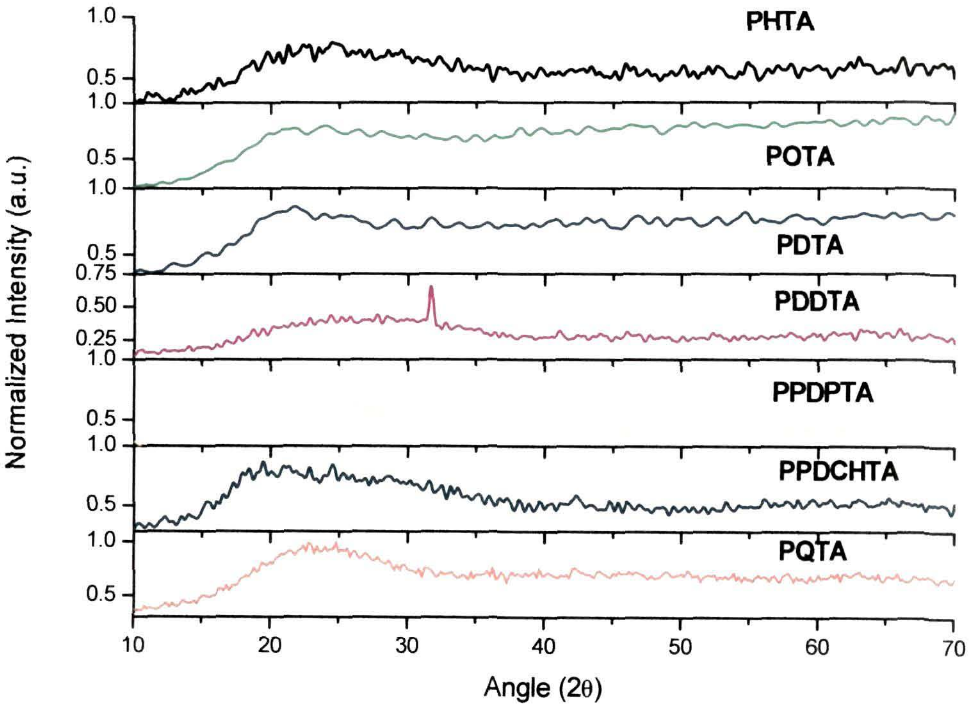


Figure 2.43: X-ray diffractograms of polymers

2.5.3 Thermal properties of polymers

2.5.3.1 Thermogravimetric analysis

The thermal properties of the polymers have been investigated by thermogravimetric analysis (TGA) under nitrogen atmosphere. The TGA curve of polymers is shown in Figure 2.44 - 2.50 and weight losses at different temperature are shown in Table 2.5. PDTA and PPDPTA polymers show 5-10% weight loss at 260° and 125 °C respectively. PHTA, POTA, PPDPTA and PPDCHTA exhibit 10-30 % weight loss at 170°, 150°, 358° and 307°C, respectively. The initial weight loss is due to the presence of oligomer compound in polymers. It is found that these polymers possess good thermal stability with the onset degradation temperature around 300-350 °C under nitrogen atmosphere and 40-60 % weight loss occurred at the temperature of 400-450 °C. The thermal stability of polymers follows the order PQTA > PDTA > PDDTA > PHTA = POTA > PPDCHTA = PPDPTA. PQTA and PDTA have found good thermal stability compared to other polymers. In case of PQTA, this is possibly due to the presence of bulky N-containing quinoline moiety attached to the thiophene backbone for high thermal stability. However, the proper explanation is not found for high thermal stability of PDTA polymer. The thermal stability increases with increasing the molecular weight of polymers.

Table2.5 Weight loss of polymers at different temperature

Polymer	Temp^r at (°C)				
	5-10 % Wt. loss	10-30% Wt. loss	40-60% Wt. loss	60-70% Wt. loss	70-80 % Wt. loss
PHTA	-	170	434	-	-
POTA	-	150	405	-	-
PDTA	260	-	410	-	-
PDDTA	-	-	430	-	-
PPDPTA	125	358	-	492	-
PPDCHTA	-	307	-	368	491
PQTA	-	-	443	-	-

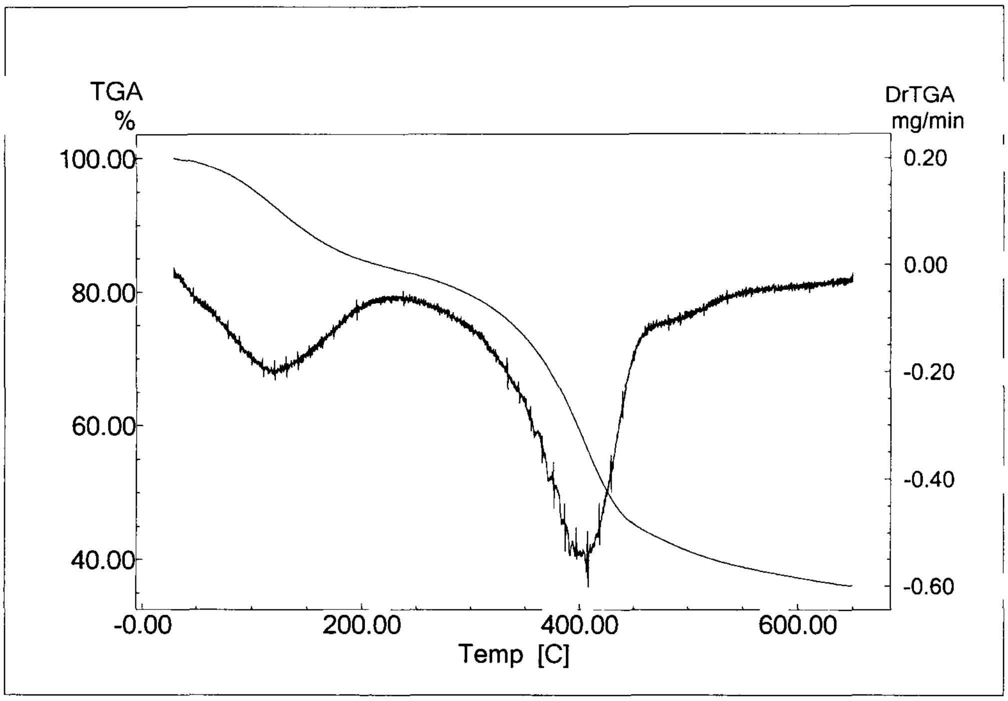


Figure 2.44: TGA curve of polymer PHTA

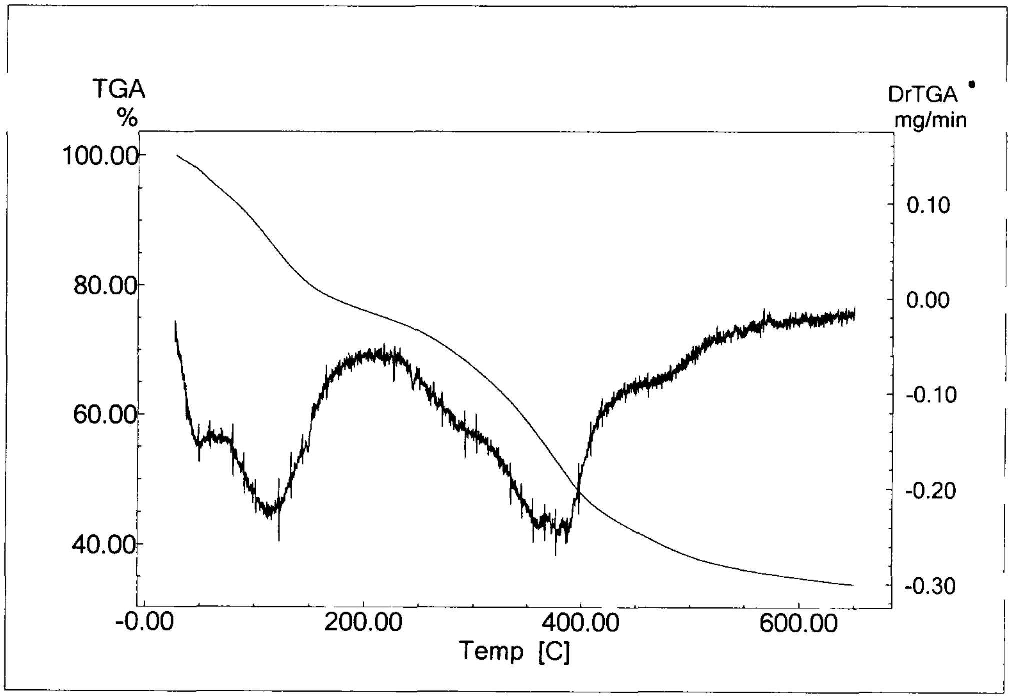


Figure 2.45: TGA curve of polymer POTA

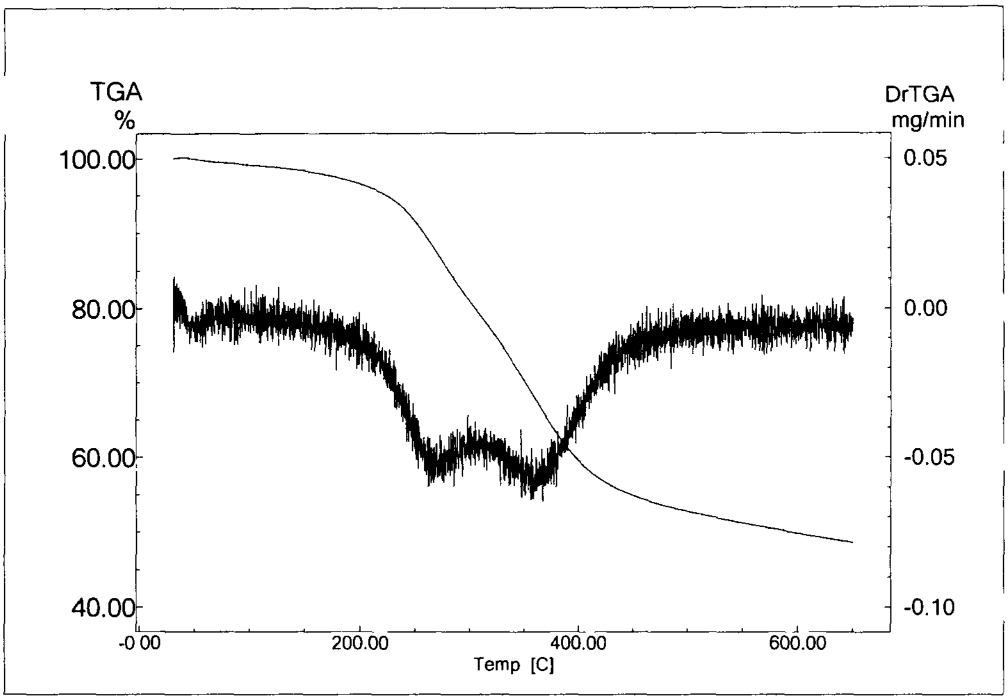


Figure 2.46: TGA curve of polymer PDTA

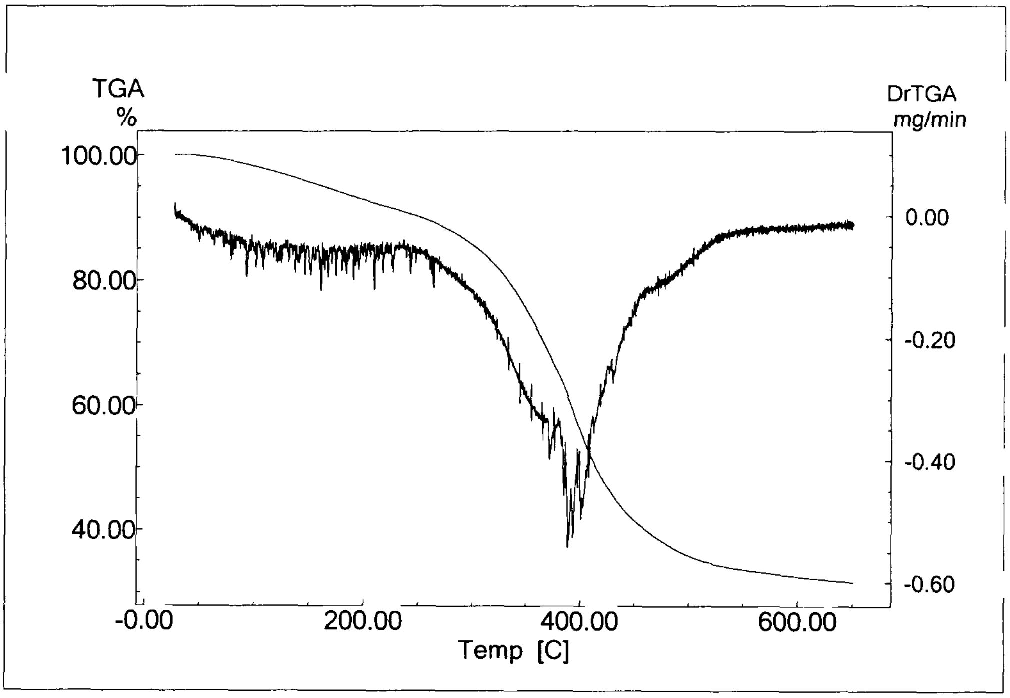


Figure 2.47: TGA curve of polymer PDDTA

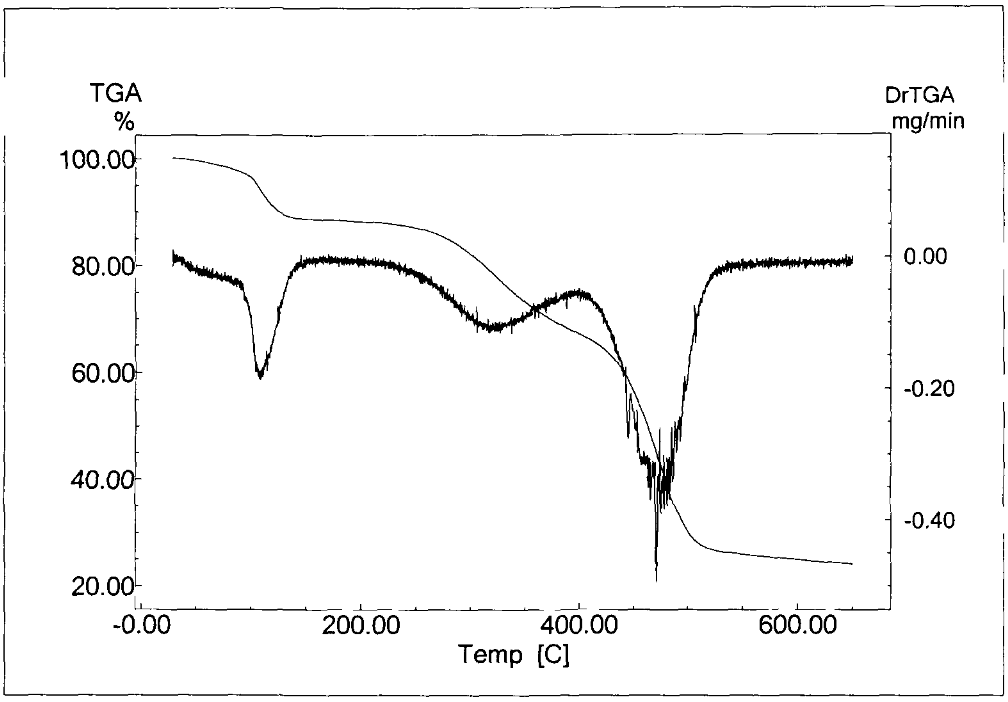


Figure 2.48: TGA curve of polymer PPDPTA

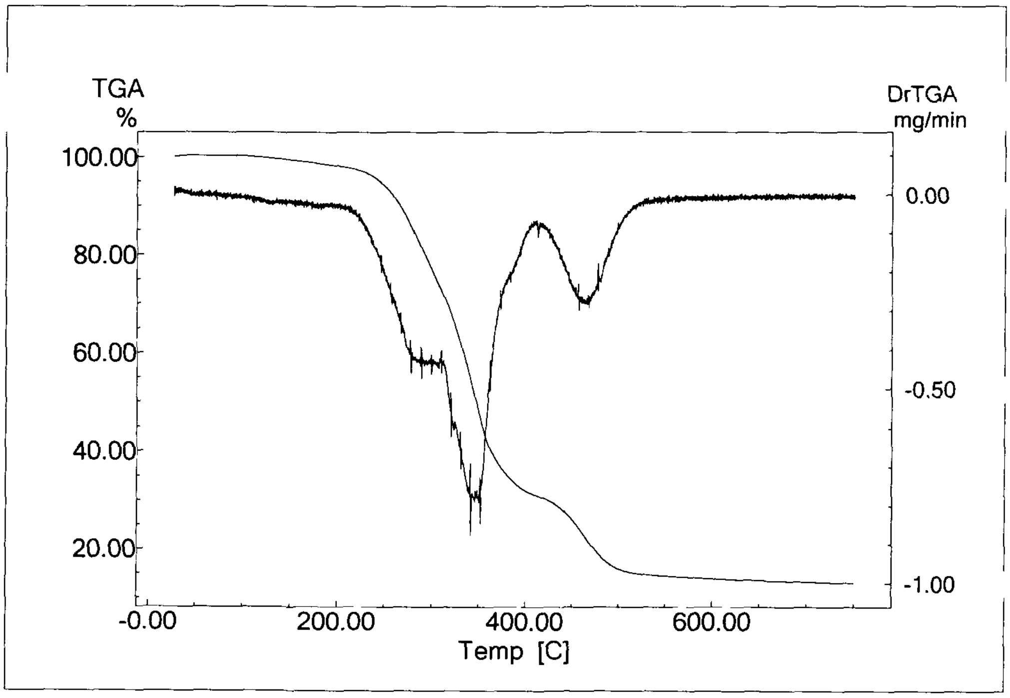


Figure 2.49: TGA curve of polymer PPDCHTA

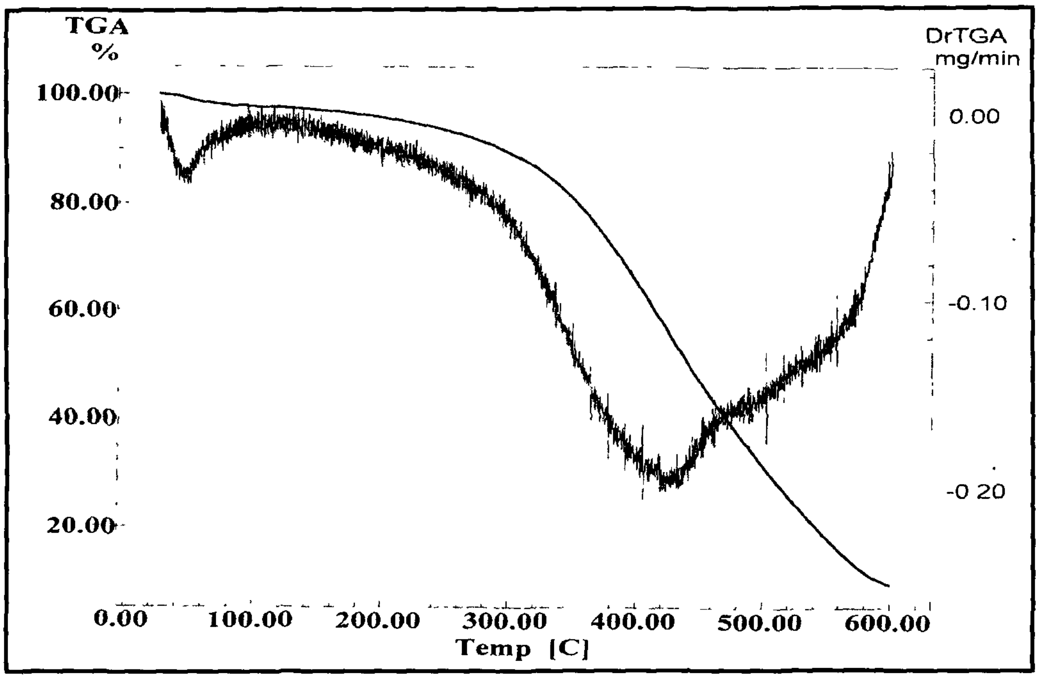


Figure 2.50: TGA curve of polymer PQTA

2.5.3.2 Differential scanning calorimetry analysis

Differential scanning calorimetry (DSC) of polymers under nitrogen atmosphere is shown in Figure 2.51- 2.57. The polymers exhibit a glass transition temperature (Tg) in the range of 66-154°C (Table 2.6). It is observed that T_g of alkyl containing ester substituted polythiophenes decrease with increasing side chain length. Further, T_g decreases with flexible pentadecyl phenyl and pentadecyl cyclo hexyl side chain attached to ester polythiophenes. PPDPTA shows the lower T_g (66°C) and PQTA shows the higher Tg(166°C). Long flexible pentadecyl chain on meta position of phenyl ring serves the internal plasticizer of polymer which lowers the Tg of PPDPTA polymer. The higher Tg of PQTA polymer is due to the presence of bulky and rigid quinoline moiety. A broad peak at105-122°C for POTA, PDTA, PDDTA, PPDPTA and PPDCHTA polymers is assigned to the melting of side chain having alkyl side chain longer than hexyl group. Similar observation has been made for polyalkylthiophenes possessing C_8 or longer alkyl side chains by other researchers [64-66]. It seems that the rigid backbone exerts strong influence on the side chain crystallization. T_g of the polymers decreases with increasing side chain length. High glass transition temperatures

(T_g) and thermal stability are required to with stand inevitable Joule heating encountered during LED operation, especially at higher electric fields and current densities [63].

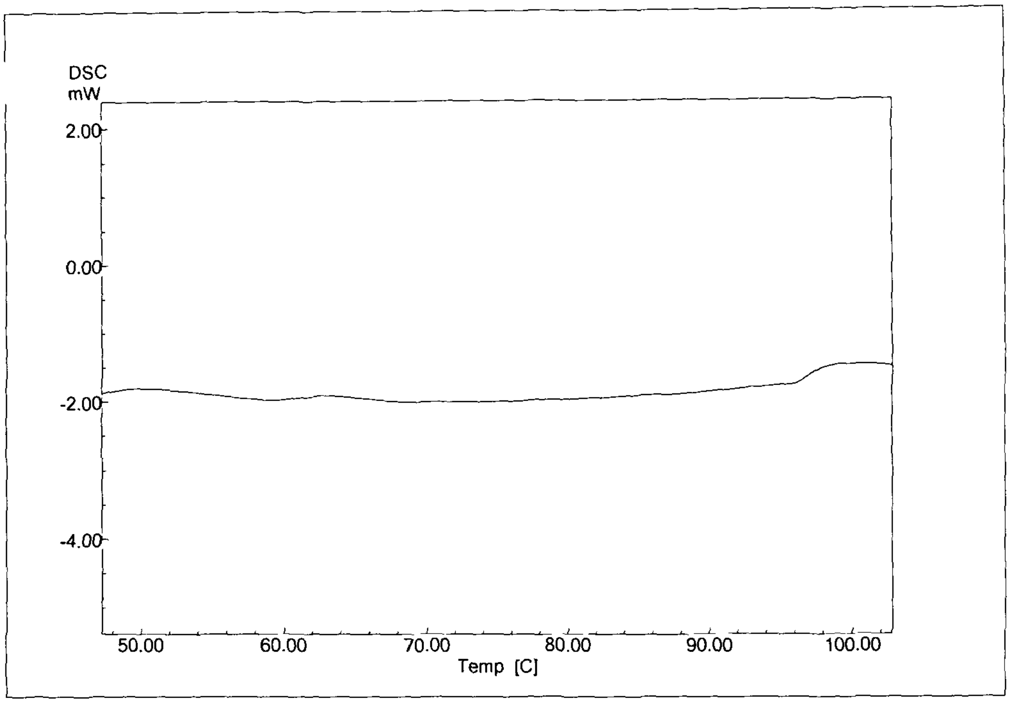


Figure 2.51: DSC curve of polymer PHTA

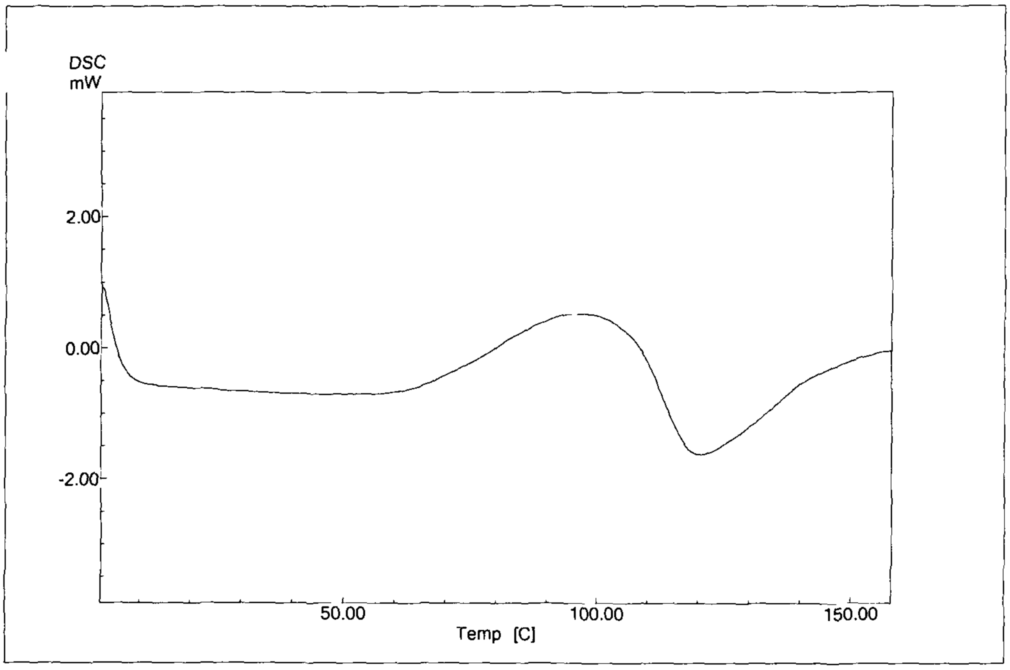


Figure 2.52: DSC curve of polymer POTA

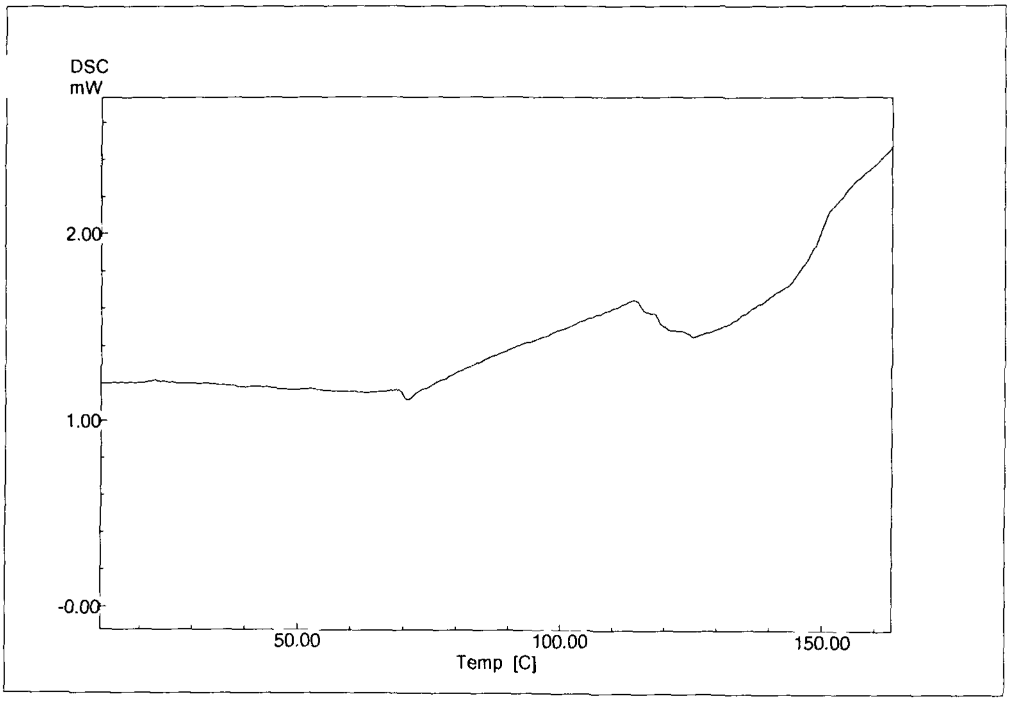


Figure 2.53: DSC curve of polymer PDTA

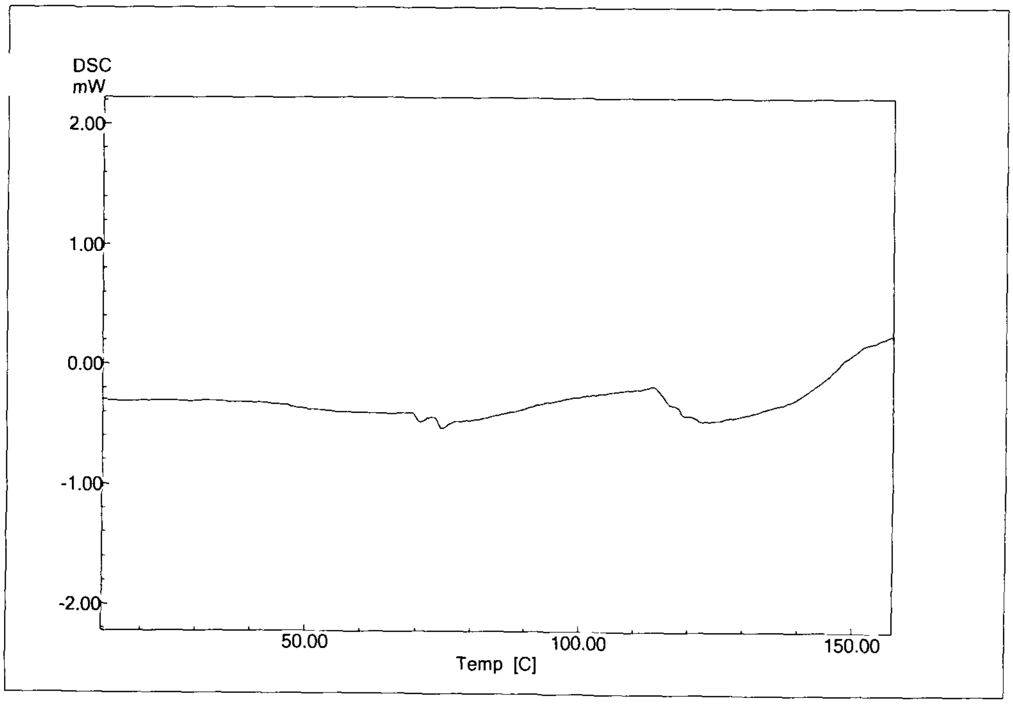


Figure 2.54: DSC curve of polymer PDDTA

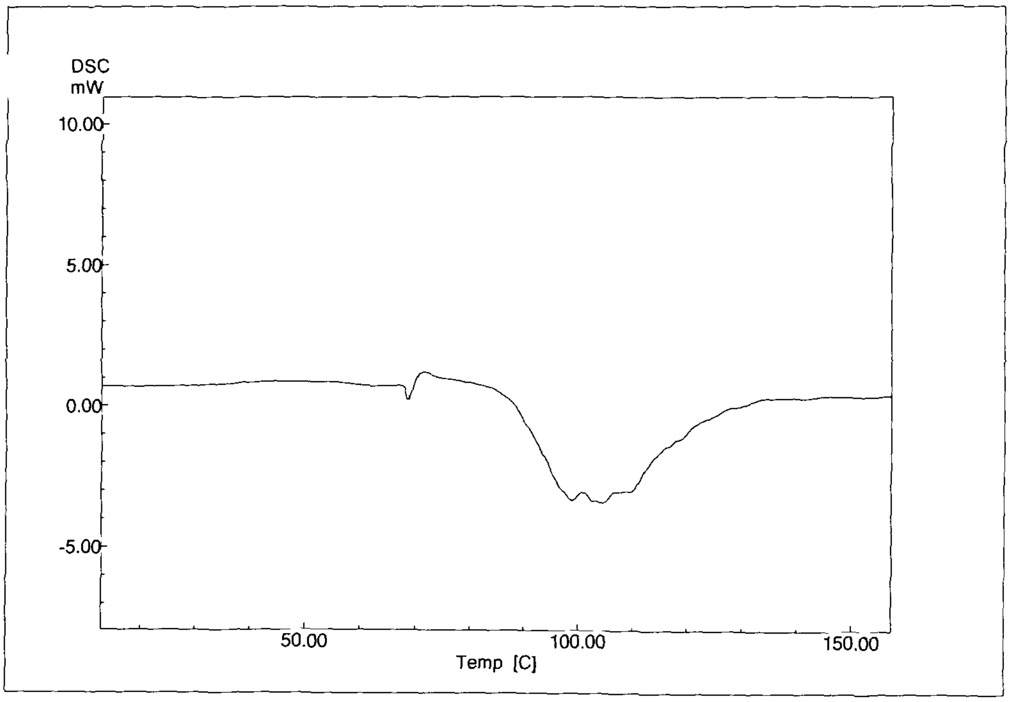


Figure 2.55: DSC curve of polymer PPDPTA

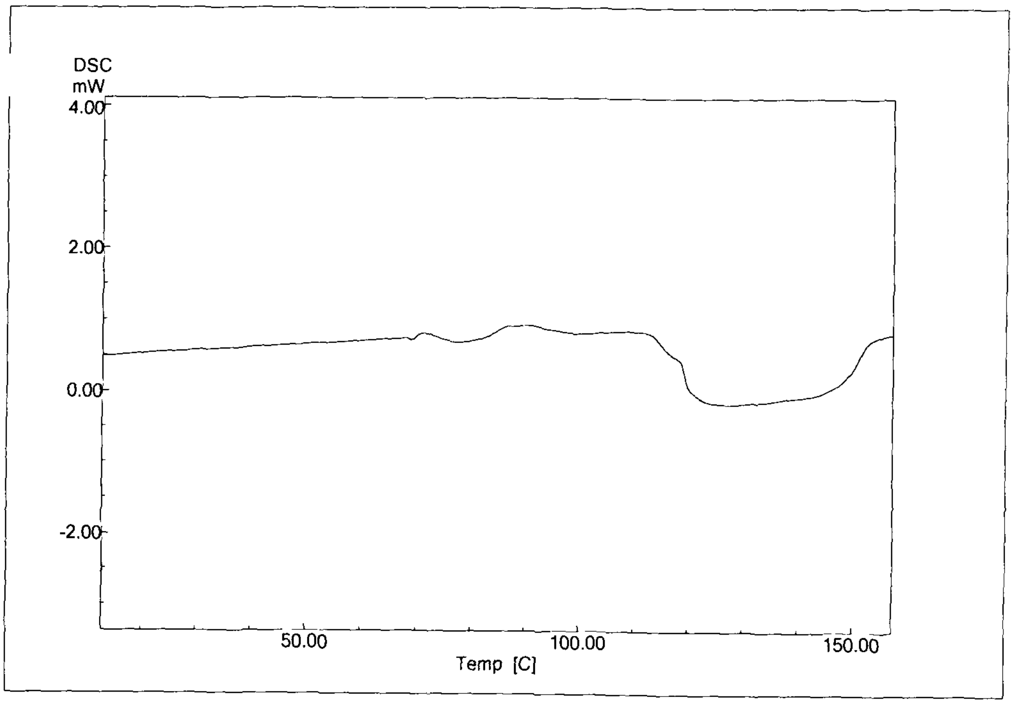


Figure 2.56: DSC curve of polymer PPDCHTA

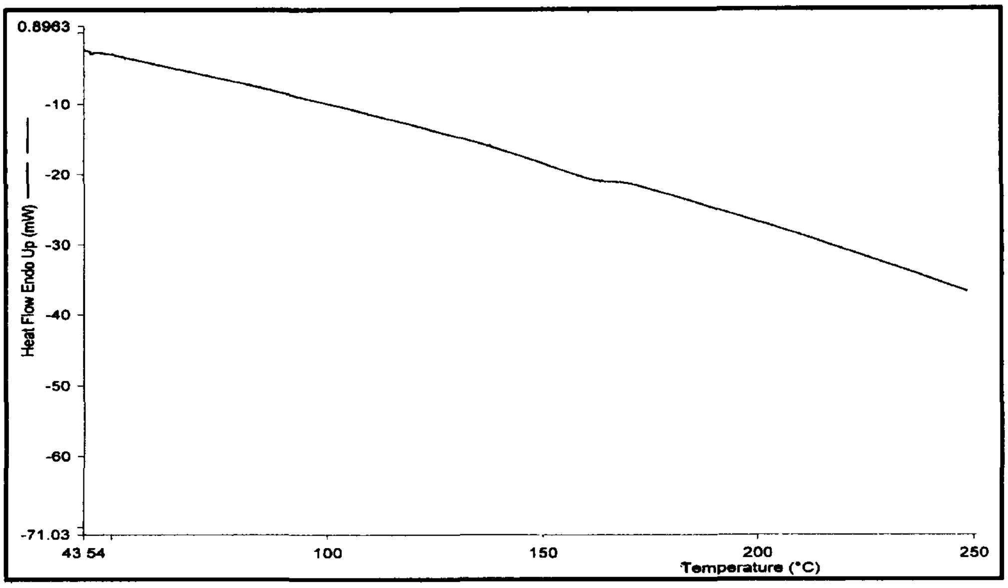
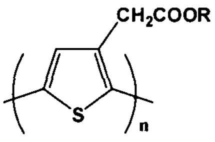
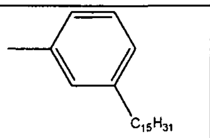
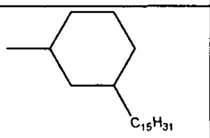
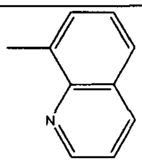


Figure 2.57: DSC curve of polymer PQTA

Table 2.6: Tg and Tm of polymers

Polymer 	Side chain moiety (R)	Glass transition temperature (Tg) (°C)	Melting temperature (Tm) (°C)
PHTA	$-C_6H_{13}$	94	-
POTA	$-C_8H_{17}$	-	120
PDTA	$-C_{10}H_{21}$	70	119
PDDTA	$-C_{12}H_{25}$	69	122
PPDPTA		63	105
PPDCHTA		67	107
PQTA		154	-

2.6 Conclusion

A series of ester substituted thiophene monomers has been synthesized by esterification reaction. The yield of the monomers is 60-80%. The formation of monomers was confirmed by FTIR, ^{1}H NMR spectroscopy. The polymers have been prepared by the oxidative polymerization using ferric chloride. The polymerization process is slow and yield of the polymer is 42-66%. The polymers show good solubility in THF, $CHCl_3$, DMF, DMAc, and DMSO. The number average molecular weights of polymers are in the range of 3154 to 22260 g / mole. The soluble part of the polymers is found to be oligomer. The absorption maximum in UV- Vis spectra of the polymers is in the range of 307-392 nm. All the polymers show red shift of absorption maximum with respect to their monomers. Optical band gap of the polymers is found to be in the range of 2.1-2.47 eV. XRD analysis reveals that polymers are amorphous in nature. Polymers possess good thermal stability with the onset decomposition temperature around 300-350 °C under nitrogen atmosphere. Thermal stability increases with the increase in molecular weight of polymers. The polymers exhibit a glass transition temperature (Tg) in the range of 63-154°C. It is observed that T_g of the polymers decreases with the increase in length of the side chain.

References

1. H. S. Nalwa, L. S. Rohwer (Eds), *Handbook of Luminescence, Display materials and Devices,* American Scientific Publisher, Stevenson Ranch, CA **(2003).**
2. T. Fuhrman, J. Salbeck, *MRS Bull, May* **(2003)** 354.
3. S. R. Forrest, *Nature, 428* **(2004)** 911.
4. B. W. D'Andrade, S. R. Forrest, *Adv Mater, 16* **(2004)** 1585.
5. M. T. Bernius, M. Inbasekaran. J. O'Brien, W. Wu, *Adv Mater, 12* **(2000)** 1737.
6. J. G. C. Veinot, T. J. Marks, *Acc Chem Res, 38* **(2005)** 632.
7. R. H. Friend, *Pure Appl Chem, 73* **(2001)** 425.
8. D. Y. Kim, H. N. Cho, C. Y. Kim, *Prog Polym Sci ,25* **(2000)** 1089.
9. T. Yamamoto, *Syn Lett,* **(2003)** 425.
10. B. Hu, Y. Wu, Z. Zhang, S. Dai, J. Shen, *J Appl Phys Lett, 88* **(2006)** 022114/1.
11. A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes, *Chem Rev, 109* **(2009)** 897.
12. I. F. Perepichka, D. F. Perepichika, H. Meng, F. Wudl, *Adv Mater, 17* **(2005)** 2281.
13. U. Mitschke, P. Bauerle, *J Mater Chem, 10* **(2000)** 1471.
14. L. Akcelrud, *Prog Polym Sci, 28* **(2003)** 875.
15. T. Yamamoto, *Macromol Rapid Commun, 23* **(2002)** 583.
16. H. S. O. Chan, S. C. Ng, *Prog Polym Sci, 23* **(1998)** 1167.
17. N. Somanathan, S. Radhakrishnan, *Int J Mod Phys B, 19* **(2005)** 4645.
18. A. Mishra, C. Q. Ma, P. Bauerle, *Chem Rev, 109* **(2009)** 1141.
19. J. Roncali, *Chem Rev, 92* **(1992)** 711.
20. R. D. McCullough, *Adv Mater, 10* **(1998)** 93.
21. R. Sugimoto, S. Takeda, H. B. Gu, K. Yoshino, *Chem Express, 1* **(1986)** 635.
22. T. A. Chen, R. D. Reike, *J Am Chem Soc, 114* **(1992)** 10087.
23. M. Rehahn, A. D. Schluter, G. Wegner, W. J. Feast, *Polymer, 30* **(1989)** 1054.
24. Z. Bao, W. Chan, L. Lu, *Chem Mater, 5* **(1993)** 2.
25. X. Hu, L. Xu, *Polymer, 41* **(2000)** 9147.
26. K. Ogawa, J. A. Stafford, S. D. Rothstein, D. E. Tallman, S. C. Rasmussen, *Synth Met, 152* **(2005)** 137.
27. V. C. Goncalves, D. T. Balogh, *Eur Polym J, 42* **(2006)** 3303.
28. B. M. W. L. Voss, R. A. J. Janssen, E. W. Meijer, *J Mol Struct ,521* **(2000)** 285.
29. T. Yamamoto, H. Hayashi, *J Polym Sci Part A Polym Chem, 35* **(1997)** 463.
30. M. R. Andersson, W. Mammo, T. Olinga, M. Svensson, M. Theander, O. Inganas, *Synth Met, 101* **(1999)** 11.
31. M. Svensson, M. Theander, O. Inganas, M. R. Andersson, *Synth Met, 119* **(2001)** 113.
32. M. Catellani, S. Luzzati, N. O. Lupsac, R. Mendichi, R. Consonni, A. Famulari, S. V. Meille, F.Giacalone, J. L. Segura, N. Martin, *J Mater Chem, 14* **(2004)** 67.
33. S. C. Ng, T. T. Ong, H. S. O. Chan, *J Mater Chem, 8* **(1998)** 2663.
34. Y. Liu, Y. Xu, D. Zhu, *Macromol Chem Phys, 202* **(2001)** 1010.
35. M. R. Andersson, M. Berggren, O. Inganas, G. Gustafsson, J. C. G. Carlberg, D. Selse, T. Hjertberg, O. Wennerstrom, *Macromolecules, 28* **(1995)** 7525.
36. K. G. Chittibabu, L. Li, M. Kamath, J. Kumar, S. K. Tripathy, *Chem Mater, 6* **(1994)** 475.
37. J. M. Xu, H. S. O. Chan, S. C. Ng, T. S. Chung, *Synth Met, 132* **(2002)** 63.
38. G. Daoust, M. Leclerc, *Macromolecules, 24* **(1991)** 455.
39. S. A. Chen, C. C. Tsai, *Macromolecules, 26* **(1993)** 2234.

40. N. Somanathan, S. Radhakrishnan, M. Thelakkat. H. W. Schmidt, *Macromol Mater Eng*, *287* **(2002)** 236.
41. M. Lanzi, P. C. Bizzarri, L. Paganin, G. Cesari, *Eur Polym J*, *43* **(2007)** 72.
42. M Zagorska, I. K. Bajer, A. Pron, P. Raimond, F. Kajzar, A. J. Attias, *Synth Met*, *102* **(1999)** 1141.
43. H. S. Ganapathy, H. S. Hwang, K. T. Lim, *Ind Eng Chem Res* *45* **(2006)** 3406.
44. M. Nicolas, F. Guittard, S Geribaldi, *J Polym Sci Part A Polym Chem*, *45* **(2007)** 4707.
45. B. Bingol, Y. Guner, A. Cirpan, L. Toppare, *Int J Polym Mater*, *54* **(2005)** 713.
46. F. Andreani, P. C. Bizzari, C. D. Casa, E. Salatelli, *Polym Bull*, *27* **(1991)** 117.
47. P. Camurlu, A. Cirpan, L. Toppare, *Synth Met*, *146* **(2004)** 91.
48. P. Camurlu, A. Cirpan, L. Toppare, *Mater Chem Phys*, *92* **(2005)** 413.
49. H. S. Ganapathy, J. S. Kim, S. H. Jin, Y. S. Gal, K. T. Lim, *Synth Met*, *156* **(2006)** 70.
50. X. Zhao, X. Hu, L. H. Gan, *Polym Adv Tech*, *16* **(2005)** 370.
51. P. C. Bizzarri, F. Andreani, C. D. Casa, M. Lanzi, E. Salatelli, *Synth Met*, *75* **(1995)** 141.
52. X. Zhao, X. Hu, C. Y. Yue, X. Xia, L. H. Gan, *Thin Solid Films*, *417* **(2002)** 95.
53. C. Lee, K. J. Kim, S. B. Rhee, *Synth Met*, *69* **(1995)** 295.
54. A. Cirpan, S. Alkan, L. Toppare, I. Cianga, Y. Yagci, *J Mater Sci*, *37* **(2002)** 1767.
55. M. Pomerantz, H. Yang, Y. Cheng, *Macromolecules, 28* **(1995)** 5706.
56. A. S. Amarasekara, M. Pomerantz, *Synthesis, 14* **(2003)** 2255.
57. A. Dass, S. Mulik, C. S. Leventis, N. Leventis, *Synth Met*, *156* **(2006)** 966.
58. S. Thomas, C. Zhang, S. H. Sun, *J Polym Sci Part A Polym Chem*, *43* **(2005)** 4280.
59. R. M. S. Maior, K. Hinkelman, H. Eckert, F. Wudl, *Macromolecules, 23* **(1990)** 1268.
60. H. Mao, B. Xu, S. Holdcroft, *Macromolecules, 26* **(1993)** 1163.
61. T. A. Chen, X. Wu, R. D. Rieke, *J Am Chem Soc*, *117* **(1995)** 233.
62. F. C. Tsai, C. C. Chasg, C. L. Liu, W. C. Chen. S. A. Jenekhe, *Macromolecules, 38* **(2005)** 1958.
63. A. P. Kulkarni, C. J. Tonzola, A. Babel. S. A. Jenekhe, *Chem Mater*, *16* **(2004)** 4556.
64. A. Bolognesi, W. Porzio, F. Provasoli, T. Ezquerra, *Makromol Chem*, *194* **(1993)** 817.
65. A. Bolognesi, W. Porzio, G. Zhou, T. Ezquerra, *Eur Polym J*, *32* **(1996)** 1097.
66. S. V. Meille, V. Romita, T. Caronna, A. J. Lovinger, M. Catellani, L. Belobrazeckaja, *Macromolecules, 30* **(1997)** 7898.

CHAPTER 3

Electrochemical, photoluminescence and electroluminescence properties of ester substituted ploythiophenes

3.1 Introduction

Recent advances in the field of electroluminescence of conjugated polymers provide a bright future for LEDs [1-13]. Conjugated polymers offer a number of advantages over conventional inorganic / organic materials. The processibility promises a significant advantage in large-area fabrication and the flexibility promises the fabrication of displays with unusual non-standard shapes [14-19]. In recent years, thiophene based polymers have been particularly exploited due to their structural versatility, solubility upon functionalization and environmental stability [20-28]. The photoluminescence properties of conjugated polythiophenes are of considerable interest due to their potential applications in light emitting diodes (LED), solar cells, chemical sensors and field effect transistor (FET) [29-32]. Solid state luminescence efficiency of polythiophenes is too low. This low efficiency is attributed to internal conversion of exciton through molecular aggregates and the existence of sulphur in the thienyl moiety which promotes intersystem crossing via spin–orbit coupling, i.e. the heavy atom effect [33-36]. The fluorescence efficiency can be enhanced by changing the substitution patterns by replacing a fraction of the thienylene moieties with groups possessing lighter atoms, e.g., phenylene or introducing steric constraints to reduce molecular aggregation of the side chain substituents on the polythiophene backbone [37-39]. Polythiophenes with suitable substituents in the 3-positions have shown tuneable photoluminescence properties [40-42]. The introduction of bulky groups like cyclohexyl, phenyl on polythiophene causes a steric twisting of the backbone and reduces the conjugation gives blue shifted emission [43-44]. Alkoxy side groups on polythiophenes backbone reduce the band gap of the polymer [45]. The incorporation of strong electron-withdrawing groups such as carboxylates is difficult because these substituents increase the potential for oxidation of the monomer and destabilize the resulting radical cation [46-47]. The devastating electron withdrawing effect of the oxygen atom in the vicinity of the thiophene can be neutralized by the intercalation of one methylene groups without any loss of polymer electroactivity. Electron-withdrawing ester groups on the thiophene ring are of considerable interest, as it may facilitate electron injection, influence electronic properties and promote triplet formation. It may also stabilize the conjugated backbone against oxidation or other unwanted degradative events [48-49]. The ester containing polythiophene derivatives show higher fluorescence quantum efficiency than that of alkyl containing derivatives [50-53].

The part of this chapter was published in **J. Luminescence, 129 (2009) 611**

The study of the electrochemical behaviour of polymers as a function of substitution can shed some light on the understanding of the reduction and oxidation process. The reduction and oxidation processes consist of several simultaneous and / or consecutive chemical and physical processes like swelling of the polymer, charge transfer between the electrode and the polymer, insertion of compensating ions into the bulk of the polymer, conformational changes of the polymer chain and change of conductivity [54]. The introduction of side groups will change several properties of the polymer and it may be difficult to confirm that oxidation and reduction potentials are entirely the result of one certain functionality. Nevertheless, some trends can be extracted that may be helpful for design and application of new materials. In addition, the energy position of HOMO and LUMO of conjugated polymers can be determined by cyclic voltammetric method. The relevance and generality of electrochemical characterization of conjugated polymers can be estimated by comparison to other methods. This is frequently done by calculating the electrochemical band gap and comparing it with optical band gap [55-56].

The operation of a light-emitting diode comprises several steps: charge injection, charge transport, charge recombination and decay of the exciton via radiative and non-radiative channels [57-63]. The electroluminescence process is strongly related to photoluminescence. In the majority of cases the same excited states are responsible for both electroluminescence (EL) and photoluminescence (PL). Electroluminescence is a combination of both optical and electrical phenomenon. Electroluminescent properties offer to choose colour for LED application. It also gives the information about quantum efficiency, stability and operating voltage required for LED.

Fabricating the state-of-the-art polymer light emitting diodes (PLEDs) involves achieving balanced and efficient injection of both electrons and holes, and therefore low work function cathodes and high work function anodes are required to minimise injection barriers. The mismatch of work function between the anode/cathode also introduces a fundamental asymmetry in the barrier heights in forward and reverse bias, which in turn leads to diode-like rectifying behaviour. The most widely used anode is indium-tin-oxide (ITO) because of its transparency and low resistivity. However, ITO is not ideal because it is not a well defined system and its physical properties are highly sensitive to the fabrication and preparation process [64]. Furthermore, the work function of ITO is often lower than desired. Improved hole injection and device performance (higher efficiency /lifetime and lower operating voltage) have been obtained by introducing a layer of poly(ethylene-dioxythiophene)/ poly(styrene sulphonic acid) (PEDOT:PSS) between the ITO and the emitting polymer [65-

68]. A similar stratagem, based on the incorporation of an interlayer between the electrode and the active layer, has also been successfully employed at the cathode/polymer interface to enhance electron injection. For example, a thin film of LiF can be inserted between an aluminium cathode and the organic emitter [69-70]. This enables fabrication of efficient diodes without resorting to low work-function metal cathodes, such as calcium and magnesium, which are reactive to the environment and detrimental to the lifetime of LEDs. The consensus over the mechanism behind electron enhancement by insulators such as LiF has not yet been achieved. The different mechanisms are enhanced electron tunnelling from the Al following hole accumulation at the polymer/ insulator junction or large voltage drops in the insulator, longer electron attenuation length, reduction of interfacial reactions with the metal electrode, reduction of the barrier height to electron injection, and dissociation of the LiF to form a low work function contact [71-74].

In this chapter, electrochemical, photoluminescence and electroluminescence properties of synthesized polymers have been discussed. The oxidation and reduction potential of different ester substituted polythiophenes were determined by cyclic voltammetry method. We have discussed the influence of substituents on the red / ox potentials. Redox stability of polymers was tested by cyclic voltammetry up to 10 cycles. Furthermore, band gap of polymers was measured by electrochemically and compared with optical method. Photoluminescence properties in solution and solid state of polymers were investigated. The relative quantum yield of polymers with respect to Rhodamine B dye was measured. The electroluminescence properties of polymers were studied by fabricating LED device with configuration ITO / PEDOT: PSS /Polymer/ LiF / Al.

3.2 Experiment

3.2.1 Materials

$LiClO_4$ (Aldrich), Poly(ethylene dioxythiophene): Poly(styrene sulfonate) (PEDOT:PSS) (Aldrich), LiF (Merck, Germany), ITO coated glass (Vin Karola, USA) were used as received.

3.2.2 Instrumentations

3.2.2.1 Cyclic voltammetry

Polymer films for electrochemical studies were spin cast from THF solution on to ITO coated glass. Cyclic voltammetric (CV) experiments were performed with a standard one compartment three-electrode configuration cell (Figure 3.1) with the polymer films deposited on ITO coated glass electrode as the working electrode, platinum as the counter electrode, and an $Ag/AgNO_3$ (0.1M) electrode as the reference electrode. The potential is measured between the reference electrode and the working electrode and the current is measured between the working electrode and the counter electrode. All potentials are reported with respect to reference electrode. Acetonitrile containing $LiClO_4$ (0.1M) was used as the electrolytic medium. The measurements were calibrated using ferrocene as the standard and the scan rate was 50 mV/s. The experiments were conducted on a Sycopel AEW2-10 cyclic voltammeter.

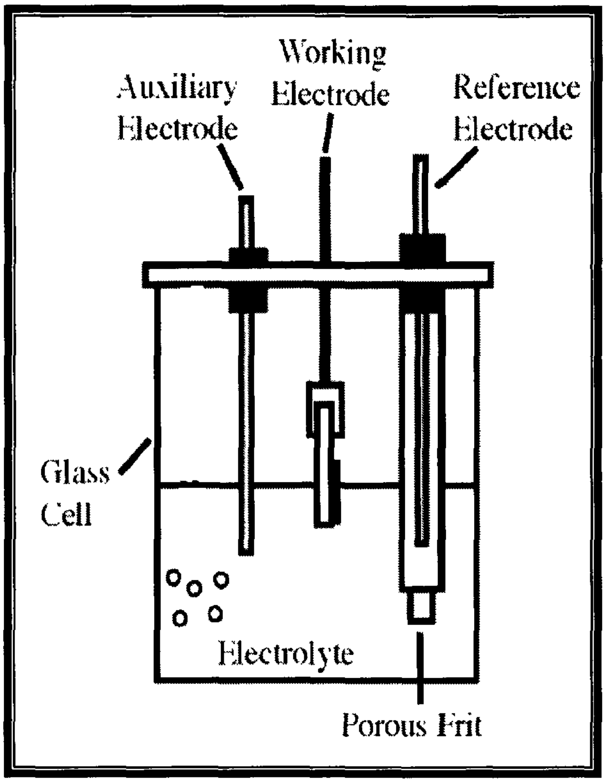


Figure 3.1: Typical 3-electrode electrochemical cell

3.2.2.2 Photoluminescence spectroscopy

Photoluminescence spectra were recorded using a Hitachi F-2500 FL Spectrophotometer, by excitation of the polymer at maximum absorption wavelength. The fluorescence spectrum of polymer at different concentration in THF solvent was recorded. Solid state PL of polymers was measured by preparing the polymer film on the glass substrate.

3.2.2.3 Device fabrication and testing

The electroluminescence (EL) devices (Figure 3.2) were fabricated on indium–tin oxide (ITO) coated glass substrate with sheet resistance of 20 Ω/cm^2. The substrate was ultrasonically cleaned with detergent, deionized water, acetone, trichloroethylene, and isopropyl alcohol, sequentially each for 20 minutes and then baked for 2h at 110°C. The ITO substrates were treated with UV–ozone for 5 min prior to film coating. Subsequently, onto the ITO glass a layer of poly(ethylene dioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) was spin–coated at 1500 rpm from its aqueous solution and then vacuum-dried for 2h 120°C. The polymer layer was spin –coated at 1500 rpm from the corresponding THF solution (1 wt %) on top of the vacuum- dried PEDOT: PSS layer and then vacuum –dried for 2h for 130°C. Under a high vacuum (1×10^{-5} Torr), a layer of LiF (1nm) at a deposition rate 0.5 A°/s was vacuum deposited and a thick layer of Al (150nm) at a deposition rate 1-4 A°/s was deposited subsequently as cathode. Thickness of the deposited layers was controlled by quartz crystal monitor. The cathode was deposited on the top of the structure. The electroluminescence (EL) spectra were measured using a high resolution spectrometer (Ocean Optics, HR-2000CG UV-NIR). I – V characteristic of LED devices were measured by Keithley 2400 programmable current voltage digital source meter.

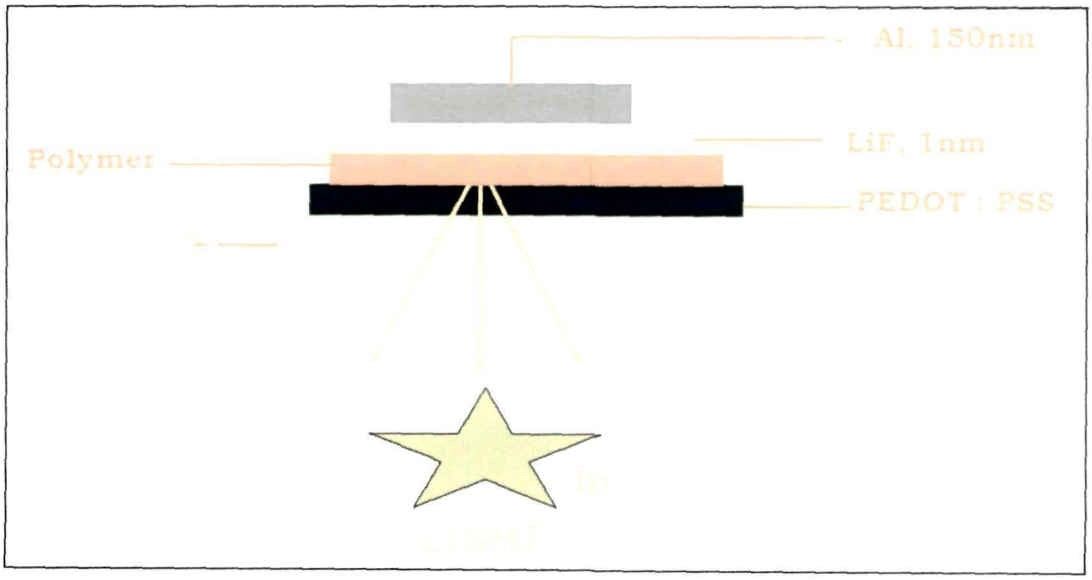


Figure 3.2: Fabrication of electroluminescence device

3.3 Results and discussions

3.3.1 Electrochemical properties of polymers

3.3.1.1 Redox properties of polymers

Electrochemical properties of synthesized polymers can be assessed in cyclic voltmmetry method. Cyclic voltammetry (CV) is a suitable way to study the redox states of polymers. The electrode potential at which a polymer undergoes reduction or oxidation can be rapidly located by CV. Cyclic voltammograms of spin cast of polymers film from THF solvent in 0.1 M $LiClO_4$ acetonitrile solution are shown in Figure 3.3 - 3.9. The oxidation and reduction potentials of polymers are listed in Table 3.1. The oxidation potentials of polymers are found to be high 2.45 V and there is no significant change with different side chains. These observations may be attributed to low molecular weight polymers [54] (molecular weight of soluble portion of polymer in THF solvent is low). On the other hand, reduction potential of polymers has been found to be altered with different side chains. The reduction potential of polymers is in the range of -0.84V to -2.25V. The reduction potential decreases with increasing alkyl side chain length and PDDTA has the lowest reduction potential (-1.2V) among alkyl ester polythiophenes. The reduction potential of PPDPTA, PPDCHTA and PQTA is -1.85 V, -1.8 V and -0.84 V respectively. It is observed that quinolinyl containing polymer PQTA have the least reduction potential amongst ester substituted polymers due to large molecular weight compared to others.

Table3.1: Oxidation and reduction potential of polymers

polymers	Oxidation potential (V)	Reduction potential (V)
PHTA	2.45	-2.1
POTA	2.45	-2.25
PDTA	2.45	-2.0
PDDTA	2.45	-1.2
PPDPTA	2.45	-1.85
PPDCHTA	2.45	-1.8
PQTA	2.47	-0.84

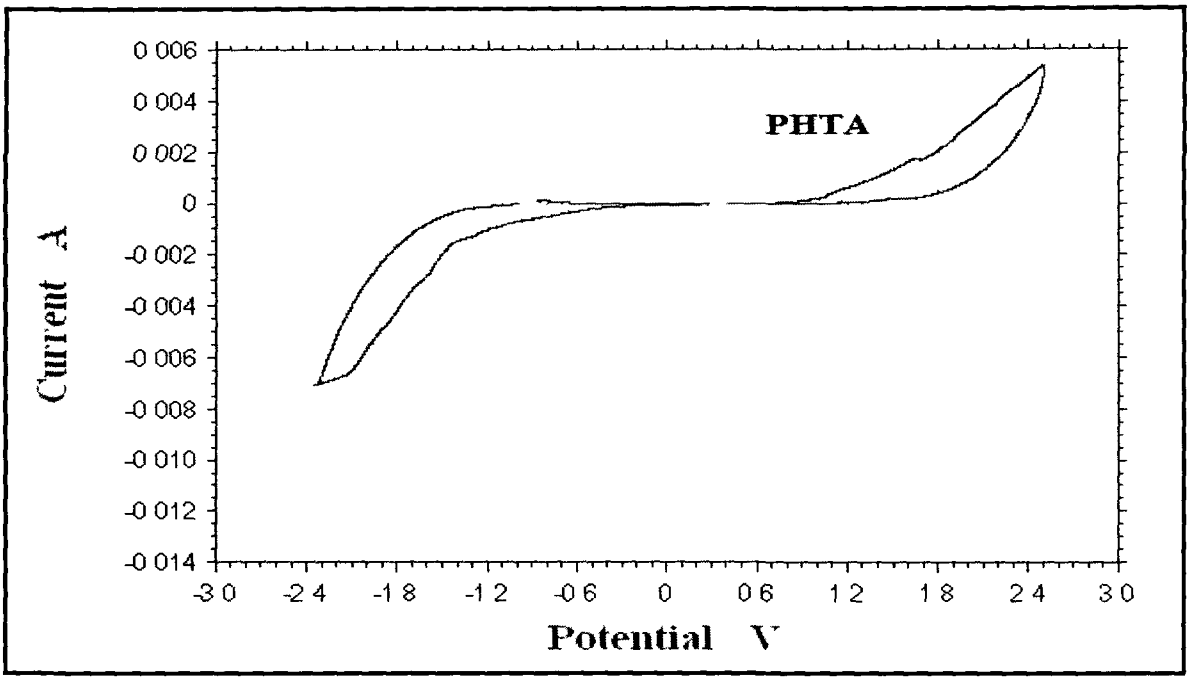


Figure 3.3: CV of polymer PHTA in thin film, Scan rate 50mV/S

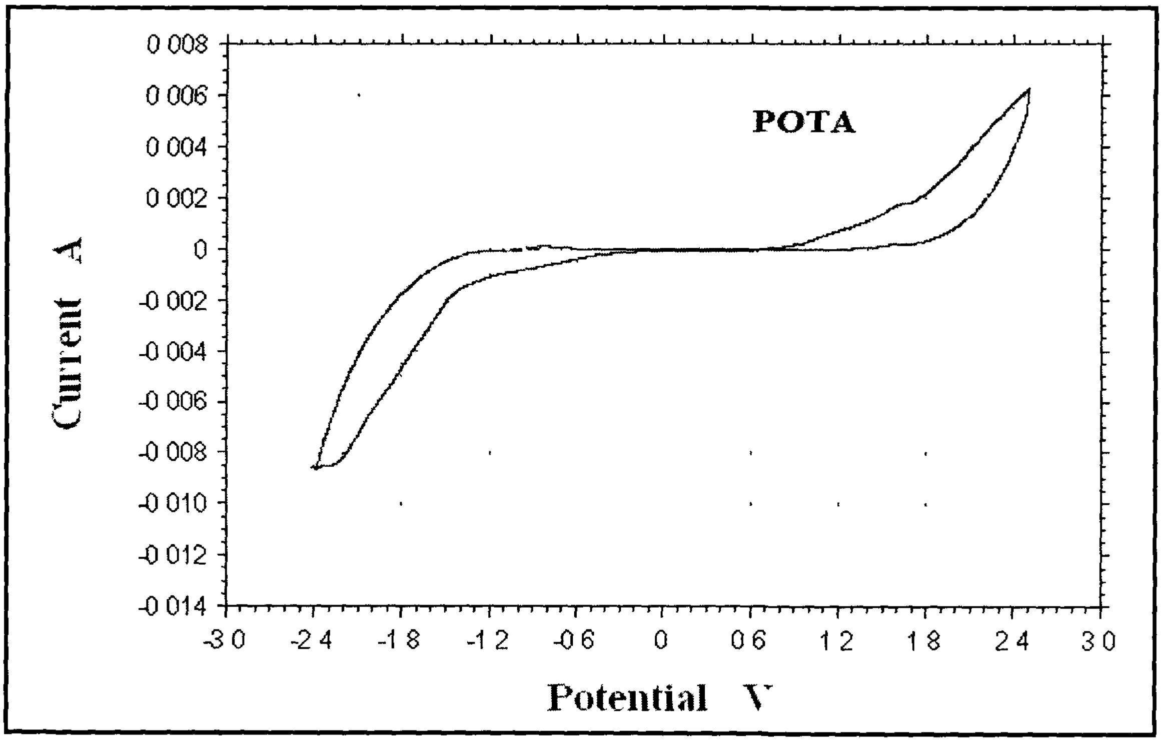


Figure 3.4: CV of polymer POTA in thin film, Scan rate 50mV/S

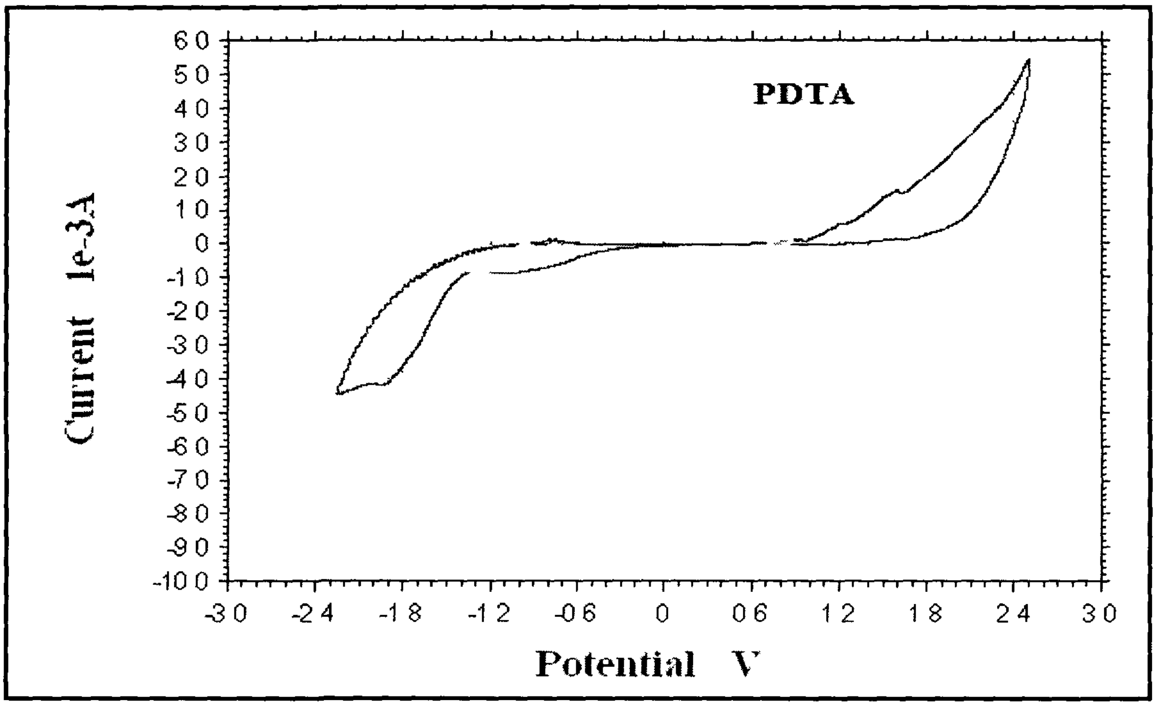


Figure 3.5: CV of polymer PDTA in thin film, Scan rate 50mV/S

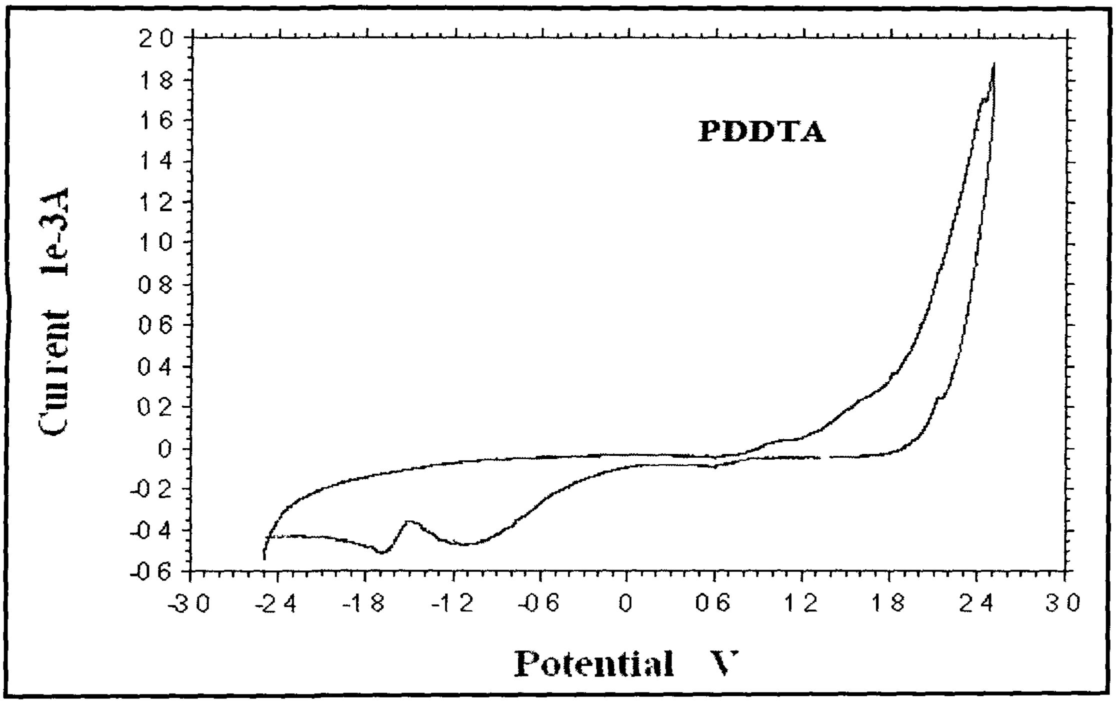


Figure 3.6: CV of polymer PDDTA in thin film, Scan rate 50mV/S

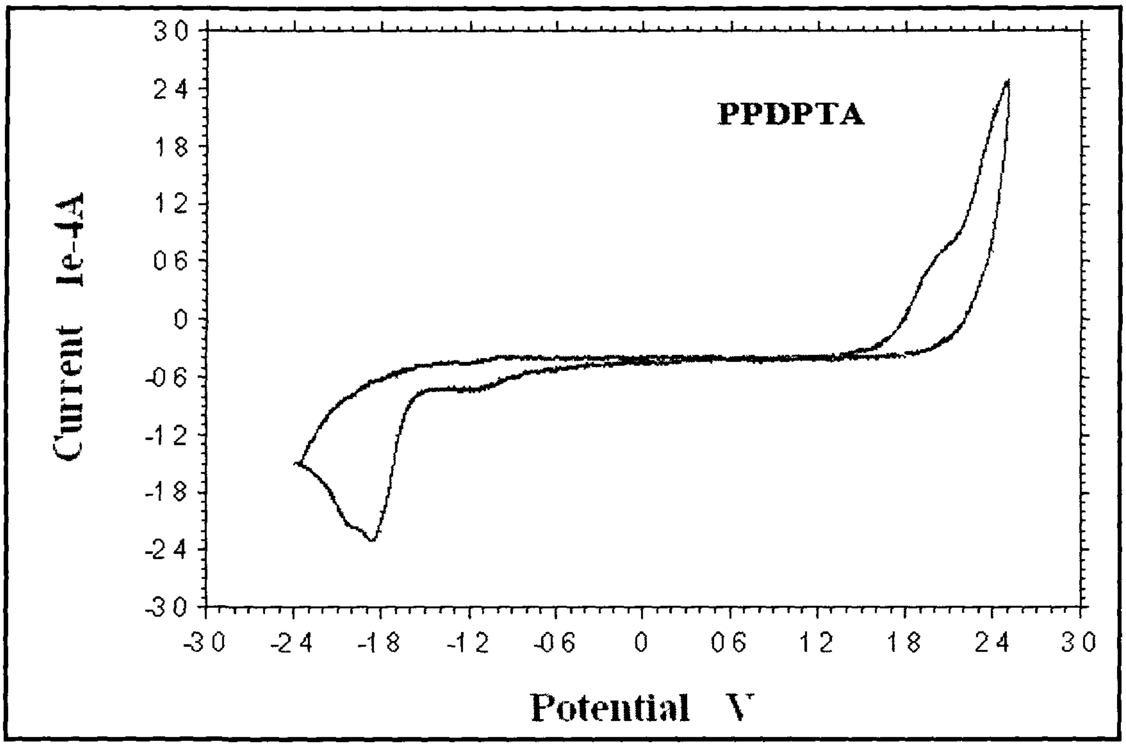


Figure 3.7: CV of polymer PPDPTA in thin film, Scan rate 50mV/S

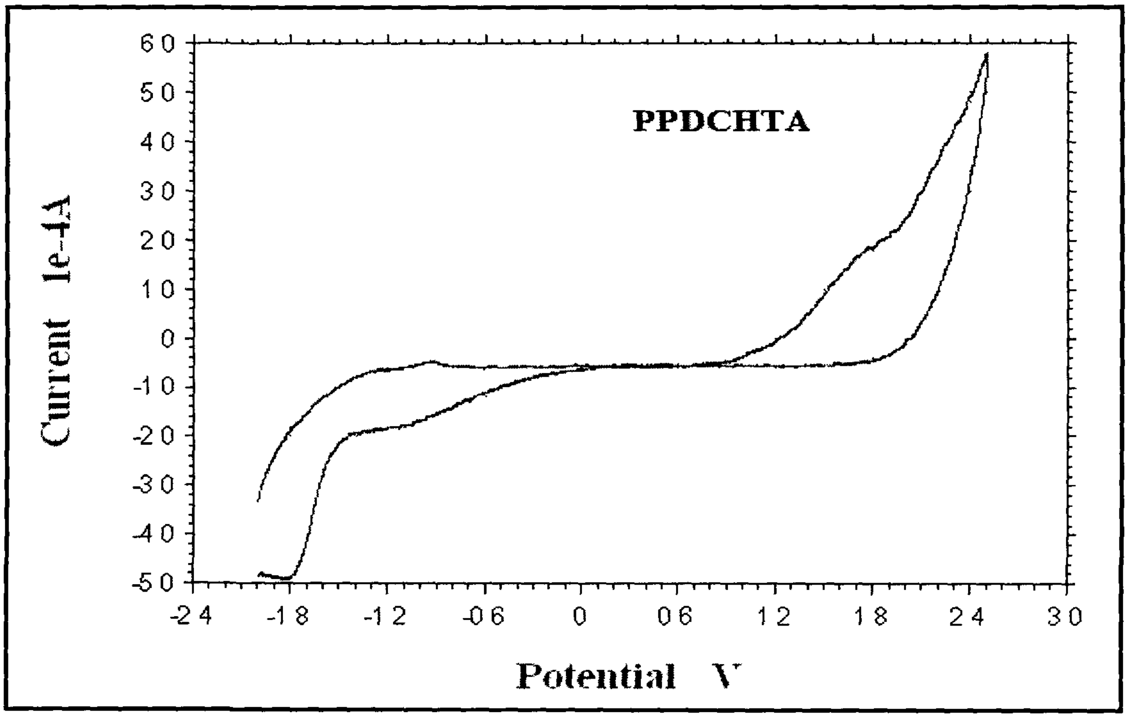


Figure 3.8: CV of polymer PPDCHTA in thin film, Scan rate 50mV/S

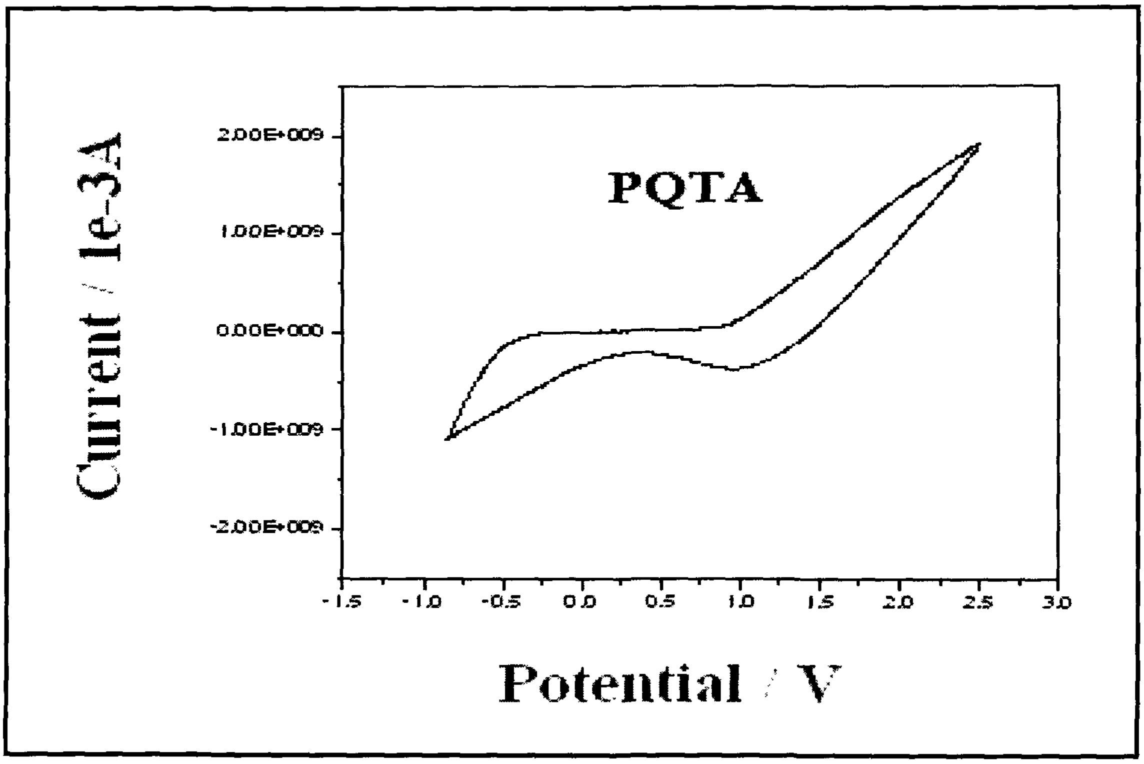


Figure 3.9: CV of polymer PQTA in thin film, Scan rate 50mV/S

3.3.1.2 Redox stability of polymers

CV provides information regarding the stability of the product during multiple redox cycles. ITO coated polymers were exposed to cyclic oxidation and reduction upto 10 cycles. Cyclic voltagrams after 10 cycles are given in figure 3.10-3.16. It is observed that there is no significant change in redox potentials. Therefore polymers are quite stable under redox potential. This is possibly due to the presence of ester group in the polymer side chains [4].

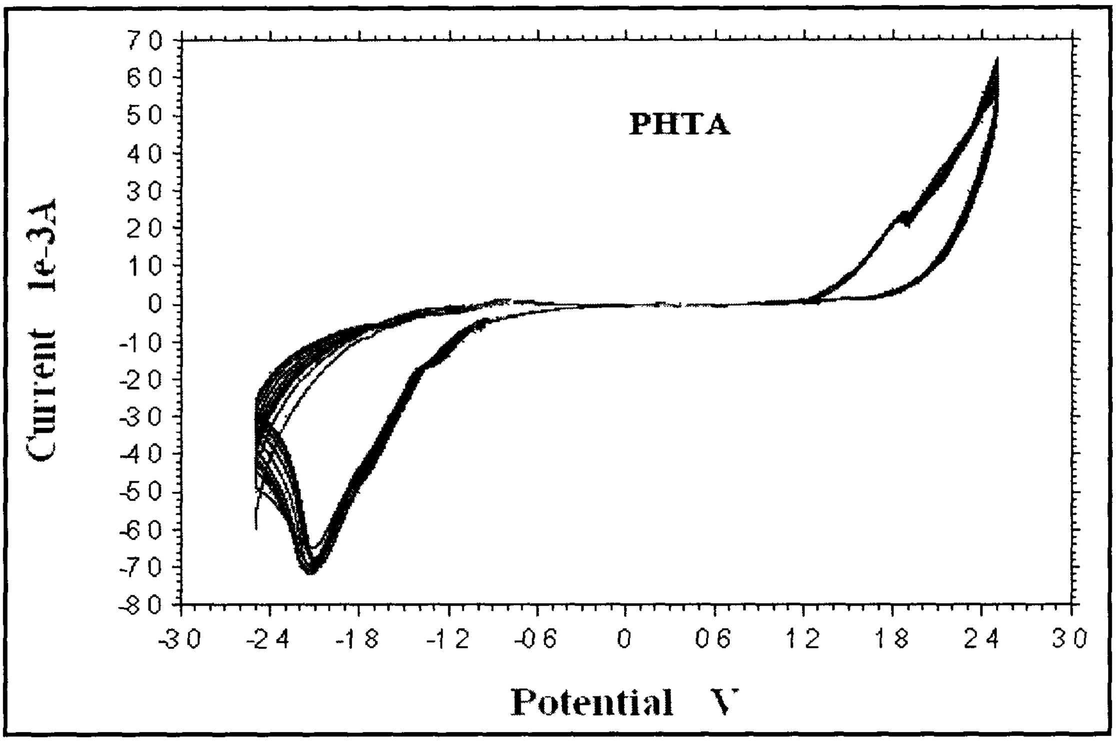


Figure 3.10: CV (10 cycles) of polymer PHTA in thin film, Scan rate 50mV/S

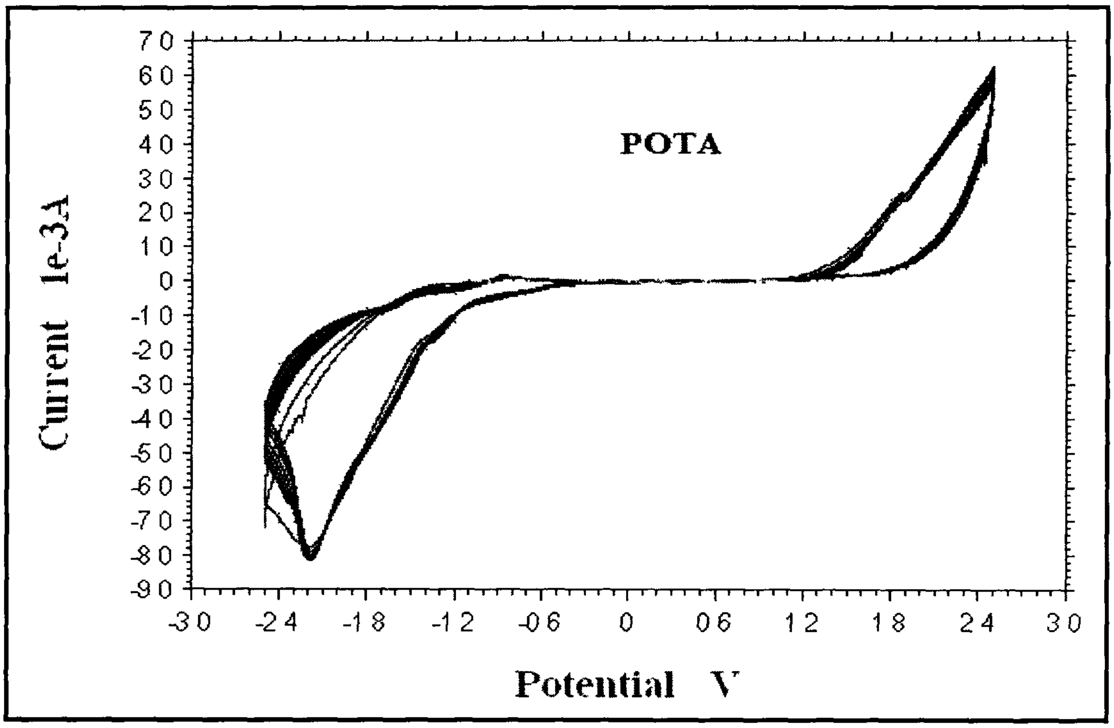


Figure 3.11: CV (10 cycles) of polymer POTA in thin film, Scan rate 50mV/S

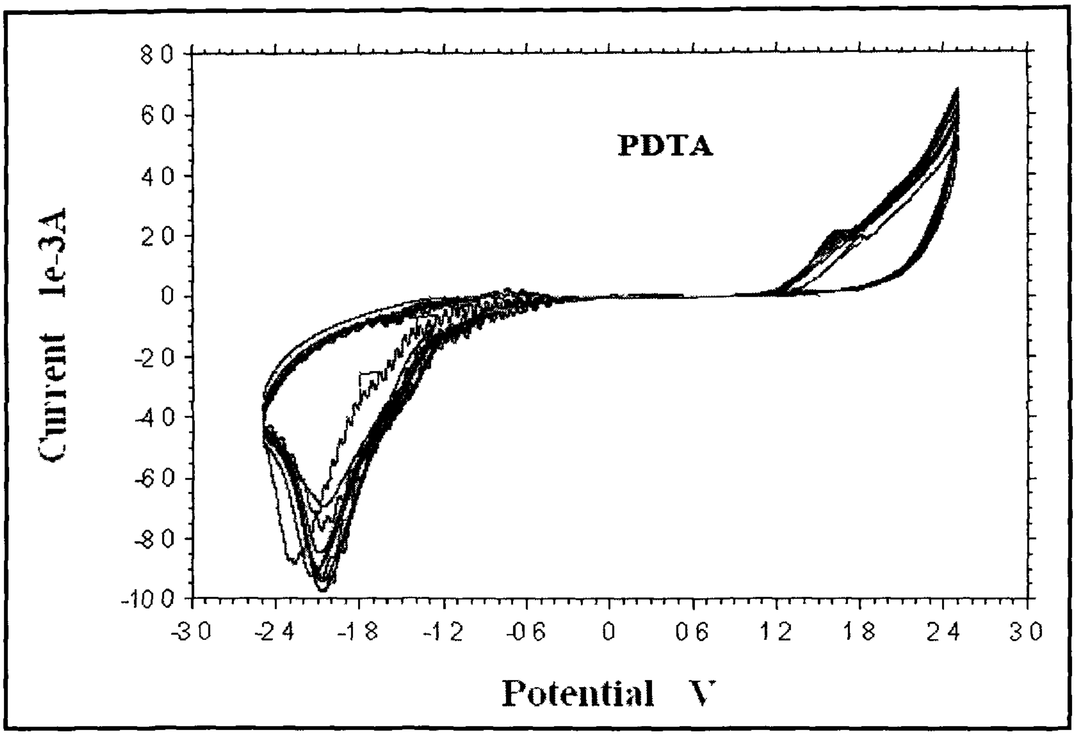


Figure 3.12: CV (10 cycles) of polymer PDTA in thin film, Scan rate 50mV/S

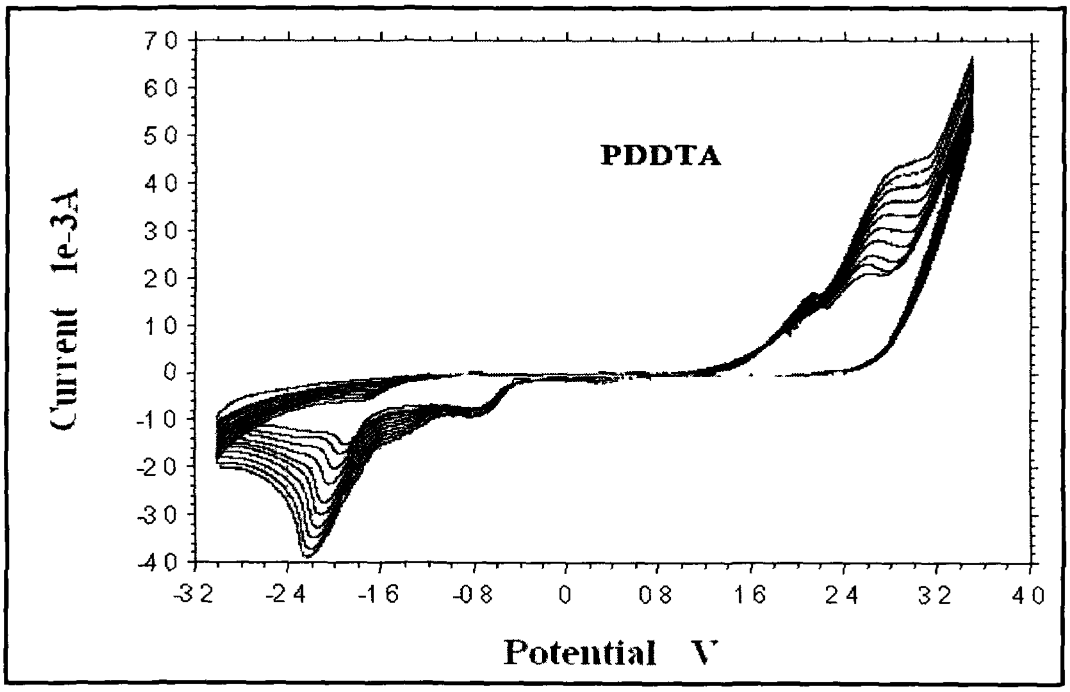


Figure 3.13: CV (10 cycles) of polymer PDDTA in thin film, Scan rate 50mV/S

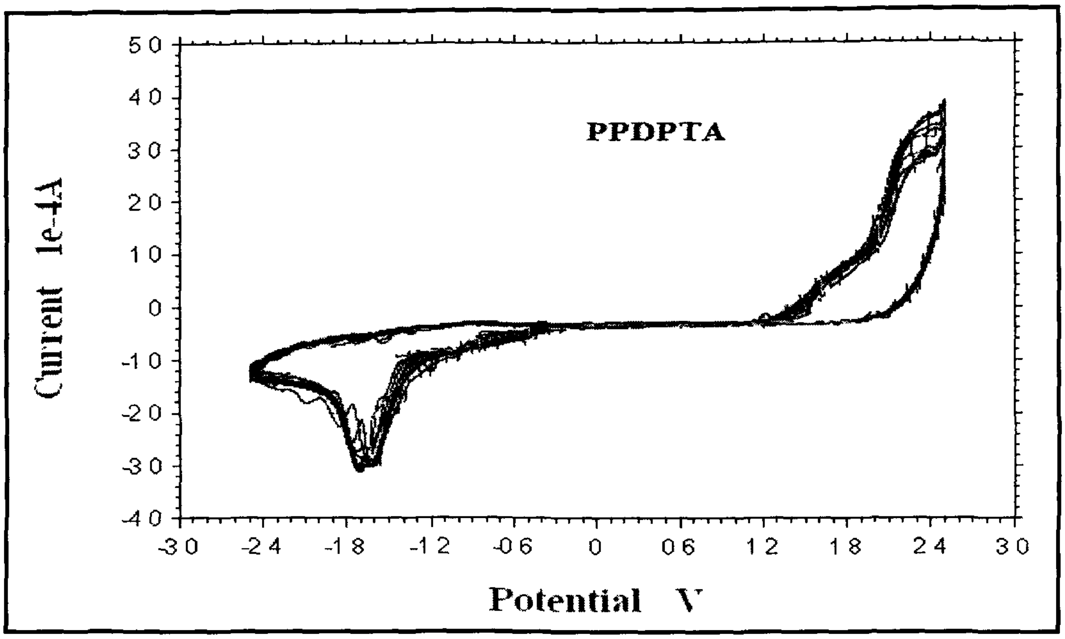


Figure 3.14: CV (10 cycles) of polymer PPDPTA in thin film, Scan rate 50mV/S

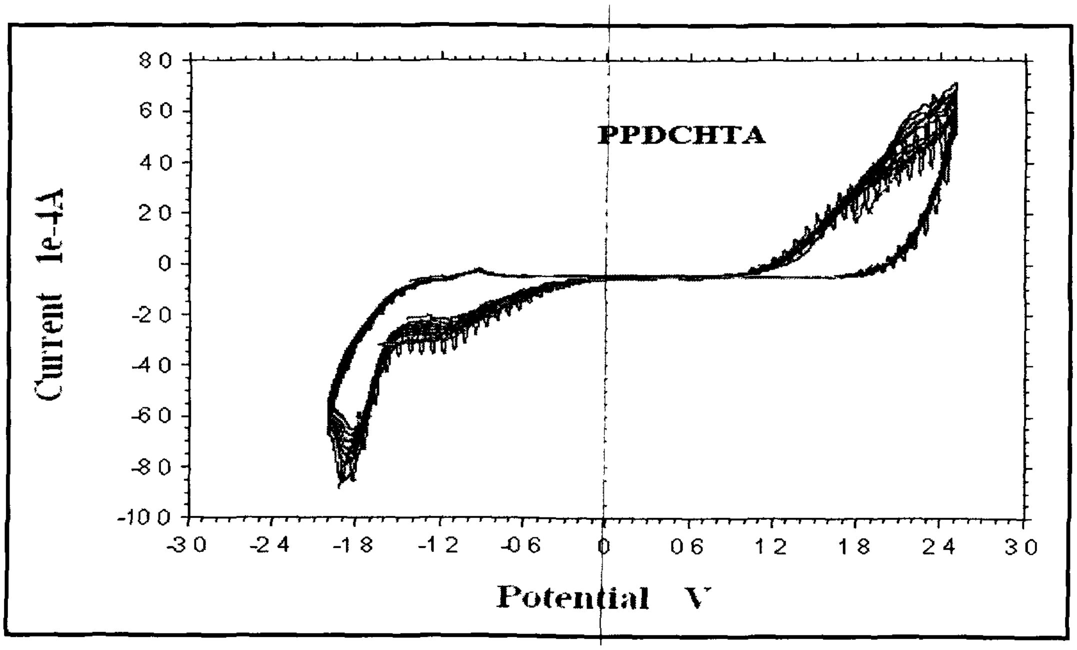


Figure 3.15: CV (10 cycles) of polymer PPDCHTA in thin film, Scan rate 50mV/S

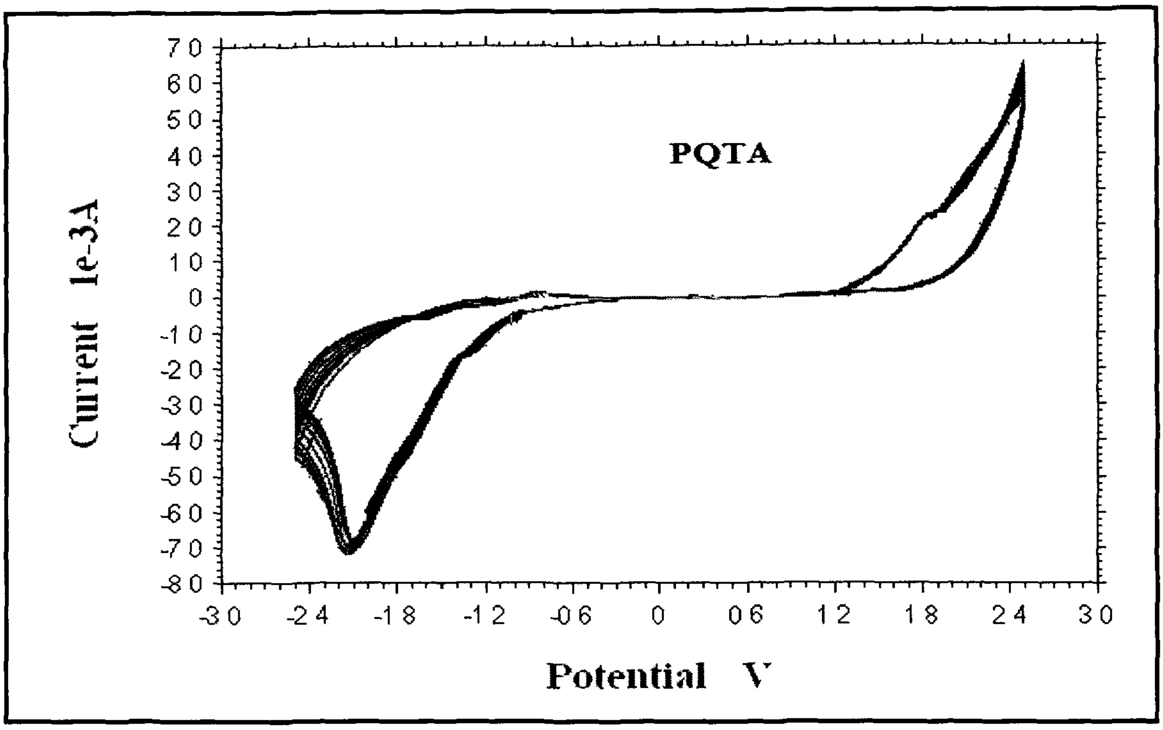


Figure 3.16 CV (10 cycles) of polymer PQTA in thin film, Scan rate 50mV/S

3.3.1.3 Estimation of energy level of polymers

The energy levels of HOMO and LUMO provide guidelines in selecting the electrode materials when constructing a LED based on these polymers. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels are estimated. Levels are calculated using the following empirical equation (3.1) [75].

$$\mathbf{HOMO = 4.4 + (E^{ox}{}_{onset}) \text{ and } LUMO = 4.4 + (E^{red}{}_{onset})} \qquad \mathbf{(3.1)}$$

The charging of the polymer during the doping process is associated with conformational reorganisation and modification of the energy levels of the polymer. From this point of view only onset potential probes injection of charges to neutral polymers in the ground state. Onset is also advantageous when two or more red / ox peaks are not fully resolved. The onset has been evaluated by drawing two tangents for each peak and is assumed to be where the two tangents cross as indicated by dashed line for $E_{pa}{}^{ox}$ in Figure 3.17.

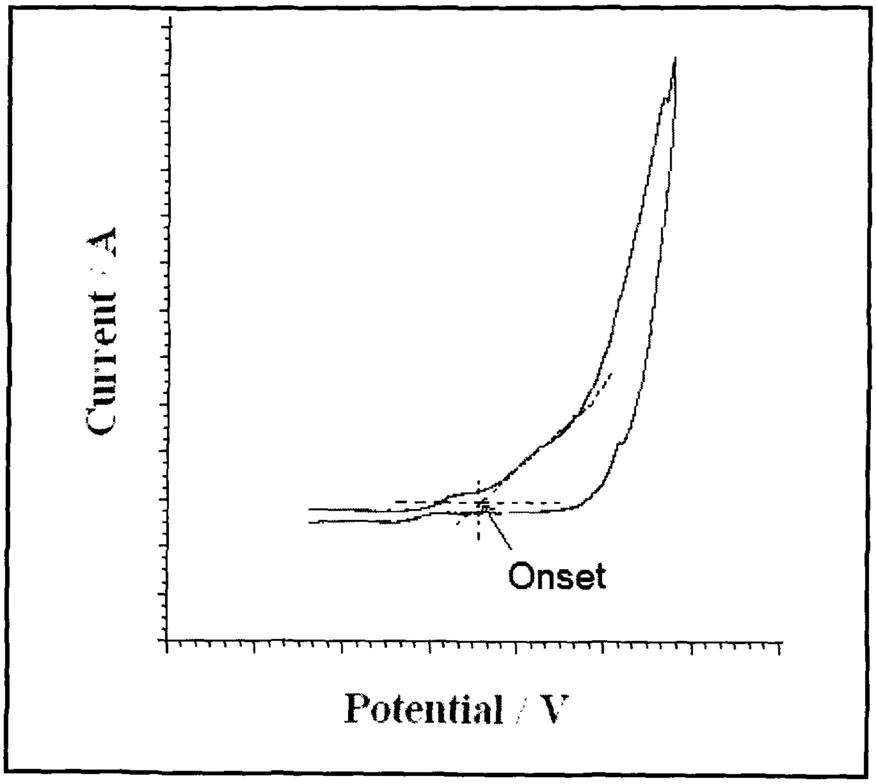
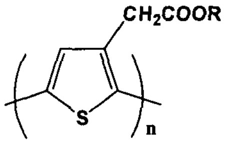
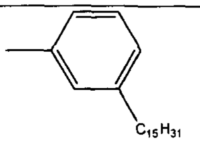
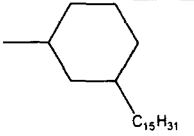
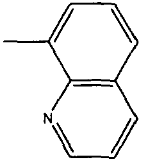


Figure 3.17 Measurement of onset in CV

The onset of oxidation and reduction potential, HOMO and LUMO of polymers are given in table 3.2. The HOMO energy level of alkyl and cyclohexyl containing polymers are same and is found to be 5.4 eV. The phenyl and quinolinyl polymers PPDPTA and PQTA, HOMO energy level are ascertained to be 5.9 eV and 6.125 eV, respectively. In case of phenyl and quinolinyl containing polymers, HOMO energy level is higher than alkyl and cyclohexyl derivative polymers. This may be due to the presence of aromatic phenyl and quinolinyl group attached to the ester polythiophenes. On the other hand, LUMO energy level of the polymers is almost identical.

Table 3.2: Onset ox/red potentials and HOMO and LUMO energy levels of polymers

Polymers 	Side chain moiety (R)	Onset of oxidation potential (V)	HOMO (eV)	Onset of reduction potential (V)	LUMO (eV)
PHTA	$-C_6H_{13}$	1.1	5.5	-0.6	3.8
POTA	$-C_8H_{17}$	1.0	5.4	-0.6	3.8
PDTA	$-C_{10}H_{21}$	1.0	5.4	-0.6	3.8
PDDTA	$-C_{12}H_{25}$	1.0	5.4	-0.57	3.83
PPDPTA		1.5	5.9	-0.6	3.8
PPDCHTA		1.0	5.4	-0.6	3.8
PQTA		1.725	6.125	-0.64	3.76

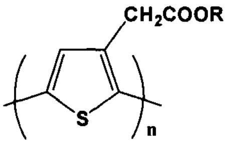
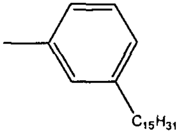
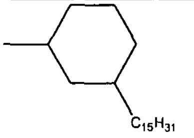
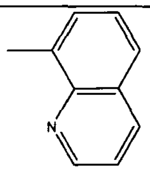
3.3.1.4 Comparison of band gap estimated from optical and electrochemical method

The band gap is an important parameter whose magnitude governs the intrinsic electronic and optical properties of conjugated polymers. The existence of a finite band gap in conjugated polymers is considered to originate principally from bond length alternation.

The electrochemical determination of band gap actually leads to the formation of charge carriers. On contrary, optical transitions do not reveal the formation of free charge carriers, as the excited state in conjugated polymers may be viewed as a bound exciton. At the same time, optical transitions cannot be directly compared to the electrochemical doping process [54].

The electrochemical and optical band gap of polymers are given in table 3.3. The band gap of alkyl and cyclohexyl containing polymers determined by optical and electrochemical method are more or less same and is found to be 1.6-1.7eV for electrochemical method and 2.29-2.38 eV for optical method. The band gap of phenyl containing polymers is found to be 2.1eV (electrochemically) and 2.45eV (optically). The band gap of quinolinyl containing polymer is found to be 2.365 eV (electrochemically) and 2.47 eV (optically). The band gap of phenyl and quinolinyl containing polymers has higher than alkyl and cyclohexyl polymers. It is seen that optical band gap gives higher values of the band gap. However, both the method establishes the same trend of band gap. Substitutes in 3-ester polythiophene have a pronounced effect on the band gap.

Table 3.3: Electrochemical and optical band gap of polymers

Polymer  	Side chain moiety (R)	Electrochemical band gap (eV)	Optical band gap (eV)
PHTA	$-C_6H_{13}$	1.7	2.36
POTA	$-C_8H_{17}$	1.6	2.36
PDTA	$-C_{10}H_{21}$	1.6	2.29
PDDTA	$-C_{12}H_{25}$	1.57	2.38
PPDPTA	 	2.1	2.45
PPDCHTA	 	1.6	2.31
PQTA	 	2.365	2.47

3.3.2 Photoluminescence behaviour of polymers

3.3.2.1 Photoluminescence in solution

The photoluminescence (PL) of the polymers in THF solution, excited at the maximum absorption wave length is measured. The emission maximum (λ^{PL}_{max}) of the polymers has been found in the range of 530nm for PPDCHTA to 547 nm for PHTA (Table 3.4), indicating difference of effective conjugation length in the relaxed excited state. The emission of light is in the yellow-green region. The Absorption, emission and stokes shifts of the polymers are shown in Figure 3.18-3.24. Stokes shifts of the polymers range from 148 nm for PQTA to 230nm for PPDCHTA. These large stokes shifts may be attributed to the configuration rearrangement upon excitation [76-77]. Here, it is observed that side chain of ester substituted polythiophenes plays no significant role for changing the colour of fluorescence emission. However, the fluorescence efficiency has been modified with the change in side chain substituents. It is well known that thiophene itself is a non-fluorescent, while oligothiophenes (T,) and oligo(alkylthiophenes) with two or more thienyl moieties are all fluorescent. *Bithiophene shows a very weak fluorescence emission band at 360 nm.* The fluorescence quantum yield of bithiophene is only about 1%. The emission maxima, fluorescence quantum yields, and fluorescence of oligothiophenes have been found to increase with increasing number of thienylene moieties [78-79].

The PL intensity of the polymers in THF solution excited at 350nm has been investigated at 0.05wt % polymer concentration (Figure 3.25). The PL intensity increases with increasing conjugation length. PL intensity is found to be high for PQTA and low for polymer PPDCHTA. It is consistent with their degree of polymerization. Here, ester spacer weakens the direct effect of side chain on polythiophene backbone.

Table 3.4: Absorption, emission and stokes shift of polymers

Polymer	Absorption (nm)	Emission (nm)	Stokes shift (nm)
PHTA	370	547	177
POTA	363	533	170
PDTA	363	545	182
PDDTA	359	543	184
PPDPTA	315	542	227
PPDCHTA	307	530	230
PQTA	392	540	148

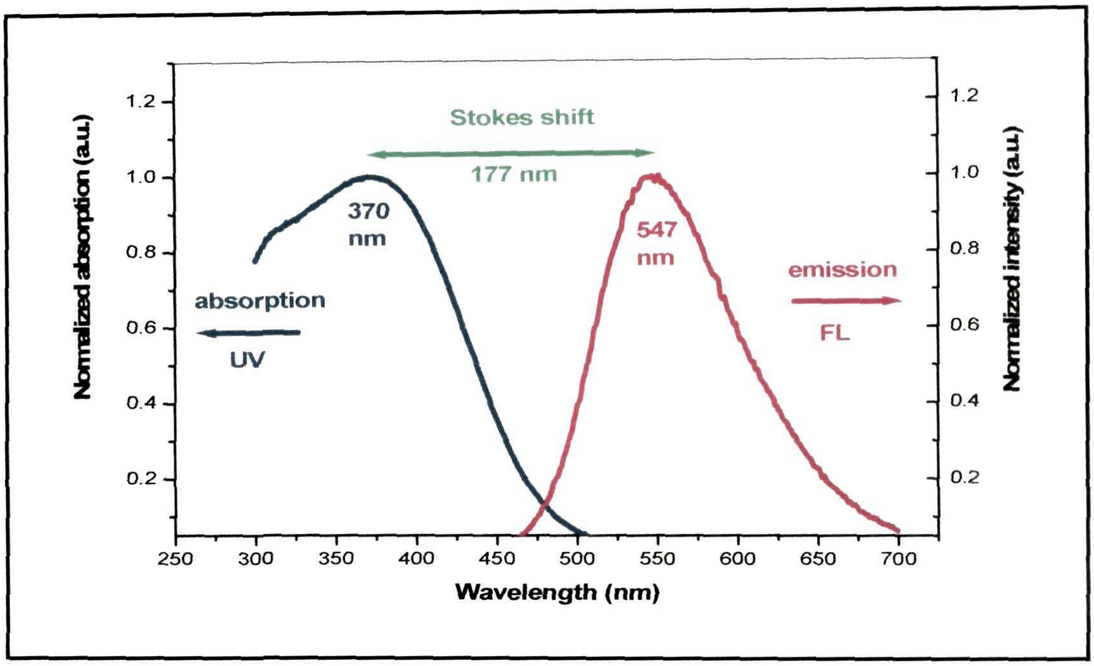


Figure 3.18: Absorption, emission and stokes shift of polymer PHTA in THF solution, excited at 370nm

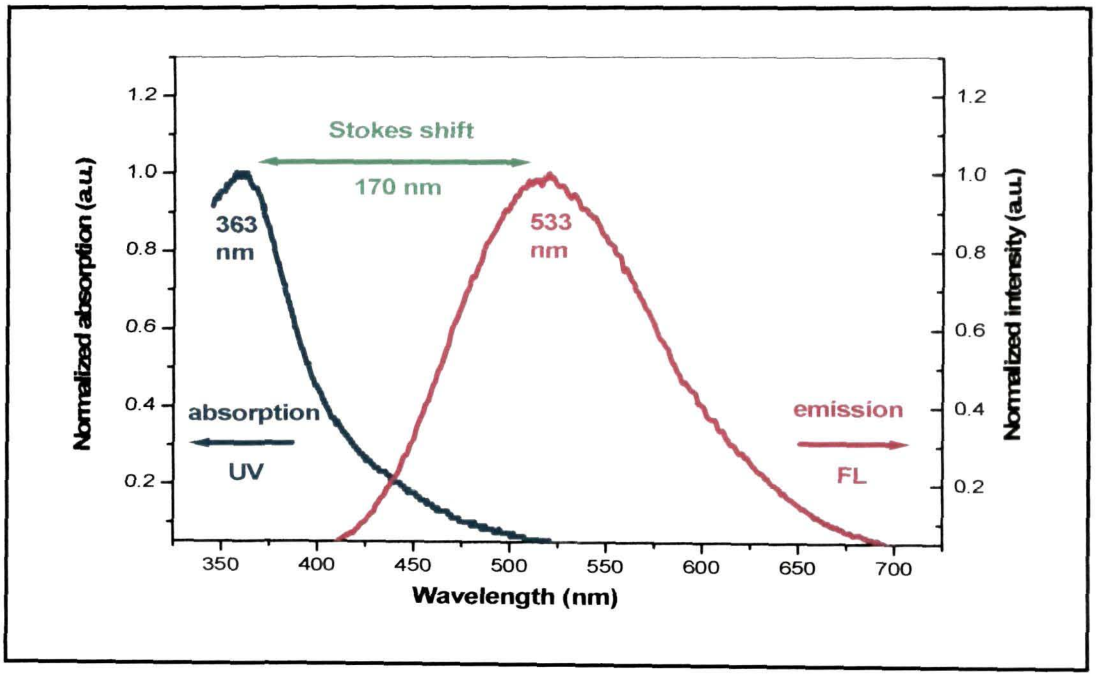


Figure 3.19: Absorption, emission and stokes shift of polymer POTA in THF solution, excited at 363 nm

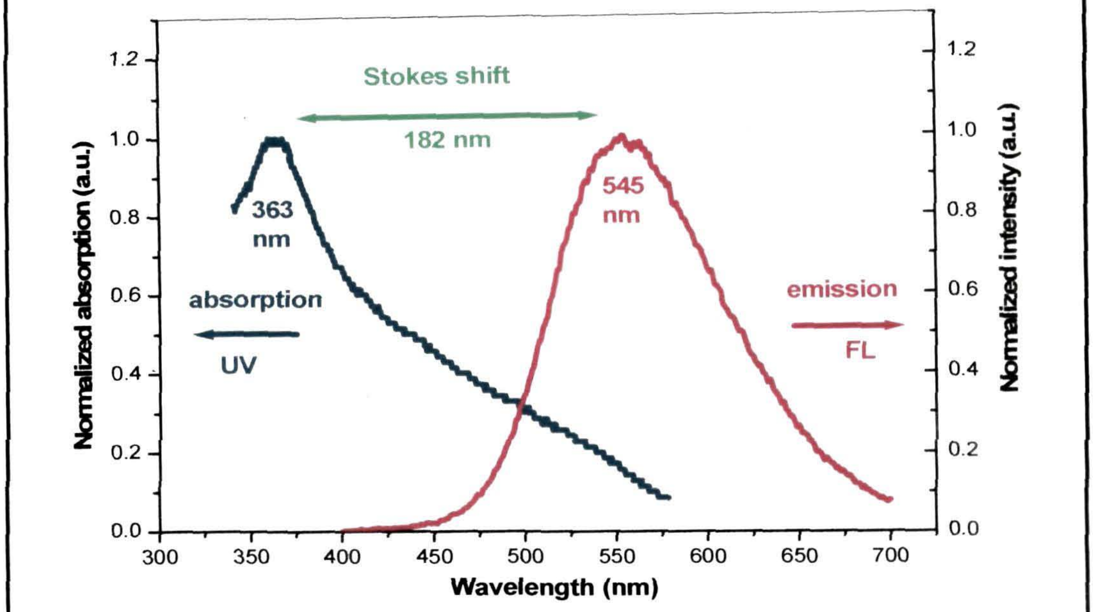


Figure 3.20: Absorption, emission and stokes shift of polymer PDTA in THF solution, excited at 363 nm

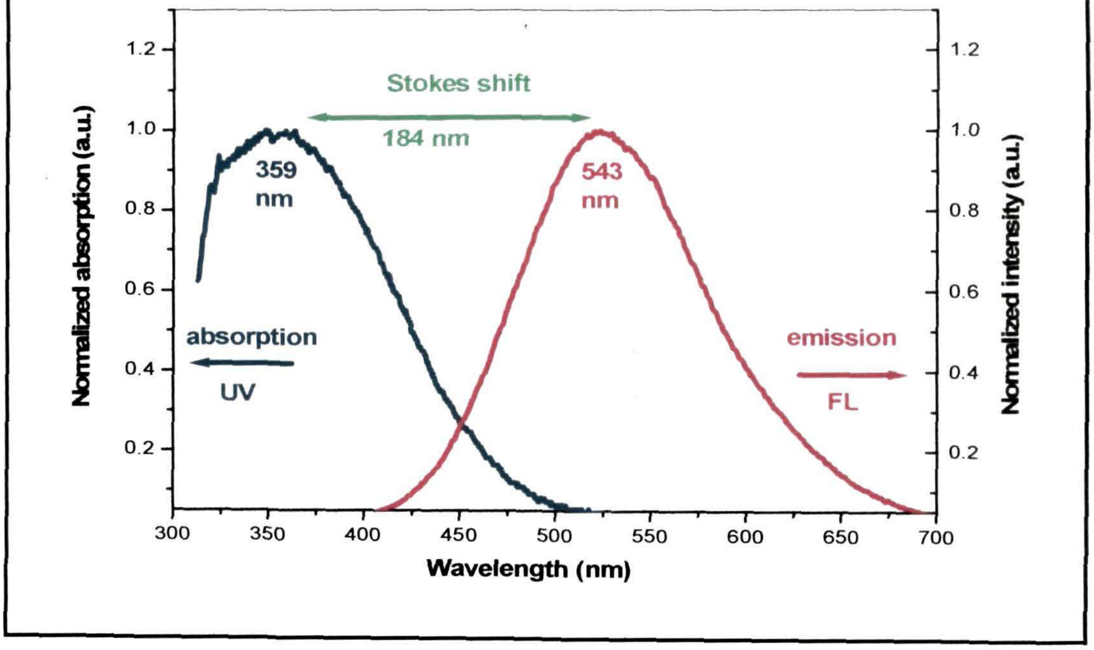


Figure 3.21: Absorption, emission and stokes shift of polymer PDDTA in THF solution, excited at 359 nm

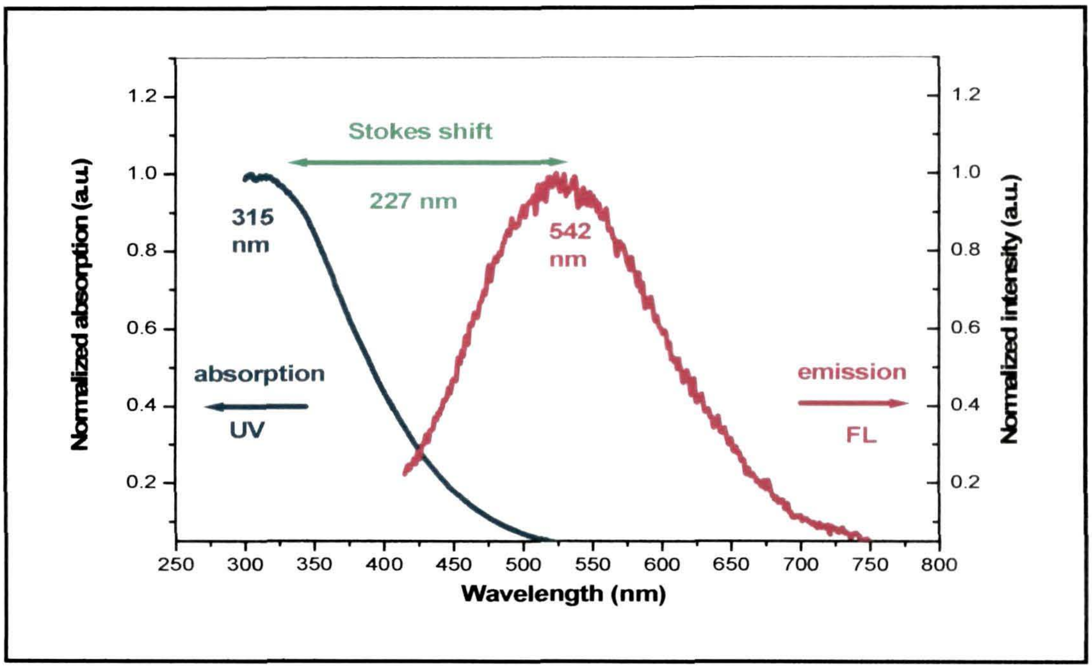


Figure 3.22: Absorption, emission and stokes shift of polymer PPDPTA in THF solution, excited at 315 nm

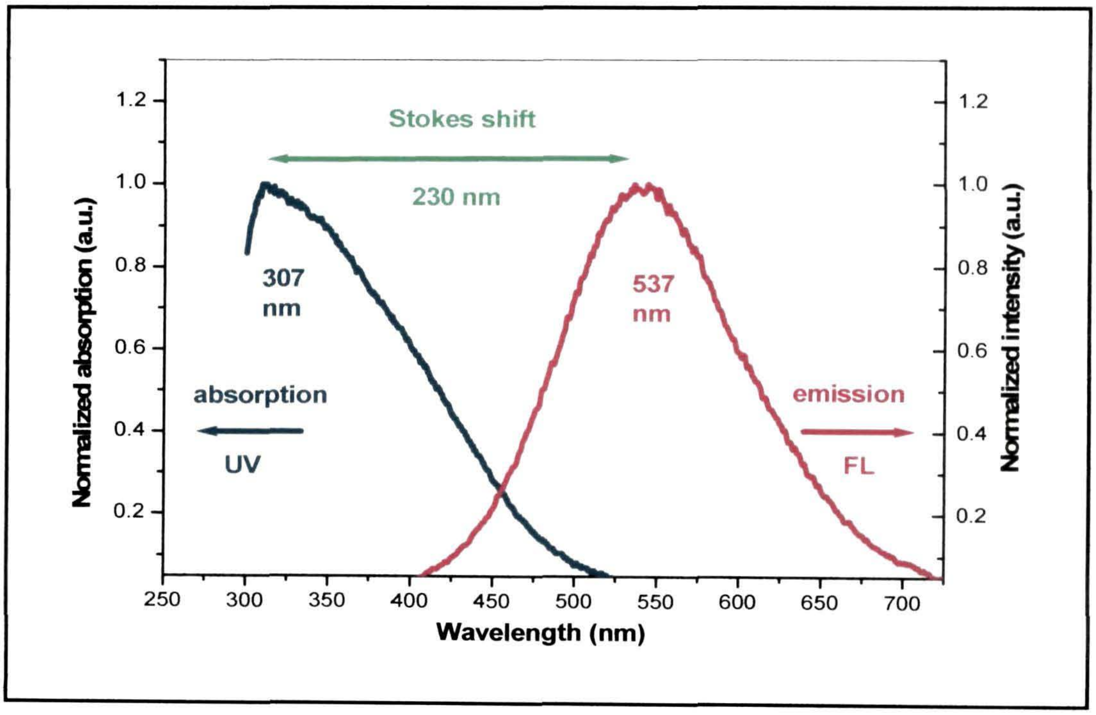


Figure 3.23: absorption, emission and stokes shift of polymer PPDCHTA in THF solution, excited at 307 nm

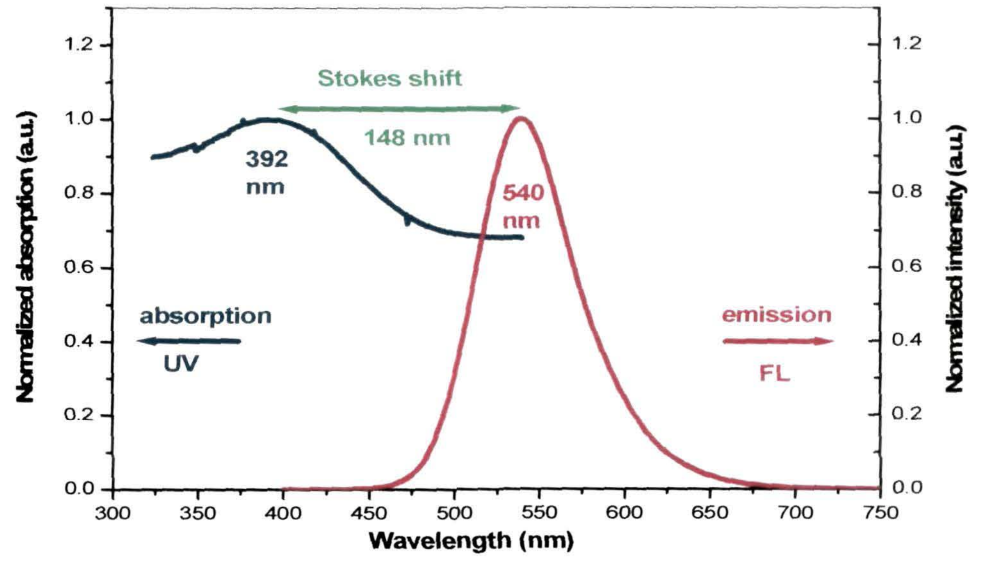


Figure 3.24: absorption, emission and stokes shift of polymer PHTA in THF solution, excited at 392 nm

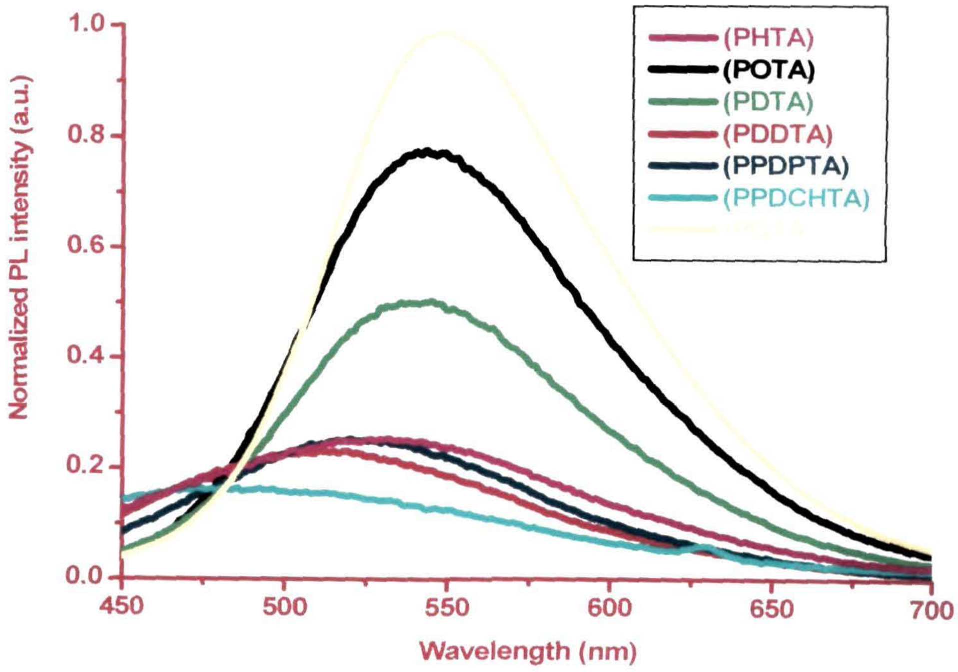


Figure 3.25: Normalized PL spectra of polymers excited at 350nm in THF solution at 0.05 wt% polymer concentration

3.3.2.2 Photoluminescence in dilute solution

The PL characteristics of the polymers in THF have been measured in different solution concentrations (Figure 3.26- 3.32). The limiting concentration of polymers is given in Table 3.5. The PL intensity increases up to 0.0125 wt% of polymers then decreases except polymer PQTA. The PL intensity of polymer PQTA increases upto 0.006 wt% of polymer and shows steady after 0.006 wt%. The limiting value of the concentration is 0.0125 wt % for all polymers except PQTA polymer which is 0.006 wt%. The result indicates that the PL intensity increases with decrease in solution concentration. This is due to fluorescence quenching at higher polymer solution concentration. This can be explained by classical concentration quenching effects due to nonemissive excimer complexes most easily formed in the more planar conjugated structure at higher concentrations [22].

Table3.5: Limiting concentration of polymers

Polymer	Limiting concentration (wt %)
PHTA	0.0125
POTA	0.0125
PDTA	0.0125
PDDTA	0.0125
PPDPTA	0.0125
PPDCHTA	0.0125
PQTA	0.006

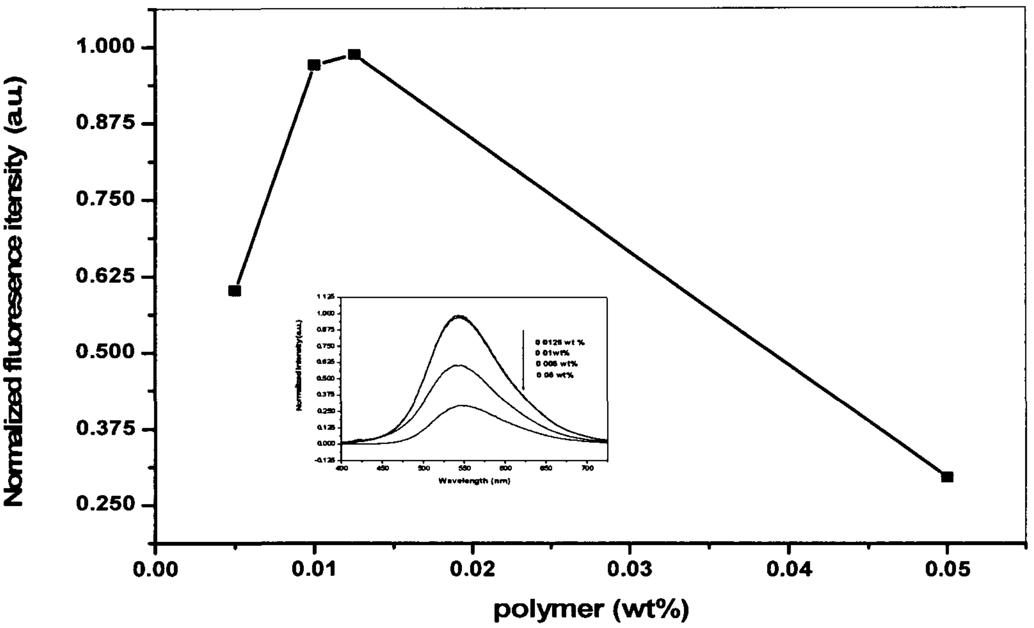


Figure 3.26: Normalized PL intensity of polymer PHTA in different concentration. The inset shows the PL intensity increasing with dilute solution up to a certain level

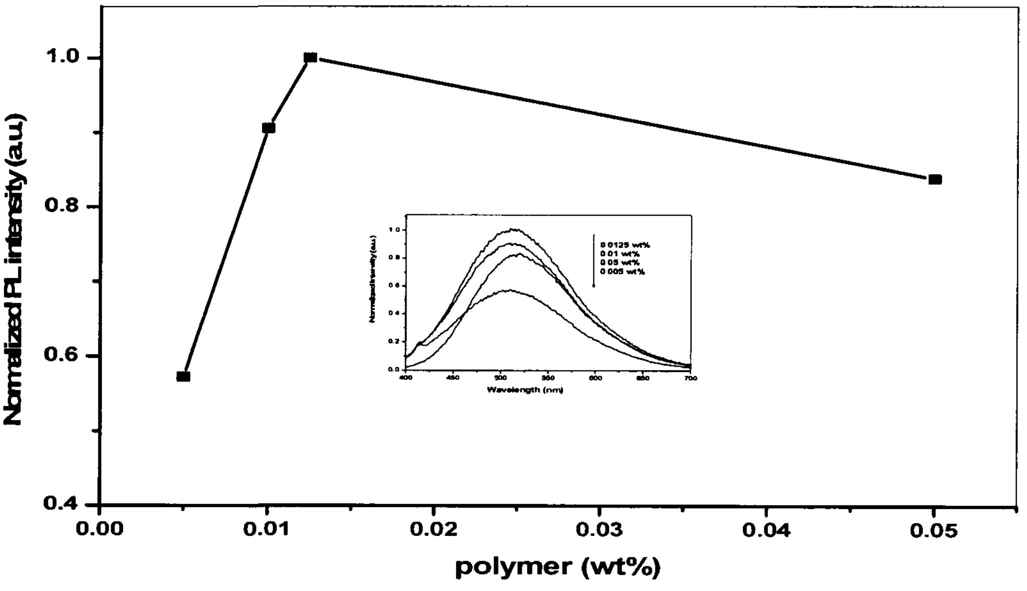


Figure 3.27: Normalized PL intensity of polymer POTA in different concentration. The inset shows the PL intensity increasing with dilute solution up to a certain level.

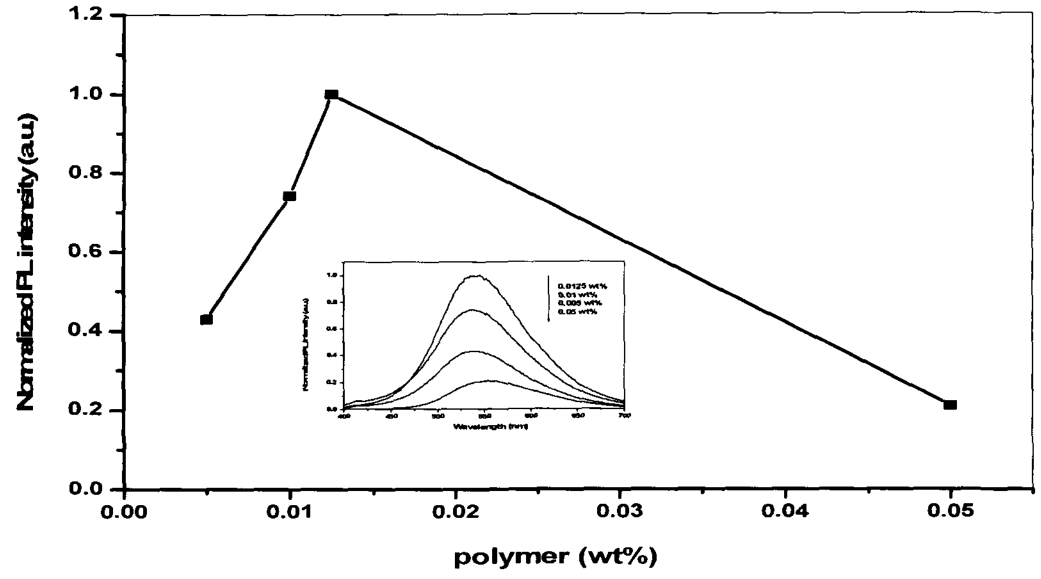


Figure 3.28: Normalized PL intensity of polymer PDTA in different concentration. The inset shows the PL intensity increasing with dilute solution up to a certain level.

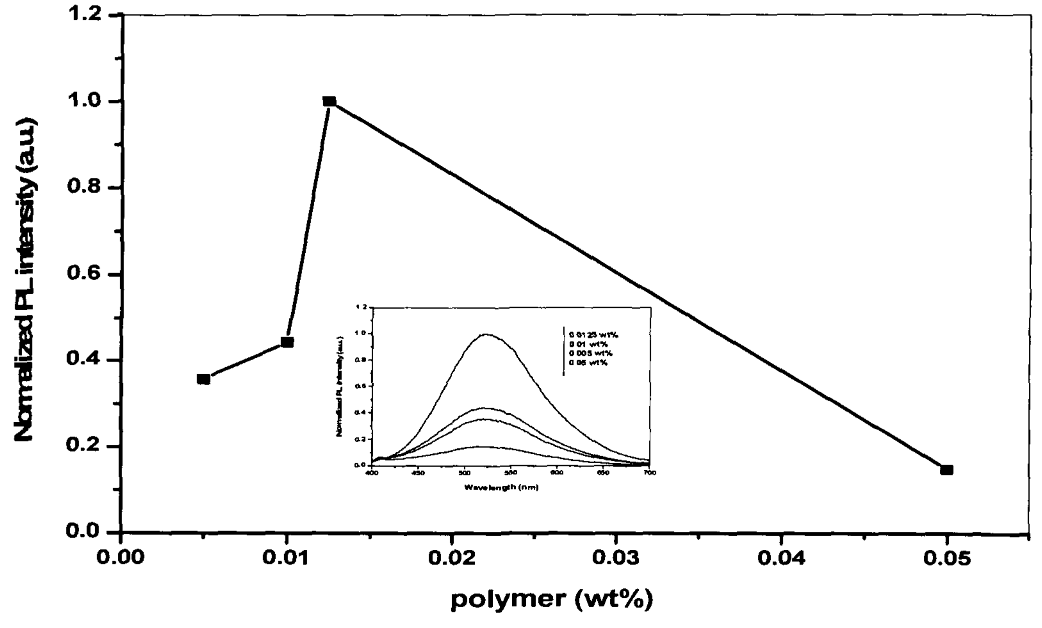


Figure 3.29: Normalized PL intensity of polymer PDDTA in different concentration. The inset shows the PL intensity increasing with dilute solution up to a certain level.

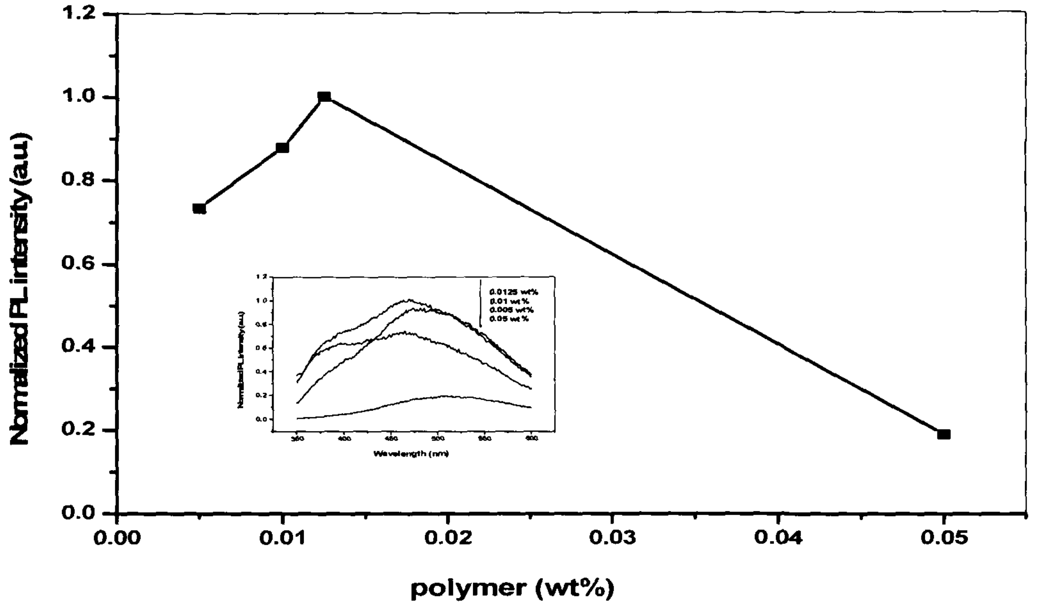


Figure 3.30: Normalized PL intensity of polymer PPDPTA in different concentration. The inset shows the PL intensity increasing with dilute solution up to a certain level.

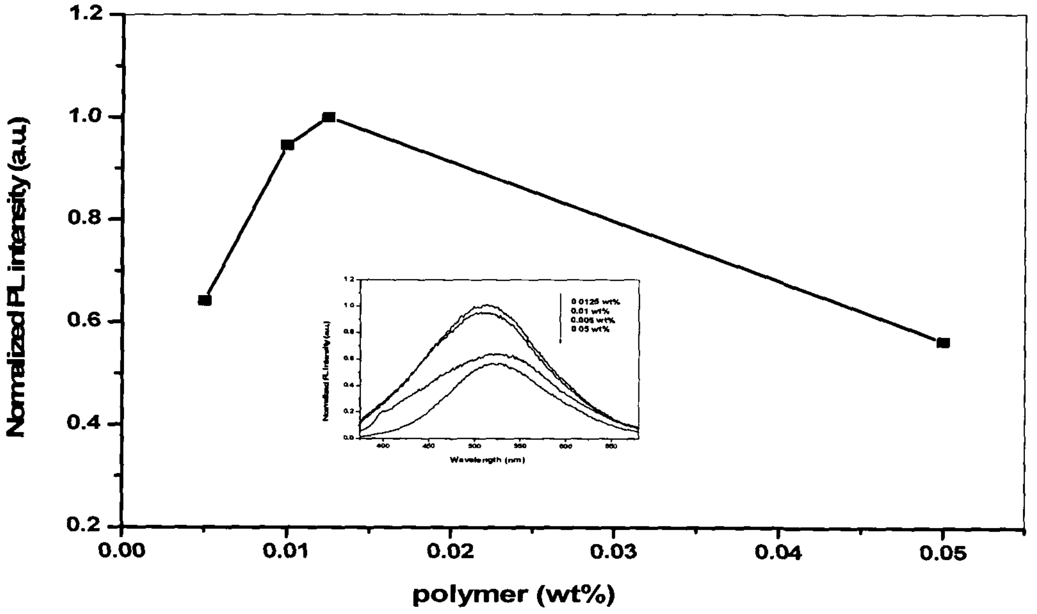


Figure 3.31: Normalized PL intensity of polymer PPDCHTA in different concentration. The inset shows the PL intensity increasing with dilute solution up to a certain level.

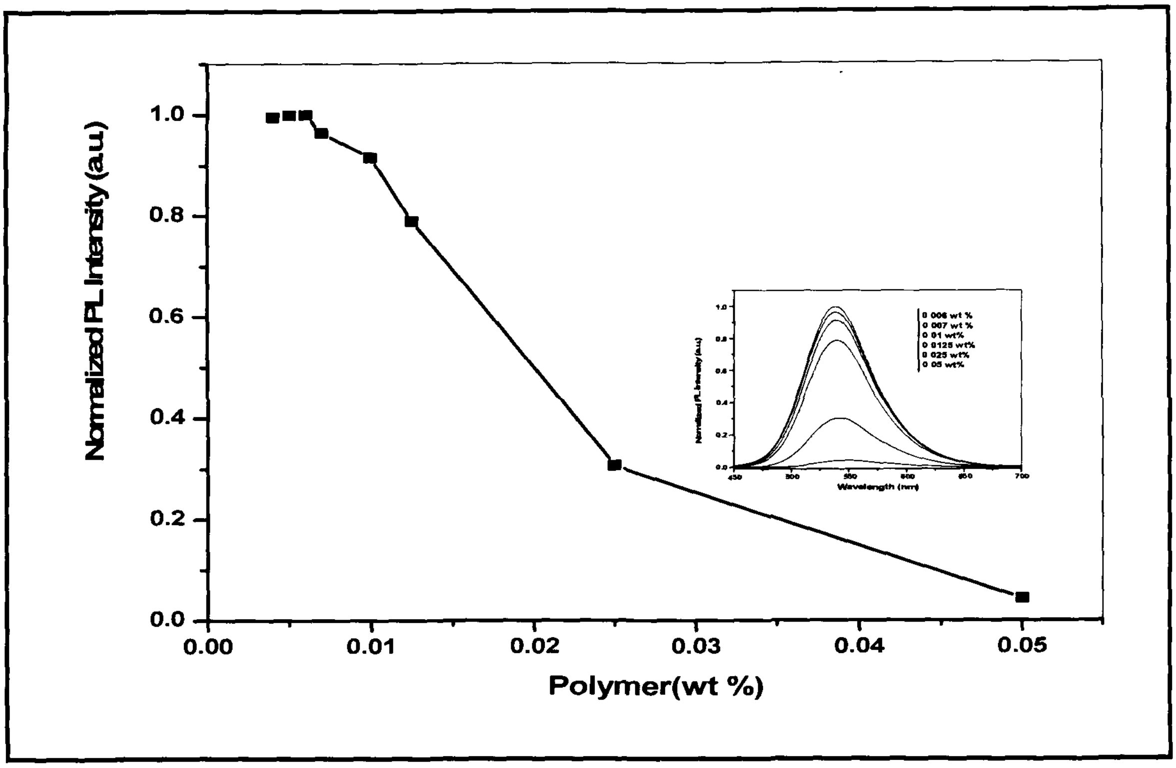


Figure 3.32: Normalized PL intensity of polymer PQTA in different concentration. The inset shows the PL intensity increasing with dilute solution up to a certain level.

3.3.2.3 Photoluminescence in solid state

The PL in solid state of polymers is measured by preparing the polymer film on the glass substrate. The PL emission of polymers films in solid state are broad and intensity is low (Figure 3.33). The fluorescence emission maximum of polymers in solution and solid state is summarized in Table 3.6. The polymers in solid state show emission band at 553- 564 nm. The fluorescence of polymer in solid state shows red shift in comparison to their solution. The low fluorescence efficiency of polymers in solid state is attributed to π- stacking [33].

Table 3.6: *PL emission maxima of polymers in solution and solid*

Polymer	Excited at (nm)	Emission maximum of polymer (0.05 wt%) in THF solution (nm)	Emission maximum of polymer in thin film (nm)
PHTA	370	547	564
POTA	363	533	549

PDTA	363	545	553
PDDTA	359	543	548
PPDPTA	315	542	557
PPDCHTA	307	530	562
PQTA	392	540	563

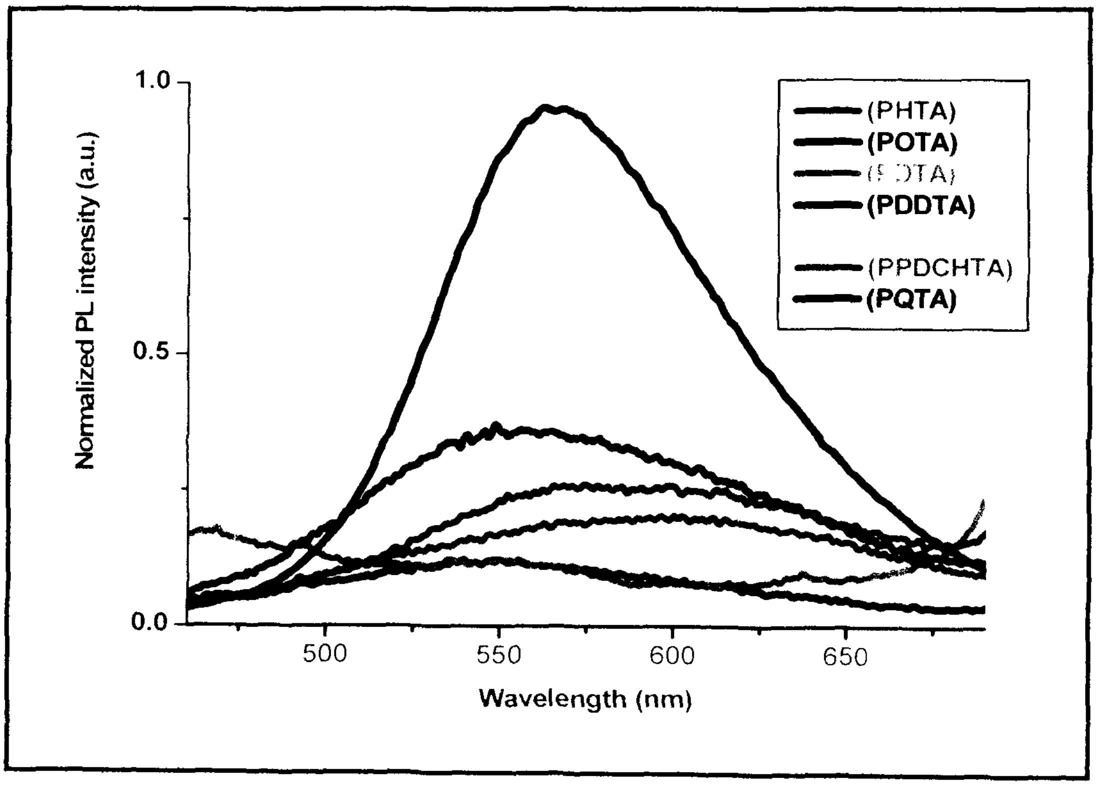


Figure 3.33: Normalized PL spectra of polymers excited at 350 nm in thin film

3.3.3 Quantum yield of polymers

The maximum fluorescence of polymers intensity value at 0.0125 wt % in THF was taken for quantum yield calculation. The standard fluorescent sample, Rhodamine B dye was chosen because it emits in a similar region to these polymers. The fluorescence spectrum of Rhodamine B dye at 0.0125 wt% in THF solvent was recorded. The quantum yield value of polymers was calculated using the standard sample Rhodamine B dye. The quantum yield of a polymer sample in solution ϕ_s relative to a reference sample of known quantum yield ϕ_r may be related by eqn. (3.2) [80]:

$$\phi_s = \phi_r (A_r/A_s \times I_s/I_r) \qquad (3.2)$$

Where A_s and A_r are the absorbance of the sample and reference solutions respectively at the excitation wavelength; I_r and I_s are the corresponding relative integrated fluorescence intensities.

The fluorescence quantum yield of polymers is measured and compared with Rhodamine B dye (Table 3.7). The relative quantum yield of polymers is found to be 0.237-2.481 with respect to Rhodamine B dye at 0.0125 wt %. The quantum yield of PQTA is two times higher than the Rhodamine B dye. The presence of quinoline moiety in the polythiophene backbone is responsible for high fluorescence efficiency of PQTA. In PPDPTA and PPDCHTA polymers, possibly inter- chain dispersive interaction exhibits enhanced aggregation which reduces the fluorescence efficiency [81-82].

Table 3.7: Relative fluorescence quantum yield of polymers

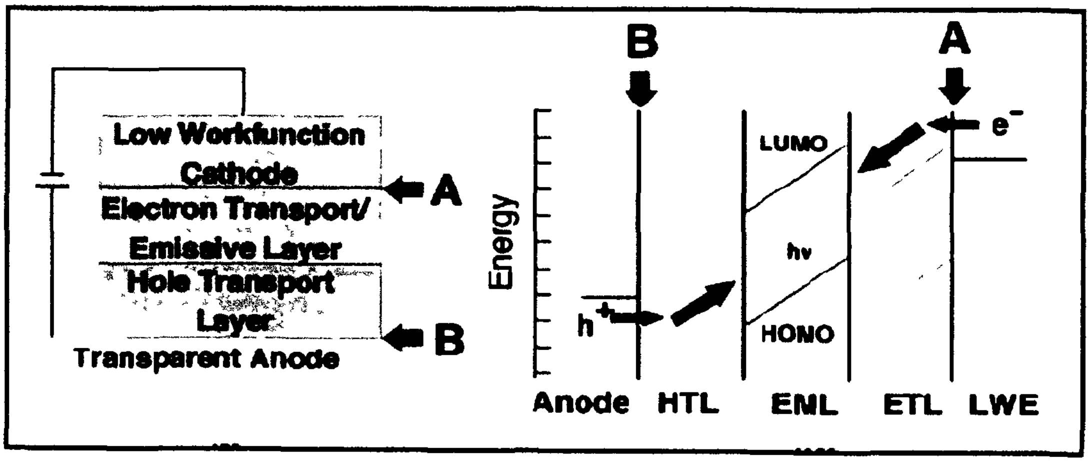
Polymer	Fluorescence Quantum yield of polymer at 0.0125 wt% (relative)*
PHTA	0.665
POTA	0.914
PDTA	0.839
PDDTA	0.586
PPDPTA	0.26
PPDCHTA	0.237
PQTA	2.481

* Relative quantum yield with respect to Rhodamine B dye (fluorescence quantum yield taken as 1)

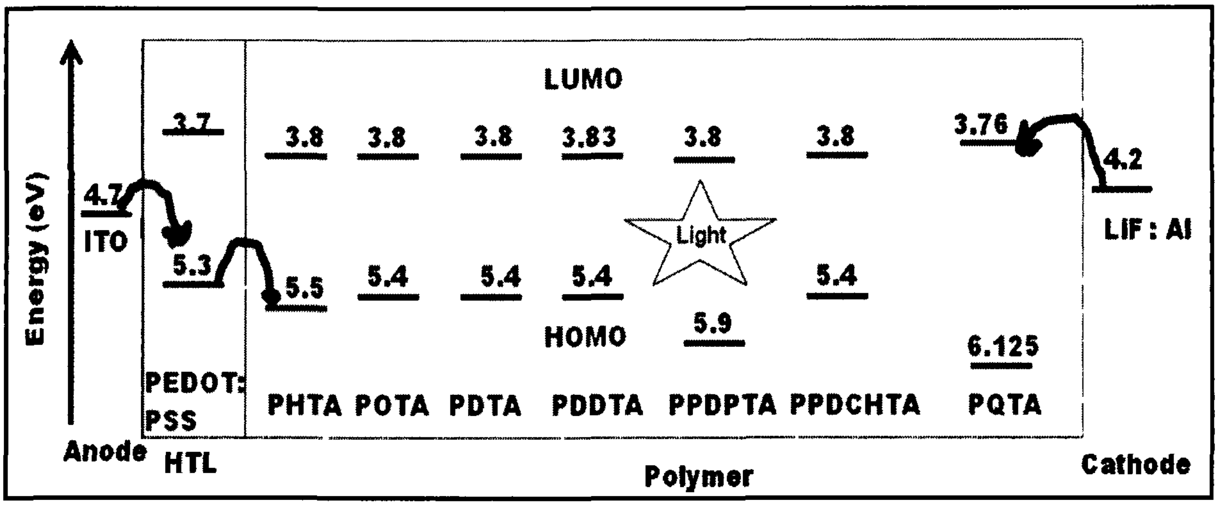
3.3.4 Electroluminescence properties of polymers

3.3.4.1 Electroluminescence of polymers

The LED device was fabricated with the configuration ITO/PEDOT:PSS/polymer/LiF/Al. PEDOT: PSS was used as a hole transporting layer. The electron injection was helped by using a thin 1 nm LiF layer followed by a thick layer of Al. By applying voltage across the thin film of polymer, h+ and e- charges from electrodes start to move in opposite directions to each other and when they meet each other in polymer chain, they produce an excited state, which subsequently emit radiation i.e. light (Scheme 3.1-3.2). Fig. 3.34 shows the EL spectra of polymers. The polymers exhibit yellowish colour in EL at 15V. The EL maxima of POTA and PQTA are 536 and 540nm respectively, which are similar to their corresponding photoluminescence maxima. Light emission of the EL device was too weak to be measured for PHTA, PDTA, and PDDTA and no emission was observed for PPDPTA and PPDCHTA. This may be due to the weak film forming capability and low intensity of PL in solid state of oligomer compound. This results in poor interaction of interfaces for charge transport of carrier in LED device [83].



Scheme 3.1: EL mechanism



Scheme 3.2: Energy level diagram of polymers

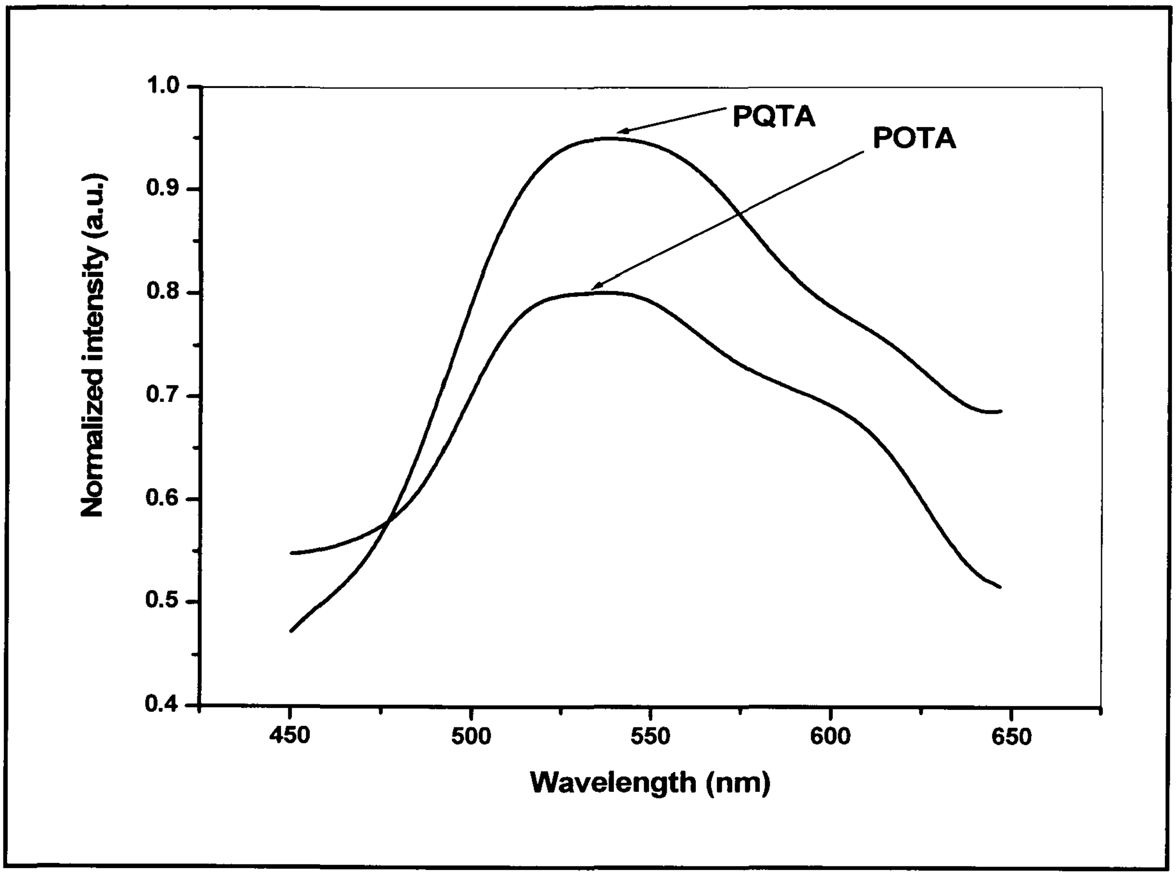


Figure 3.34: EL spectra of polymers at 15 V

3.3.4.2 Current - Voltage characteristic of device

Figure 3.35-3.41 shows the current voltage characteristic of the devices. The turn on voltage of the devices is in the range of 5.4V to 7V for current injection (Table 3.8). The turn on voltage is low (5.4 V) for POTA and is high (7 V) for PPDPTA. The current density i.e. charge carrier capacity of POTA and PQTA is higher than the other polymers. This is effective for light emission in LED device.

Table 3.8: Turn on voltage of polymers

Polymer	Turn on voltage for current injection(V)
PHTA	5.5
POTA	5.4
PDTA	6.0
PDDTA	6.1
PPDPTA	7.0
PPDCHTA	6.0
PQTA	5.5

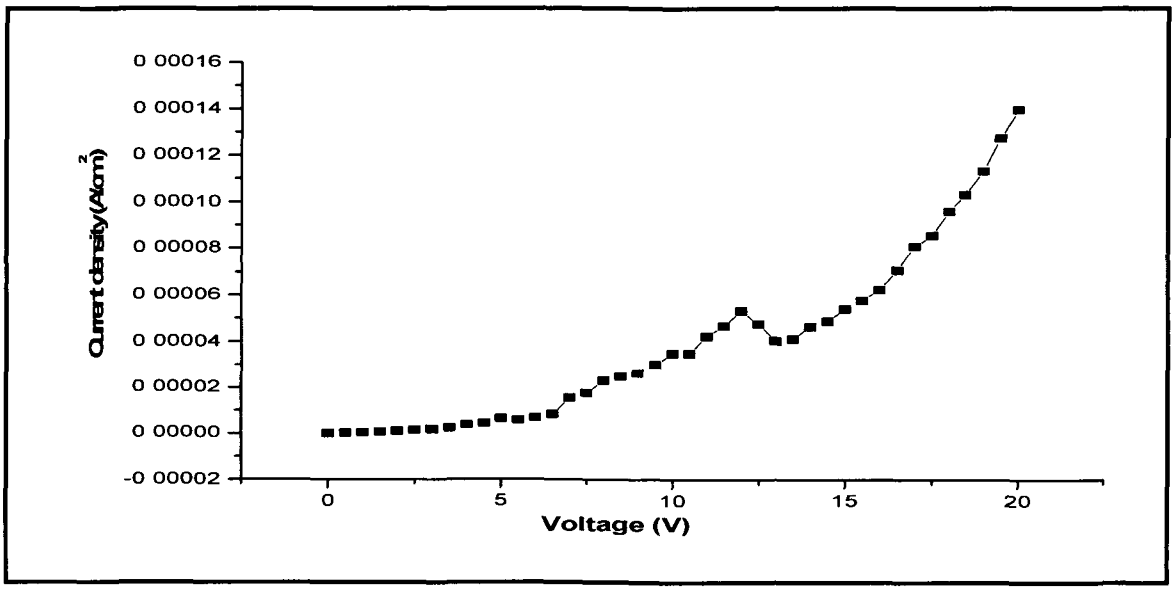


Figure 3.35: I-V characteristic of polymer PHTA

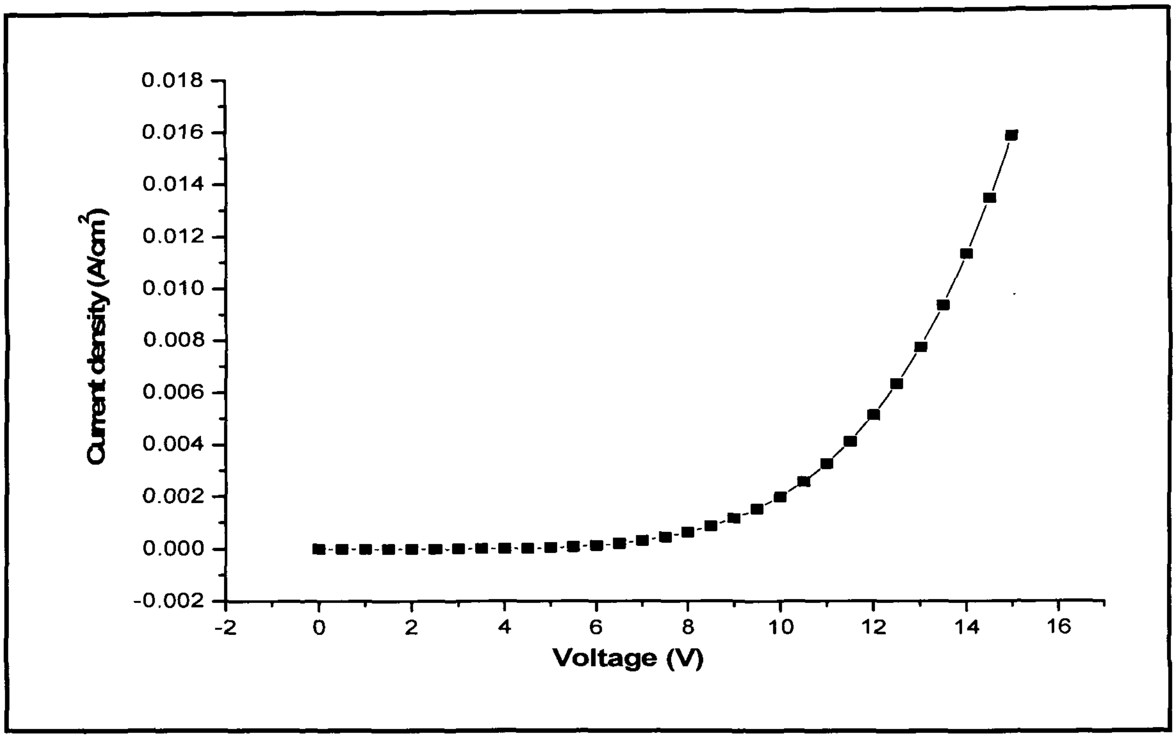


Figure 3.36: I-V characteristic of polymer POTA

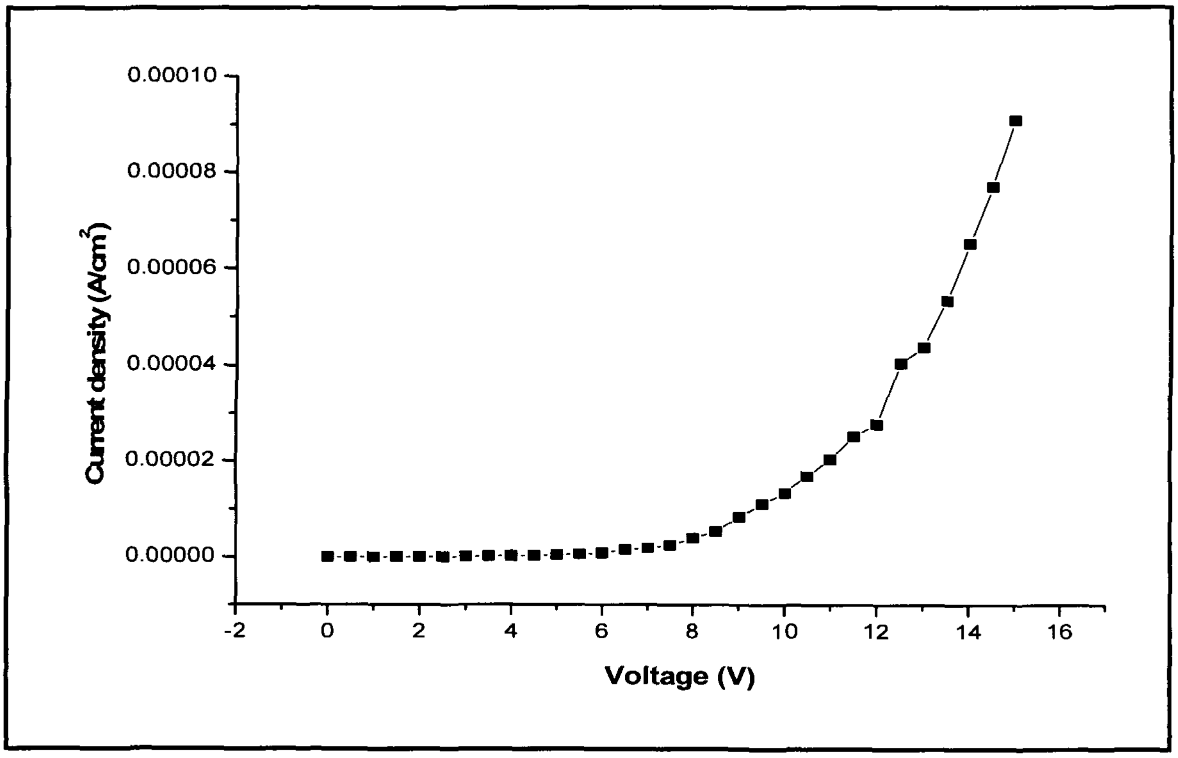


Figure 3.37: I-V characteristic of polymer PDTA

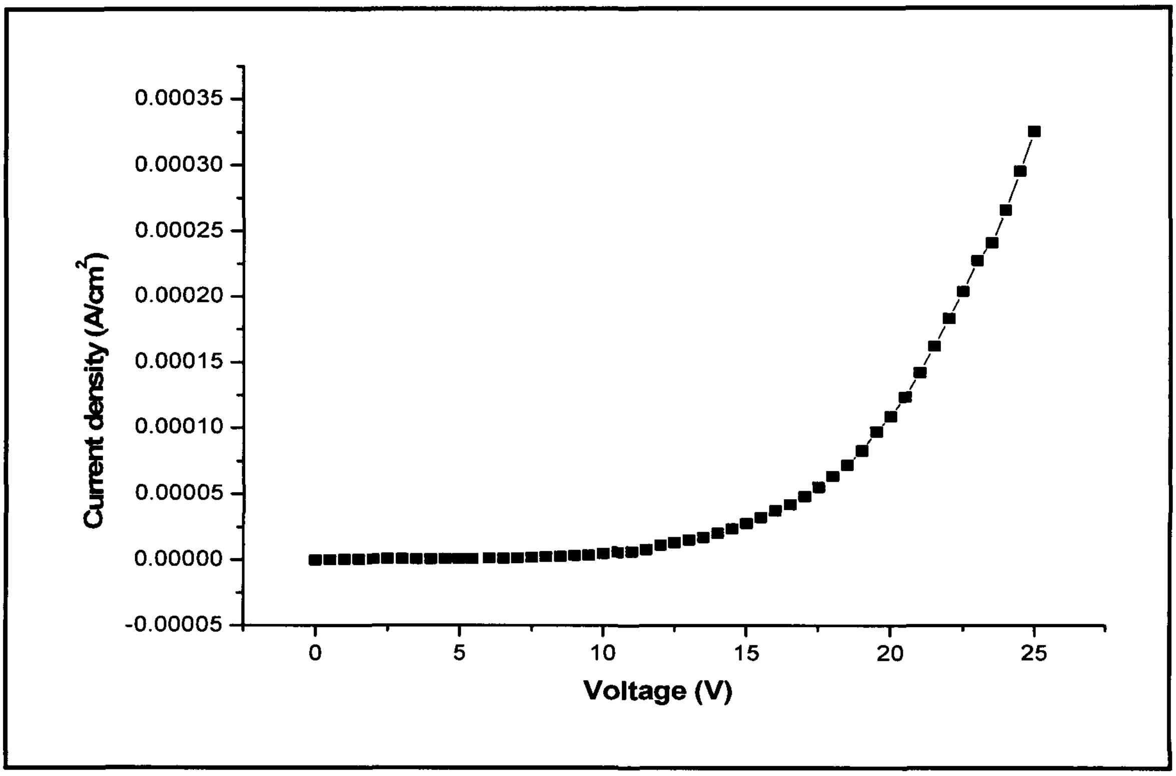


Figure 3.38: I-V characteristic of polymer PDDTA

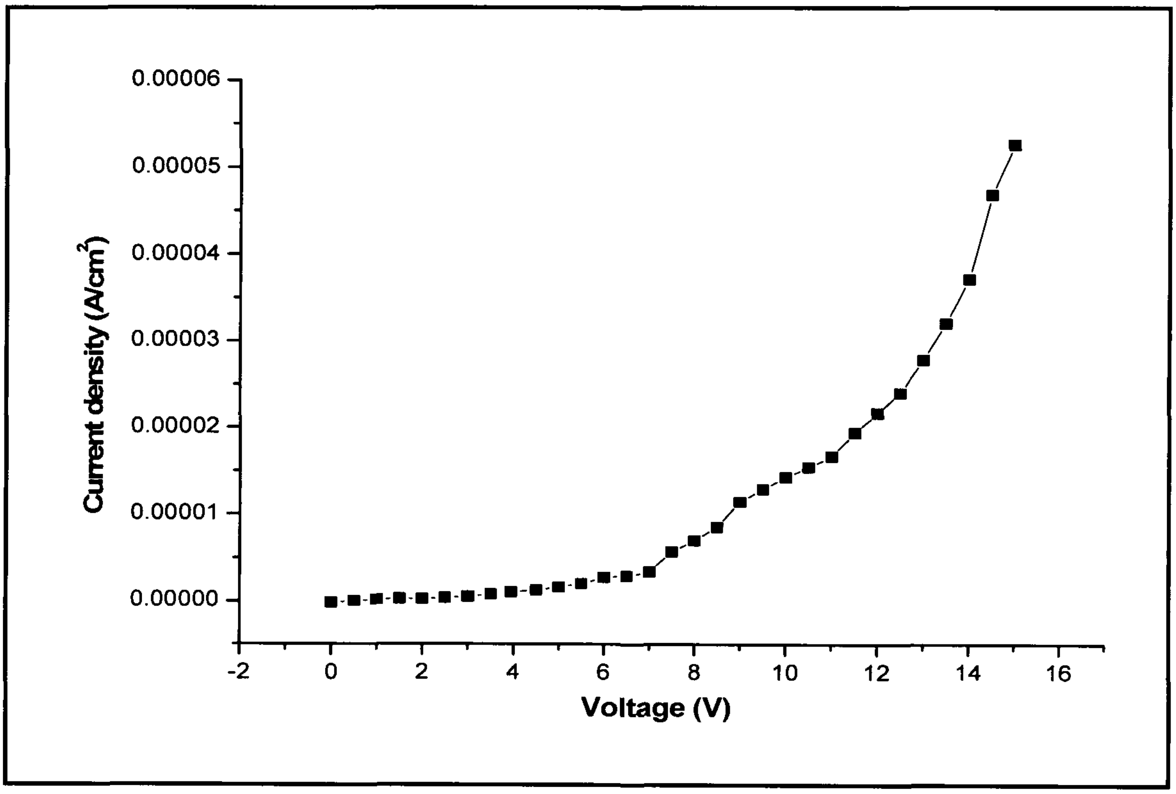


Figure 3.39: I-V characteristic of polymer PPDPTA

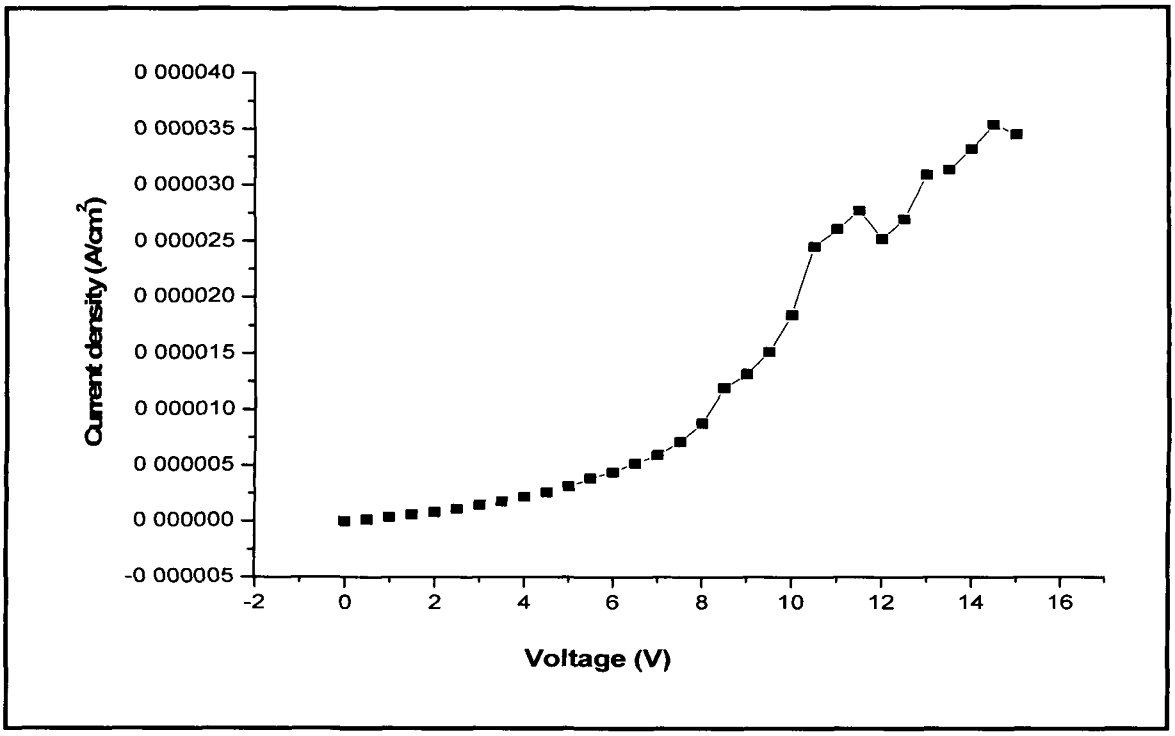


Figure 3.40: I-V characteristic of polymer PPDCHTA

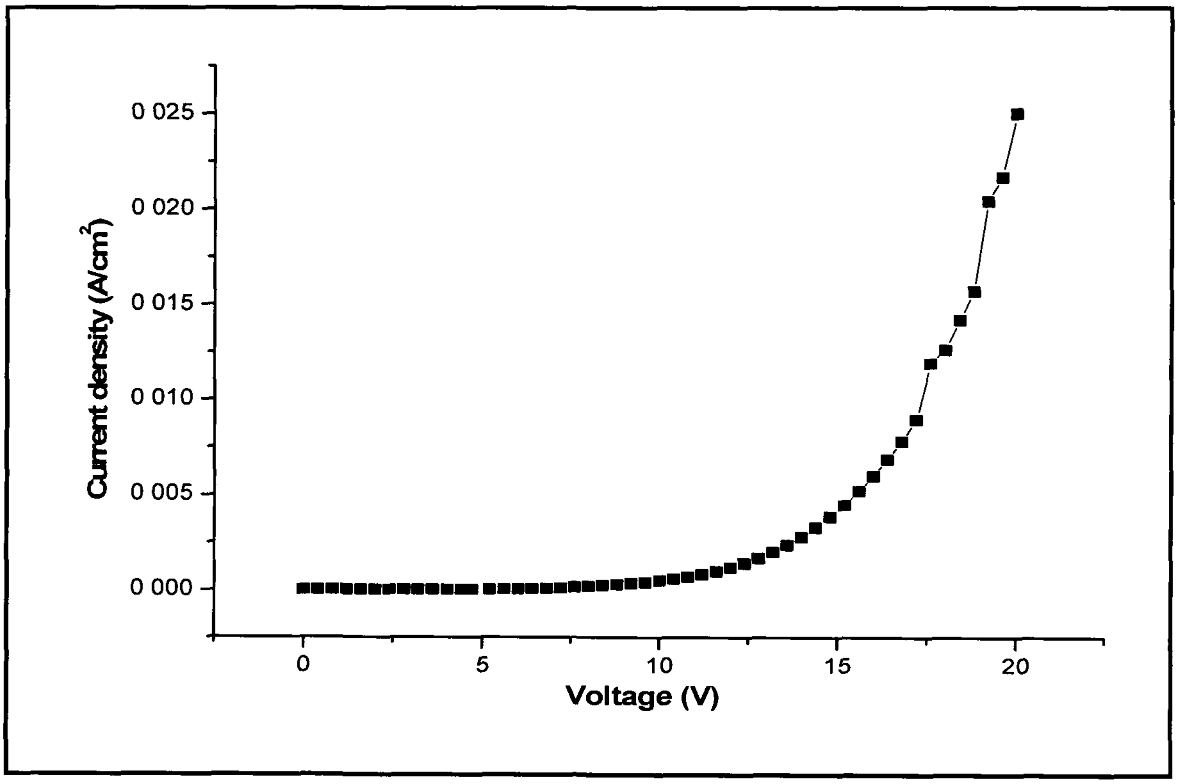
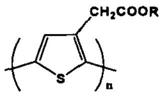
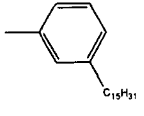
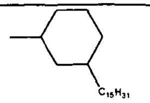
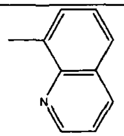


Figure 3.41: I-V characteristic of polymer PQTA

3.4 Summery of properties in table

All the properties of polymers are summarized in Table 3.9.

Table 3.9: All the properties of polymers

Polymer 	**Side chain moiety (R)**	**Mn (g/mol)**	**(DP)**	**Solubility (%)**	**Tg (°C)**	**λ_{max}^{abs} (nm)**	**λ_{max}^{abs} (nm)**	**PL (nm)**	**PL (nm)**	**E_{ox} (V)**	**E_{red} (V)**	**HOMO (eV)**	**LUMO (eV)**	**E_g^{elec} (eV)**	**E_g^{opt} (eV)**	**ϕs**	**EL (nm)**	**Turn on voltage (V)**
PHTA	**$-C_6H_{13}$**	**5372**	**24**	**24**	**94**	**255**	**370**	**547**	**564**	**2.45**	**-2.1**	**5.5**	**3.8**	**1.7**	**2.36**	**0.665**	**-**	**5.5**
POTA	**$-C_8H_{17}$**	**3338**	**13**	**27**	**-**	**254**	**363**	**533**	**549**	**2.45**	**-2.25**	**5.4**	**3.8**	**1.6**	**2.36**	**0.914**	**536**	**5.4**
PDTA	**$-C_{10}H_{21}$**	**1589**	**6**	**36**	**70**	**254**	**363**	**545**	**553**	**2.45**	**-2.0**	**5.4**	**3.8**	**1.6**	**2.29**	**0.839**	**-**	**6.0**
PDDTA	**$-C_{12}H_{25}$**	**8418**	**27**	**37**	**69**	**254**	**359**	**543**	**548**	**2.45**	**-1.2**	**5.4**	**3.83**	**1.57**	**2.38**	**0.586**	**-**	**6.1**
PPDPTA		**6852**	**16**	**87**	**63**	**272**	**315**	**542**	**557**	**2.45**	**-1.85**	**5.9**	**3.8**	**2.1**	**2.45**	**0.26**	**-**	**7.0**
PPDCHTA		**3154**	**7**	**90**	**67**	**253**	**307**	**537**	**562**	**2.45**	**-1.8**	**5.4**	**3.8**	**1.6**	**2.31**	**0.237**	**-**	**6.0**
PQTA		**22260**	**83**	**15**	**154**	**256**	**392**	**540**	**563**	**2.47**	**-0.84**	**6.125**	**3.76**	**2.36**	**2.47**	**2.481**	**540**	**5.5**

3.5 Conclusions

Cyclic voltammetry study indicates that the oxidation potentials of polymers are high (2.45V) and there is no significant change with substituents. At the same time, change in side chain plays a significance role for altering the reduction potential of polymers. The reduction potential of the polymers is in the range of -0.84V to -2.25 V. It is observed that quinolinyl containing polymer PQTA have the least reduction potential amongst ester substituted polymers due to large molecular weight compared to others. All the polymers seem to be stable under cyclic oxidation and reduction potential (up to 10 cycles). The phenyl and quinolinyl containing polymers have higher band gap and HOMO energy level than alkyl and cyclohexyl derivative polymers. LUMO energy level is same for all polymers. The electrochemical band gap of the polymers is in the range of 1.57 -2.365 eV and the value is lower than the optical band gap.

The fluorescence emission maximum of the polymers is found to be in the range of 530nm for PPDCHTA to 547 nm for PHTA. The light emission is in the yellow-green region. Stokes shifts of the polymers are in the range of 148 nm for PQTA to 230nm for PPDCHTA. The PL intensity increases with increasing the degree of polymerization. It is found to be high for PQTA and low for polymer PPDCHTA. It is consistent with their degree of polymerization. The enhanced fluorescence efficiency of polymers is achieved at the cost of their solubility. Here, ester spacer weakens the direct effect of side chain on polythiophene backbone. Also, PL intensity increases with dilution and the limiting value of the concentration is 0.0125 wt % for all polymers except PQTA which is 0.006 wt%. The PL intensities increase with dilution which indicates fluorescence quenching at higher polymer solution concentration. Polymers in solid state show emission band at 553- 564 nm. The fluorescence of polymers in solid state shows red shift in comparison to their solution. The relative fluorescence quantum yield of polymers in THF solution is in the range of 0.237 to 2.481 with respect to Rhodamine B dye. The high fluorescence quantum yield of PQTA polymer is due to the presence of quinoline moiety in the polythiophene backbone.

The polymers show yellowish colour in EL spectra. The turn on voltage of devices is in the range of 5.4V to 7V for current injection. Turn on voltage of POTA is low (5.4 V) and is high (7V) for PPDPTA. The emission maxima of EL devices based on POTA and PQTA are 536 and 540nm respectively, which are similar to their corresponding photoluminescence maximum. Light emission of the EL device was too weak to be measured for PHTA, PDTA, and PDDTA and no emission was observed for PPDPTA and PPDCHTA. This may be due to the weak film forming capability and low intensity of PL in solid state of oligomer compound. This results in poor interaction of interfaces for charge transport of carrier in LED device.

References

1. T. A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds (Eds), Hand book of conducting polymers, Marcel Dekker, New York, 2nd *edition*, **(1998).**
2. G. Hadziioannou and G. G. Malliaras (Eds), Semiconducting Polymer: Chemistry, Physics and Engineering, Wiley- VCH, Germany, 2nd *edition, Volume 1 &2*, **(2007).**
3. K. Mullen, U. Scherf (Eds), Organic Light –Emitting Devices, Wiley- VCH, Germany, **(2006).**
4. A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz, and A. B. Holmes, *Chem. Rev., 109* **(2009)** 897.
5. A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem. Int. Ed., 37* **(1998)** 402.
6. R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dossantos, J. L. Bredas, M. Logdlund & W. R. Salaneck, *Nature, 397* **(1999)** 121.
7. L. S. Hung and C. H. Chen, *Mater. Sci. Eng. R, 39* **(2002)** 143.
8. I. D. Rees, K. L. Robinson, A. B. Holmes, C. R. Towns, and R. O'Dell, *MRS Bull., June* **(2002)** 451.
9. A. Misra, L. Kumar, P. Kumar, S. K. Dhawan, M. N. Kamalasanan, S. Chandra, *Ind. J. Pure and Appl. Phys., 42* **(2004)** 793.
10. T. Y. Luh, S. Basu, R. M. Chen, *Cur. Sci., 78* **(2000)** 1352.
11. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks. K. Mackay. R. H. Friend. P. L. Burns. A. B. Holmes, *Nature, 347* **(1990)** 539.
12. G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, A. J. Hegger, *Nature, 357* **(1992)** 477.
13. M. C. Choi, Y. Kim, C. S. Ha, *Prog. Polym. Sci., 33* **(2008)** 581.
14. U. Mitschke, P. Bauerle, *J. Mater. Chem., 10* **(2000)** 1471.
15. L. Akcelrud, *Prog. Polym. Sci., 28* **(2003)** 875.
16. H. E. Katz, *J. Mater. Chem., 7* **(1997)** 369.
17. A. J. Heeger, *Solid State Comm., 107* **(1998)** 673.
18. S. Maiti, *Ind. J. Chem., 33A* **(1994)** 524.
19. T. B. Singh, N. S. Sariciftci, *Annu. Rev. Mater. Res., 36* **(2006)** 199.
20. J. Roncali, *Chem. Rev., 92* **(1992)** 711.
21. R. D. McCullough, *Adv. Mater., 10* **(1998)** 93.
22. H. S. O. Chan, S. C. Ng, *Prog. Polym. Sci., 23* **(1998)** 1167.
23. T. Yamamoto, *Macromol. Rapid Commun., 23* **(2002)** 583.
24. I. F. Perepichka, D. F. Perepichka, H. Meng, F. Wudl, *Adv. Mater., 17* **(2005)** 2281.
25. G. Barbella, M. Melucci, G. Sotgiu, Adv. *Mater., 17* **(2005)** 1581.
26. T. Torroba, M. V. Garcia, *Angrew. Chem. Int. Ed., 45* **(2006)** 8092.
27. A. R. Murphy, J. M. J. Frechet, *Chem. Rev., 107* **(2007)** 1066.
28. A. Mishra, C. Q. Ma, P. Bauerle, *Chem. Rev., 109* **(2009)** 1141.
29. D. Fichou (Ed), *Handbook of Oligo and Polythiophenes*, Wiley –VCH, Germany, **(1999).**
30. D. Fichou, *J. Mater. Chem., 10* **(2000)** 571.
31. M. Leclerc, H. A. Ho, *Syn. Lett., 2* **(2004)** 380.

32. W. Porzio, S. Destri, M. Pasini, A. Bolognesi, A. Angiulli, P. Digianvincenzo, D. Natali, M. Sampietro, M. Caironi, L. Fumagalli, S. Ferrari, E. Peron, F. Perissinotti, *Mater. Sci. Eng. C: Bio. Supra. Sys., 26* **(2006)** 996.
33. B. Xu, S. Holdcroft, *Macromolecules, 26* **(1993)** 4457.
34. R. E. Gill, G. G. Malliaras, J. Wildeman, G. Hadziioannou, *Adv. Mater., 6* **(1994)** 132.
35. N. C. Greenham, I. D. W. Samuel, G. R. Hayes, R. T. Phillips, Y. A. R. R. Kessener, S. C. Moratti, A. B. Holmes, R. H. Friend, *Chem. Phys. Lett., 241* **(1995)** 89.
36. T. Kodaira, A. Watanable, M. Fujitsuku, O. Ito, *Polymer, 39* **(1997)** 3793.
37. M. Leclerc, K. Faid, *Adv. Mater., 9* **(1997)** 1087.
38. W. A. Goedel, N. S. Somanathan, V. Enkelmann, G. Wegner, *Makromol. Chem., 193* **(1992)** 1195.
39. M. Theandher, O. Inganas, W. Mammo, T. Olinga, M. Svensson, M. R. Andersson, *J. Phys. Chem. B, 103* **(1999)** 7771.
40. N. Somanathan, S. Radhakrishnan, *Int. J. Mod. Phys. B, 19* **(2005)** 4645.
41. X. Xu, L. Xu, *Polymer, 41* **(2000)** 9147.
42. X. Zhao, X. Hu, L. H. Gan, *Polym. Adv. Technol., 16* **(2005)** 370.
43. M. R. Anderson, M. Beggren, O. Inganas, G. Gustafsson, *Macromolecules, 28* **(1995)** 7525.
44. M. R.Anderson, O. Thomas, W. Mammo, M. Svensson, M. Theander, O. Inganas, *J. Mater. Chem., 9* **(1999)** 1933.
45. G. Daoust, M. Leclerc, *Macromolecules, 24* **(1991)** 455.
46. M. Pomerantz, H. Yang, Y. Cheng, *Macromolecules, 28* **(1995)** 5706.
47. M. Pomerantz, Y. Chang. R. K. Kasim, R. L. Elsenbaumer, *J. Mater. Chem., 9* **(1999)** 2155.
48. M. Lanzi, P. C. Bizzarri, L. Paganin, G. Cesari, *Eur. Polym. J., 43* **(2007)** 72.
49. A. R. Murphy, J. Liu, C. Luscombe, D. Kavulak, J. M. Frechet, R. J. Kline, M. D. McGehee, *Chem. Mater.,17* **(2005)** 4892.
50. T. K. Kang, J. Y. Kim, K. J. Kim, C. Lee, S. B. Rhee, *Synth. Met., 69* **(1995)** 377.
51. C. Lee, K. J. Kim, S. B. Rhee, *Synth. Met., 69* **(1995)** 295.
52. S. Lee, S. I. Hong, C. Lee, S. B. Rhee, T. J. Kang, *Mol. Cryst. Liq. Cryst., 295* **(1997)** 19.
53. A. Bolognesi, C. Botta, Z. Geng, C. Flores, L. Denti, *Synth. Met., 71* **(1995)** 2191.
54. T. Johansson, W. Mammo, M. Seensson, M. A. Andersson, O. Inganas, *J. Mater. Chem., 13* **(2003)** 1316.
55. M. Skompska, A. Szkurlat, *Electrochim. Acta, 46* **(2001)** 4007.
56. A. R. Hillman, I. Efimov, M. Skompska, *Faraday Discuss.,121* **(2002)** 423.
57. J. Kalinoswki, *J. Phys. D:Appl. Phys., 32* **(1999)** R179.
58. A. Pron, P. Rannou, *Prog. Polym Sci., 27* **(2002)** 135.
59. J. Li, C. Ma, J. Tang. C. S. Lee, S. Lee, *Chem. Mater., 17* **(2005)** 615.
60. J. L. Bredas, D. Beljonne, V. Coropceanu, J. Cornil, *Chem. Rev., 104* **(2004)** 4971.
61. A. P. Kulkarni, C. J. Tonzola, A. Babel, S. A. Jenekhe, *Chem. Mater., 16* **(2004)** 4556.
62. D. Dini, *Chem. Mater., 17* **(2005)** 1933.
63. J. Kalinoswki, *Opt. Mater., 30* **(2008)** 792.
64. J. S. Kim, M. Granstrom, R. H. Friend, N. Johansson, W. R. Salaneck, R. Dair, W. J. Feast, F. Cacialli, *J. Appl. Phys., 84* **(1998)** 6859.
65. A. J. Campbell, D. D. C. Bradley, H. Antoniadis, M. Inbasekaran, W. S. W. Wu, E. P. Woo, *Appl. Phys. Lett., 76* **(2000)** 1734.
66. S. A. Carter, M. Angelopoulos, S. Karg, P. J. Brock, J. C. Scott, *Appl. Phys. Lett.,70* **(1997)** 2067.

67. J. S. Kim, R. H. Friend, F. Cacialli, *Appl. Phys. Lett., 74* **(1999)** 3084.
68. B. Ballarin, A. F. Morgera, D. Frascaro, S. Marazzita, C. Piana, L. Setti, *Synth. Met., 146* **(2004)** 201.
69. L. S. Hung, C. W. Tang, M. G. Mason, *Appl. Phys. Lett., 70* **(1997)** 152.
70. Y. D. Jin, X. B. Ding, J. Reynaert, V. I. Arkhipov, G. Borghs, P. L. Heremans, M. V. D. Auweraer, *Org. Electro., 5* **(2004)** 271.
71. Y. E. Kim, H. Park, J. J. Kim, *Appl. Phys. Lett., 69* **(1996)** 599.
72. T. M. Brown, F. Cacialli, *IEE Proc.-Optoelectron., 148* **(2001)** 74.
73. K. R. Choudhury, J. H. Yoon, F. So, *Adv. Mater., 20* **(2008)** 1456.
74. D. Hohertz. J. Gao, *Adv. Mater., 20* **(2008)** 3298.
75. A. K. Agrawal, S. A. Jeneka, *Chem. Mater., 8* **(1996)** 579.
76. H. Chosrovian, S. Rentsch, D. Grebner, D. U. Dahm, E. Brickner, *Synth. Met., 60* **(1993)** 23.
77. M. Bellete, L. Mazerolle, N. Desrosier, M. Leclerc, G. Durocher, *Macromolecules, 28* **(1995)** 8587.
78. J. K. Herrema, P. F. V. Hutten, R. E. Gill, J. Wildeman, R. H. Wierringa, G. Hadziioannou, *Macromolecules, 28* **(1995)** 8102.
79. Y. Kanemitsu, K. Suzuki, Y.Tomiuchi, Y. Shiraishi, M. Kuroda, O. Nabeta, *Synth. Met., 71* **(1995)** 2209.
80. A. P. Davey, S. Elliott, O. O'Connor, W. Blau, *J. Chem. Soc. Chem. Commun.,* **(1995)** 1433.
81. C. G. Wu, Y. C. Lin, C. E. Wu, P. H. Huang, *Polymer,46* **(2005)** 3748.
82. R. Cagnoli, A. Mucci, F. Parrenti, L. Schenetti, M. Borsari, A. Lodi, G. Ponterrini, *Polymer, 47* **(2006)** 775.
83. X. Zhang, S. A. Jenekhe, *Macromolecules, 33* **(2000)** 2069.

CHAPTER 4

Fluorescence quenching of Ester substituted ploythiophenes and their application as chemical sensor

4.1 Introduction

There is a growing interest in the design and development of chemical sensors for acids and metal ions because of their toxic effect on human health and the environment [1-2]. Inorganic acids and metals contamination arises from industrial affluent released into the water and environments [3]. Acids and metals can accumulate in the human body causing a wide variety of diseases [4]. The use of conjugated polymers (CP) as biosensor devices is a rising research field, and the detection of small quantities of biomolecules is of great importance. Areas in which detection of nucleotides is of importance are for example forensic science, medical diagnostics, and the study of mutation [5-7]. In recent years, there has been an interest in exploiting thiophene based polymers as chemical and biological sensors due to their strong fluorescence quenching [8-12]. One of the advantages with this type of sensor is the collective system response given by the series of chromophores building block in the polymer chain [13-14]. Therefore, CPs can be used as the optical platforms in highly sensitive chemical and biological sensors [15-18]. The interchain interactions of the CPs lead to formation of tight aggregates, which results in fluorescence quenching because of π-stacking between main chains of the CPs [19-20]. The fluorescence efficiency can be controlled by changing the substitution patterns on the polythiophene backbone [21-23]. Generally, fluorescence efficiency is the highest in dilute solution, where the emitting species are isolated from each other. In most cases, increasing the concentration of polymer in solution decreases efficiency of fluorescence due to concentration quenching [24]. The quenching efficiency increases with increasing tendency of the polymer to associate with the quencher in solution. This association can occur either through the formation of a nonluminescent complex between the polymer and the quencher (static quenching) or due to collisions between the photoluminescent macromolecule and the quencher (dynamic quenching). For both mechanisms, the quantitative measure of the luminescence quenching efficiency is given by the Stern-Volmer constant K_{SV} defined by [25]

$$\phi^{o}/\phi = 1 + K_{sv}[quencher] \qquad (4.1)$$

Where ϕ^{o} is the intensity of fluorescence in the absence of the quencher and ϕ is the intensity

---

The part of this chapter was published in **Sens. Actuators B: Chem., (2009) doi:10.1016/j.snb.2009.07.008 (article in press)** of fluorescence in the presence of the quencher and [quencher] is the concentration of quencher. The equation reveals that ϕ^0/ϕ increases in direct proportion to the concentration of the quenching moiety, and the constant K_{sv} defines the efficiency of quenching. When all the other variables are held constant, higher the K_{sv}, lower is the concentration of quencher.

This chapter includes the fluorescence quenching and application of polymers as chemical sensor. The behaviour of photoluminescence property was studied in presence of acids, metals ions, nucleotides and protein (l-proline). The polymers showed both fluorescence quenching in the presence of acids, copper, cadmium and lead metal ions and enhancement in presence of analytes such as aluminium and zinc metals ions, nucleotides and protein (l-proline). The detection limit of HCl acid, copper, lead and cadmium ions has been evaluated by optical quenching method

4.2 Experiment

Photoluminescence spectra of polymers were recorded using Hitachi F- 2500 Fluorescence spectrophotometer, by excitation of the polymer at their absorption maximum. The polymers in THF solution were treated in various acidic solutions (acetic acid, sulphuric acid, nitric acid and hydrochloric acid) at room temperature and photoluminescence response was analysed. Also, PQTA polymer in THF solution was treated in various metal ions (Al^{3+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}) , nucleotides and l-proline. The treatment was carried out in ultrasonically at room temperature for 1 hour and their photoluminescence response was recorded.

4.3 Results and Discussion

4.3.1 Fluorescence quenching at acid medium of polymers

In order to detect the fluorescence quenching behaviour of polymers, the polymers (0.0025 wt %) were treated with 0.5M 10ml HCl acids. Only quinolinyl containing polymer PQTA shows fluorescence quenching behaviour in presence of HCl and other polymers does not show any significant fluorescence quenching in presence of HCl (Figure 4.2-4.6). All the polymers have three different groups: one group is thiophene, second group is ester, and third group is alkyl for PHTA, POTA, PDTA, PDDTA polymers, pentadecyl phenyl for PPDPTA polymer, pentadecyl cyclohexyl for PPDCHTA polymer and quinolinyl for PQTA polymer.

The ester group does not serve as quenching site of the excited state in poly (3-alkyl ester thiophene)s (PAET)[26]. Therefore, it is evident that quinolinyl moiety serves as the quenching site for PQTA polymer (Figure 4.1).

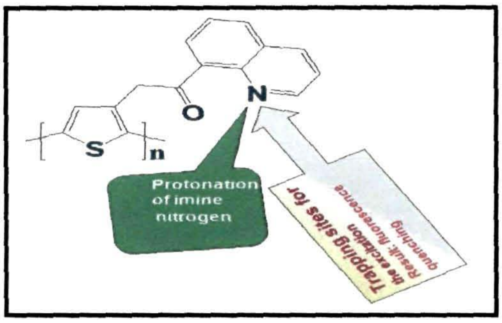


Figure 4.1: Fluorescence quenching of PQTA polymer

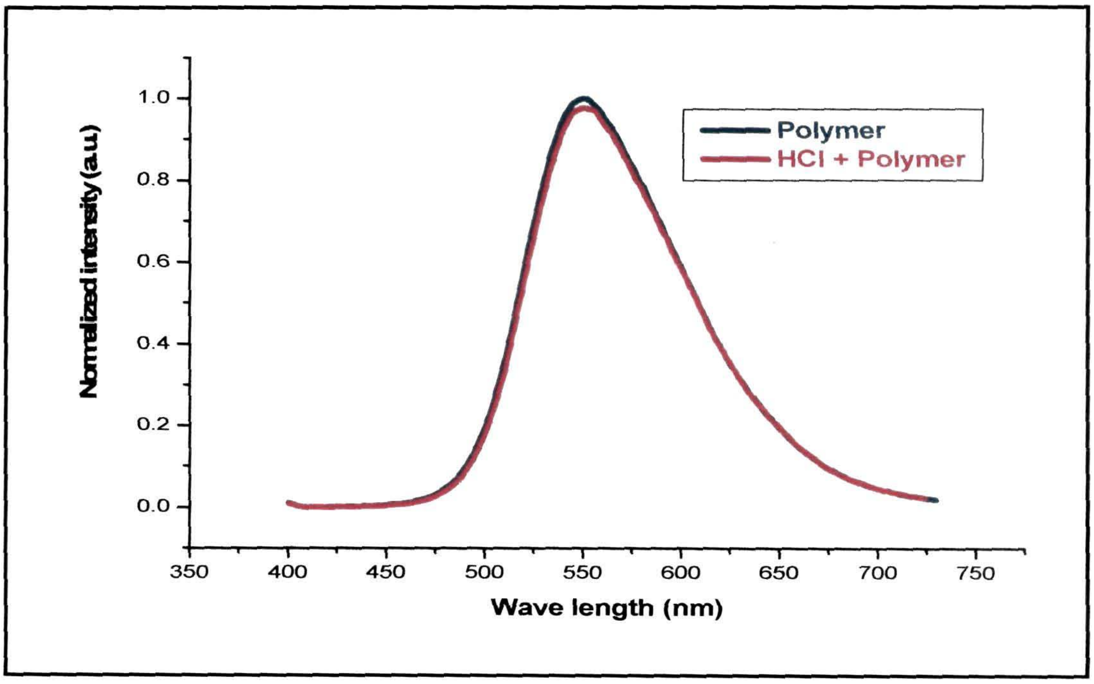


Figure 4.2: Fluorescence of PHTA polymer (0.0025 wt %) in presence of HCl acid (0.5M 10ml), THF solvent, excited at 370 nm

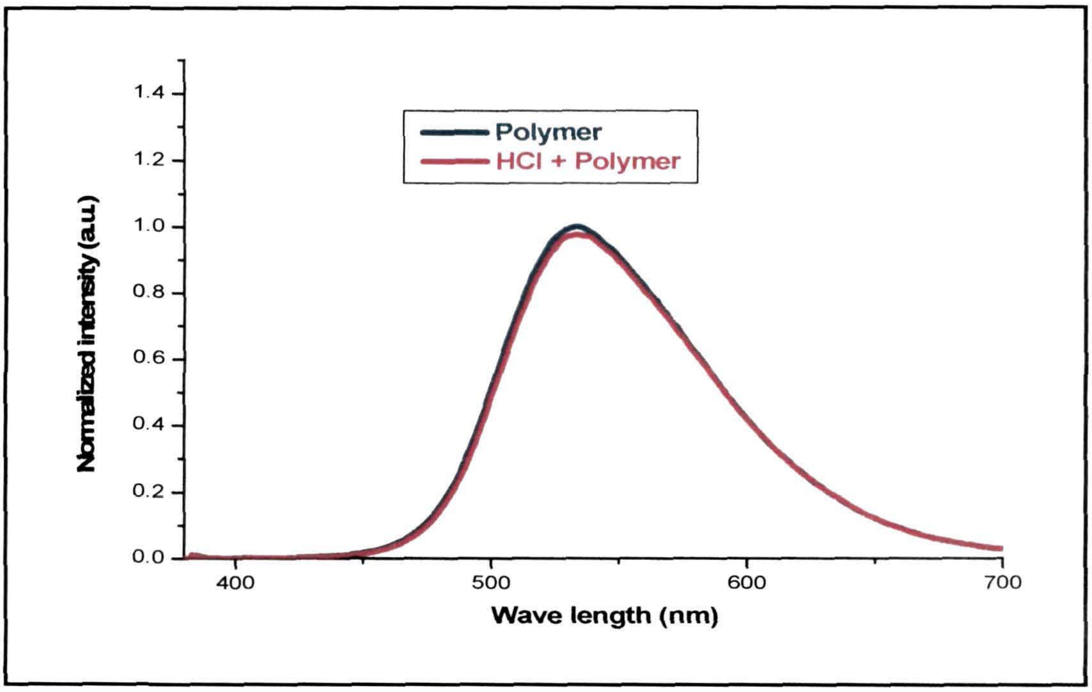


Figure 4.3: Fluorescence of POTA polymer (0.0025 wt %) in presence of HCl acid (0.5M 10ml), THF solvent, excited at 363nm.

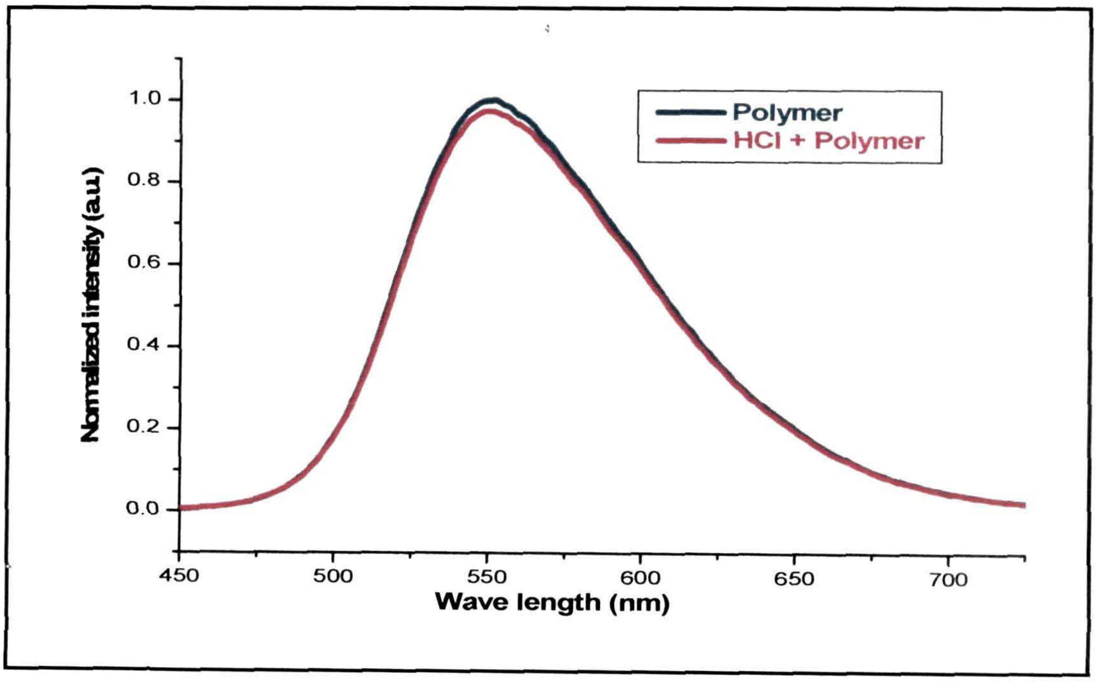


Figure 4.4: Fluorescence of PDTA polymer (0.0025 wt%) in presence of HCl acid (0.5M 10ml),THF solvent, excited at 363nm.

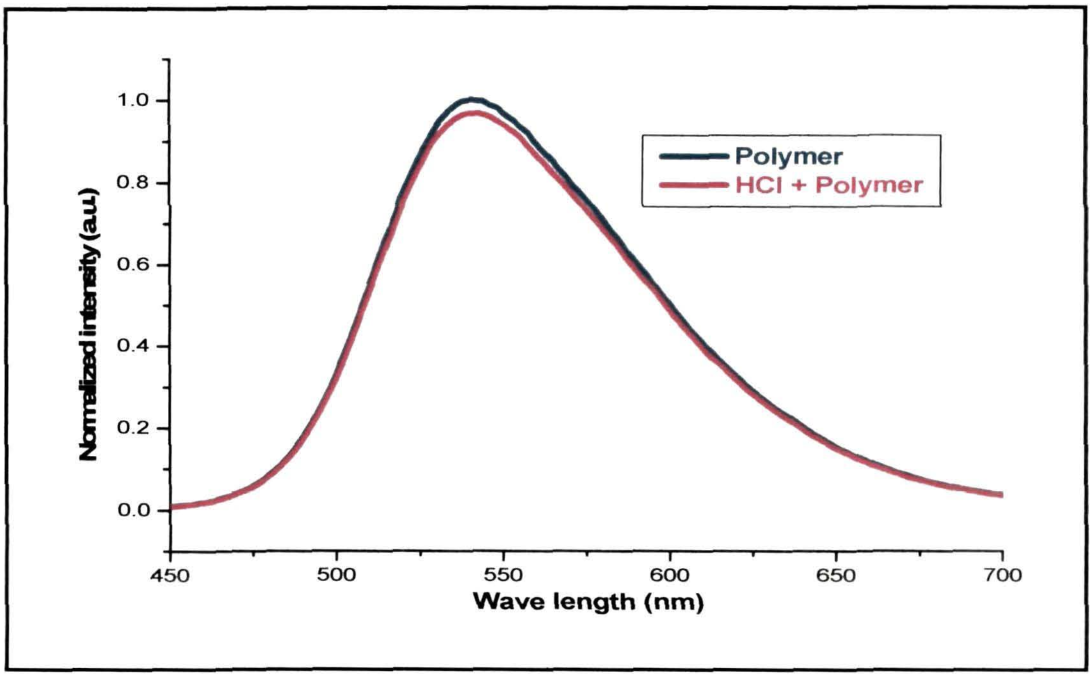


Figure 4.5: Fluorescence of PDDTA polymer (0.0025 wt %) in presence of HCl acid (0.5M 10ml),THF solvent, excited at 359 nm

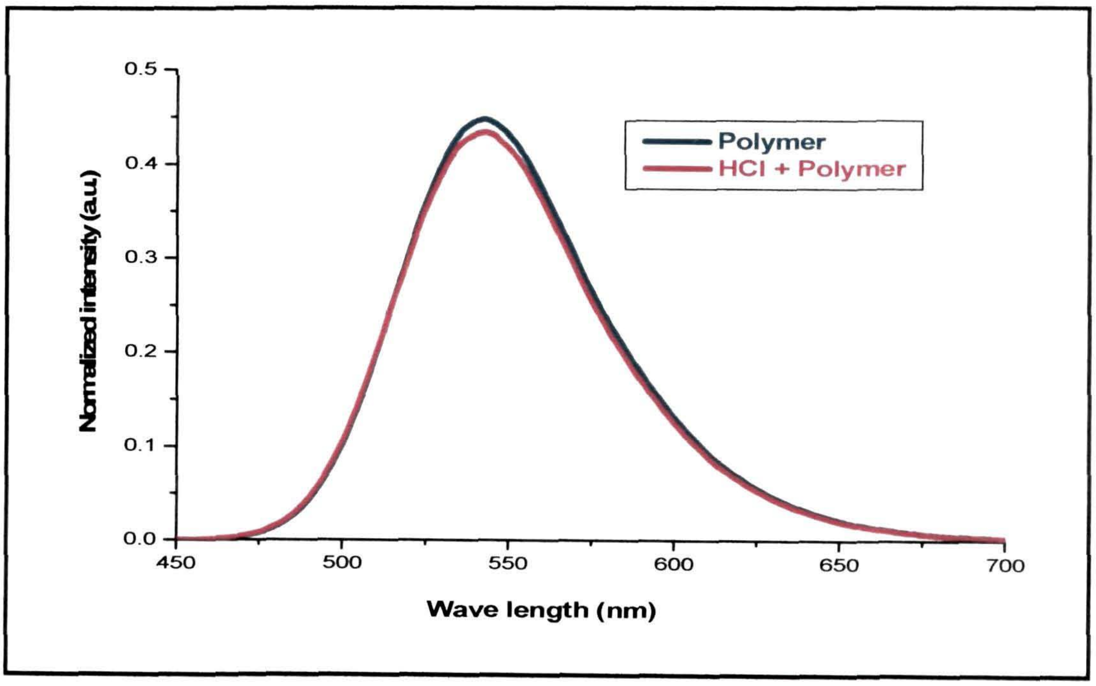


Figure 4.6: Fluorescence of PPDPTA polymer (0.0025 wt %) in presence of HCl acid (0.5M 10ml), THF solvent, excited at 315nm.

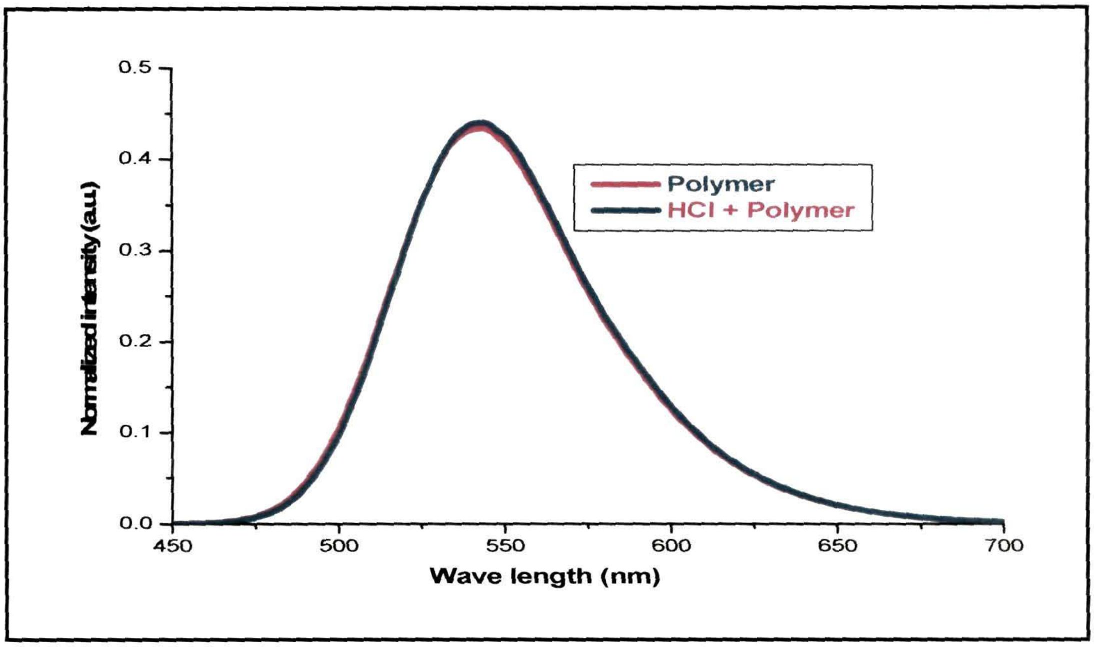


Figure 4. 7: Fluorescence of PPDCHTA polymer (0.0025 wt%) in presence HCl acid (0.5M 10ml), THF solvent, excited at 307nm.

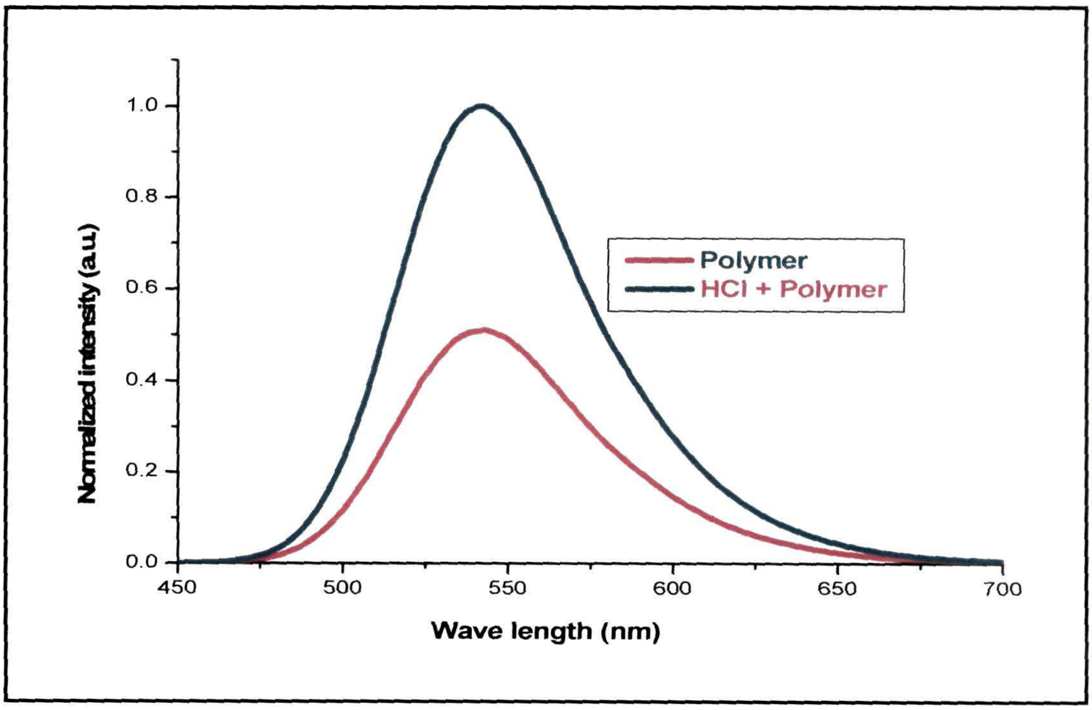


Figure 4.8: Fluorescence of PQTA polymer (0.0025 wt%) in presence HCl acid (0.5M 10ml) THF solvent, excited at 392nm.

We have studied detail fluorescence quenching properties of PQTA polymer due to its good quenching capability in presence of HCl acid. The fluorescence quenching of PQTA polymer is observed in different acid medium (Figure 4.9). Treatment of PQTA polymer (0.0025 grams) in various 0.5M 10ml acids (CH_3COOH, H_2SO_4, HNO_3 and HCl) does not show any wavelength shift but it reduces 50 % fluorescence intensity of the PQTA polymer (Figure 4.9). These acids will form quaternium salts with quinoline. Acid treatment disrupts the coplanarity of the polymer chain due to the protonation of imine nitrogen in quinolinyl group which produces trapping sites for the excitation [27]. It implies that the fluorescence quenching of PQTA polymer originates from the changes in the electron density along the polymer backbone [27]. Among the acids, HCl is the most pronouncing quenching medium for PQTA polymer. The acids can be used as a quenching medium for PQTA polymer.

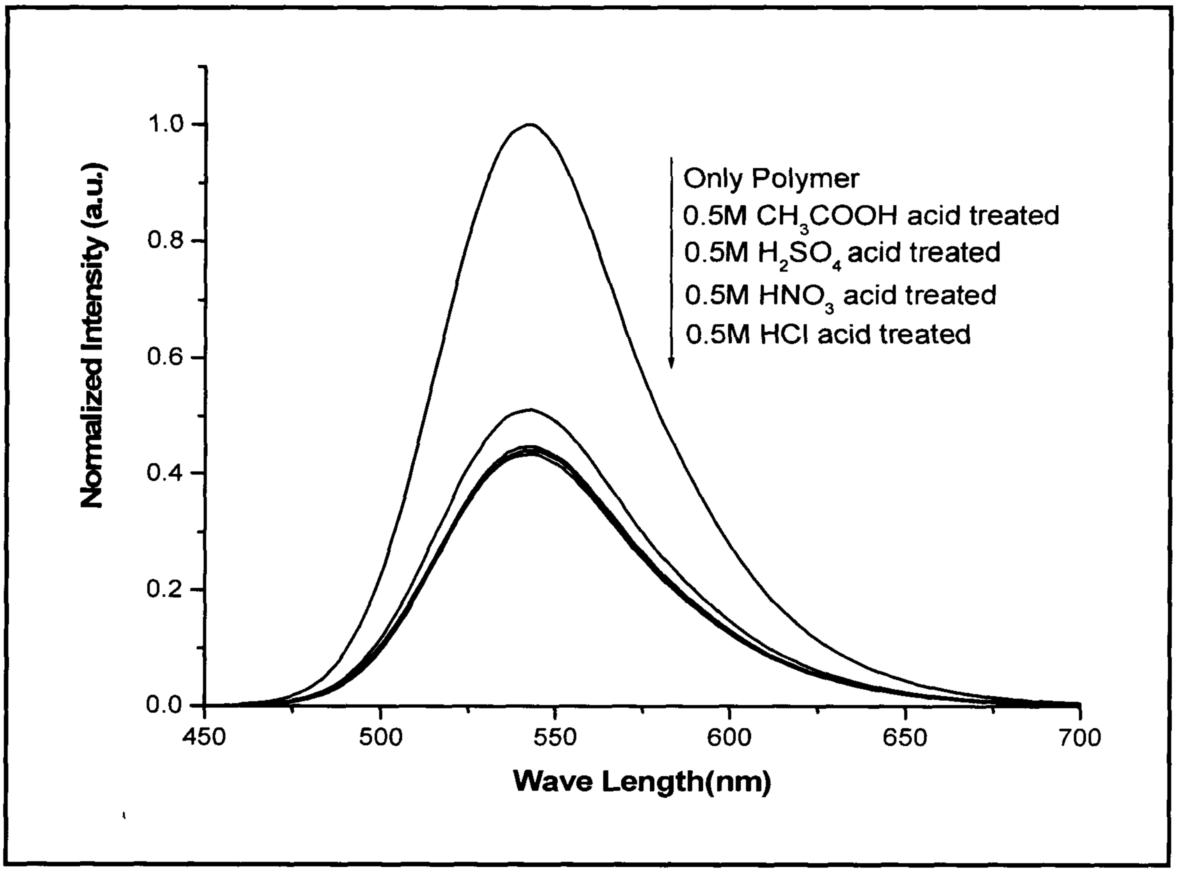


Figure 4.9: Normalized PL spectra of various acids (10ml) treated with PQTA polymer (0.0025 wt %) in THF, excited at 392 nm

4.3.2 Acid sensing properties of PQTA polymer

Fluorescence emission of the polymer (0.006 wt%) with different concentrations of hydrochloric acid shows fluorescence quenching increases with increasing acid concentration (Figure 4.10). Subsequently, fluorescence of polymer is recovered to 70% of original value by the addition of equivalent amount of sodium bi-carbonate (Figure 4.11). Addition of alkali recovers its lost coplanarity and the polymer regains its original fluorescence. The Stern-Volmer coefficient (K_{sv}) of polymer for HCl acid is calculated by using equation 1 and found to be 141 M^{-1} (Figure 4.12). The small K_{sv} value indicates the dynamic quenching [25] of polymer. From the correlation graph, concentration of HCl acid can be measured quantitatively. The detection limit of HCl acid is found to be 0.08 -10 mole L^{-1} (Table 4.1). Also, polymer regains its fluorescence intensity after treated with equal amount of $NaHCO_3$. This shows polymer can be reused. By using different techniques and materials, HCl concentrations can be measured in the range of 0.03 - 1000 mol L^{-1} [28-34]. However, HCl acid concentration detection limit is found in the range of 0.1 -10 mol L^{-1} using polymer based fluorescent sensors [35-36]. From this point of view, hydrochloric acid sensing properties of this polymer is quite impressive not only the low level of detection but also reusability of polymer.

Table 4.1: K_{sv} and detection limit of PQTA polymer for HCl acid

Quencher	K_{sv} (M^{-1})	Detection limit (mole L^{-1})
HCl acid	141	0.08 - 10

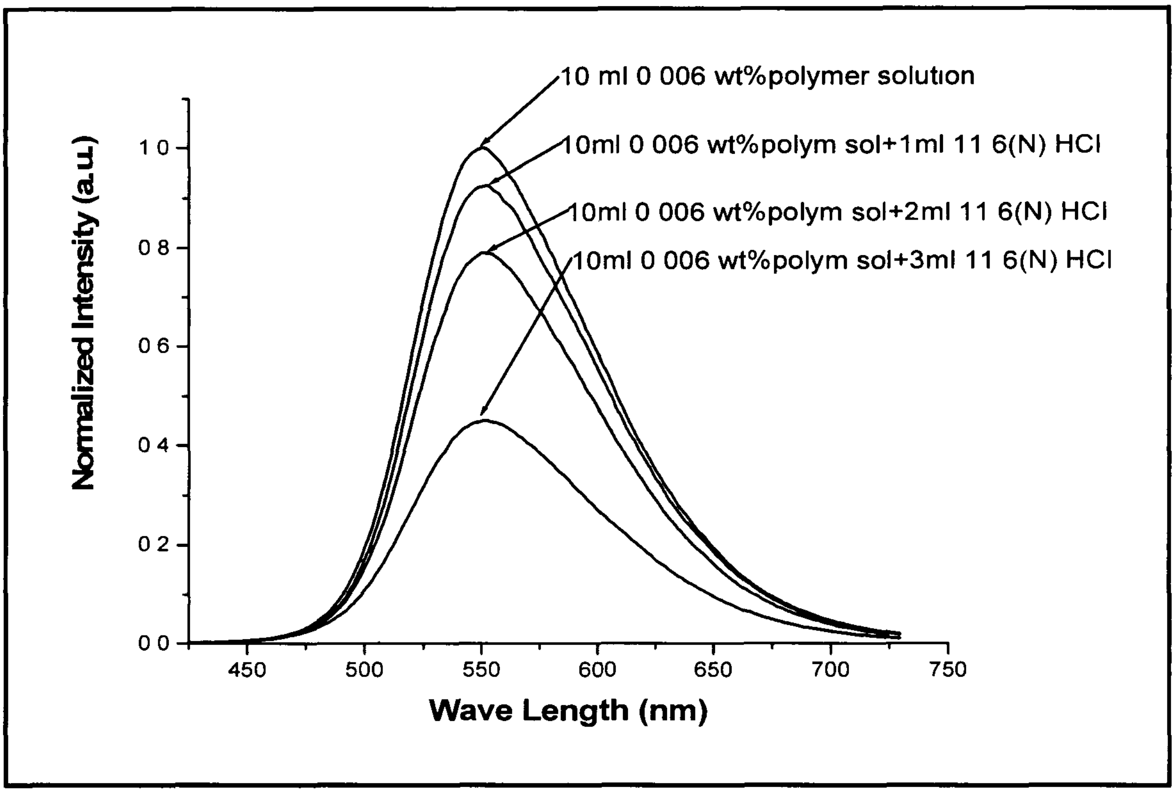


Figure 4.10: Fluorescence of PQTA polymer in different concentration of hydrochloric acid, excited at 392 nm

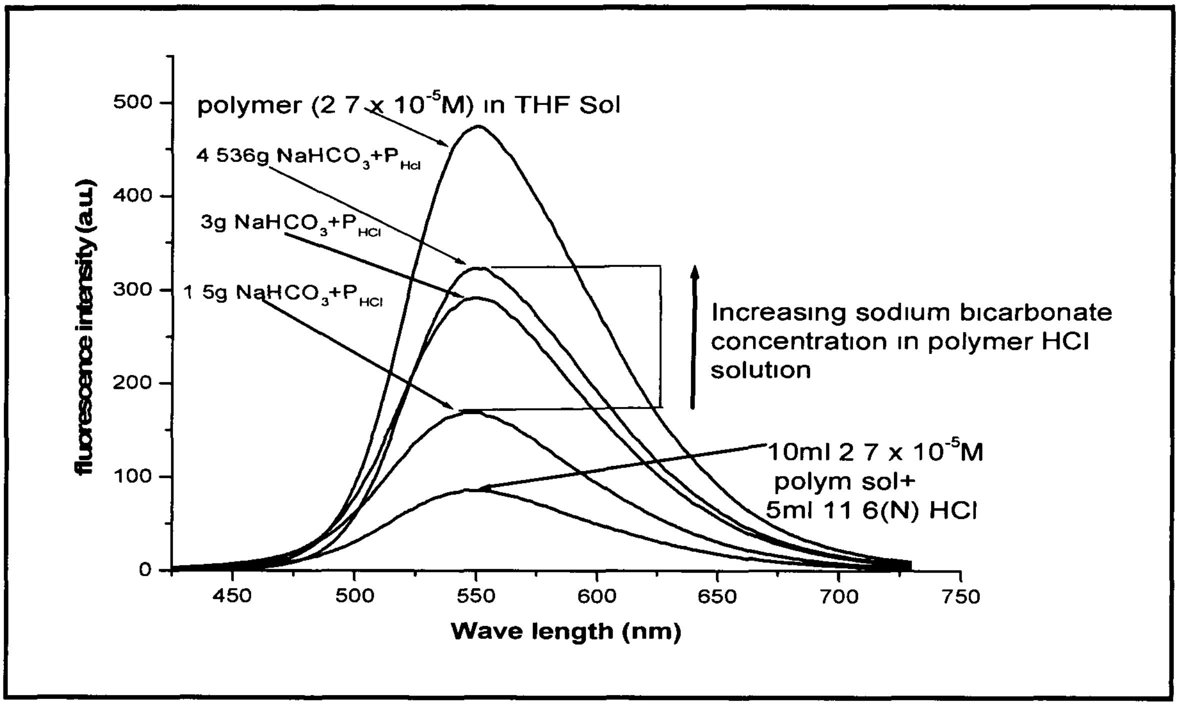


Figure 4.11: Fluorescence intensity versus different concentration of $NaHCO_3$ in PQTA polymer HCl solution in THF excited at 392nm. P_{HCl} = *10ml 2.7* × 10^{-5} M *polymer solution in THF + 5ml 11.6 (N) HCl*

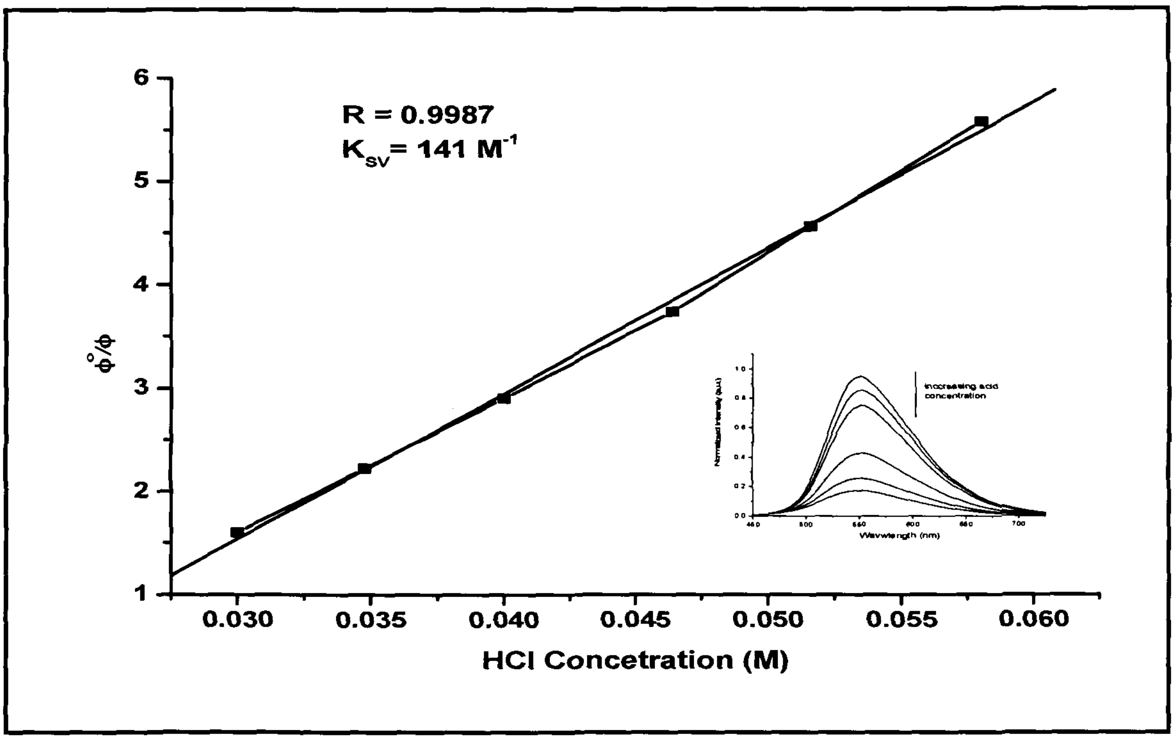


Figure 4.12: Stern - Volmer plot of PQTA polymer (2.7 × 10^{-5} M) in HCl acid. The inset shows curve of fluorescence intensity of polymer in THF solution versus various concentration of HCl excited at 392nm.

4.3.3 Metal ions sensing properties of PQTA polymer

The fluorescence of polymer was studied in the presence of Al^{3+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} ions (Figure 4.13). The fluorescence of polymer is quenched by the addition of Cu^{2+} , Cd^{2+} and Pb^{2+} ions, the values of the fluorescence quenching efficiency of polymer for Cu^{2+} (Figure 4.14), Cd^{2+} (Figure 4.15) and Pb^{2+} (Figure 4.16) ions are 2.285×10^3 , 2.287×10^3 and 3.7×10^4 M^{-1} respectively (Table 4.2). The high quenching efficiency value indicates the static quenching [25] of polymer that leads to the formation of a nonluminescent complex between the polymer and the metal ions. From the correlation graph, concentration of metal ions can be calculated quantitatively. In the case of Cu^{2+} ions, the overall detection range lies between 2.5×10^{-6} and 100×10^{-6} mole L^{-1}, while for Cd^{2+} ions the overall sensing range is 5×10^{-6} - 100×10^{-6} mole L^{-1}, and for Pb^{2+} ions overall detection range is 4×10^{-6} - 100×10^{-6} mole L^{-1} (Table 4.2). These results indicate that the polymer possesses recognition ability for specific metal ions at low level of concentrations. However the fluorescence of polymer is exorbitantly enhanced by the addition of Al^{3+} and Zn^{2+} and does not depend on the concentration (Figure 4.17). The excessive fluorescence increased of polymer in the presence of Al^{3+} and Zn^{2+} metal ions may be due to the formation of stable luminescence complex [37] between the polymer and Al^{3+} and Zn^{2+} metal ions. The peak emission in the presence of copper ions at concentration (1×10^{-4} M) has blue shifted to 20nm. The blue shifts caused by the coordination of specific copper ions are attributed to a deconjugation effect on the polymer back bone [38]. But further study is needed to know the actual mechanism of blue shifting emission of polymer in the presence of specific copper ions and exorbitantly increased fluorescence of this polymer in the presence of Al^{3+} and Zn^{2+} metal ions.

Table 4.2: K_{sv} and detection limit of PQTA polymer for metal ions (Cu^{+2}, Cd^{+2}, Pb^{+2})

Quencher	K_{sv} (10^3 M^{-1})	Detection limit (10^{-6} mole L^{-1})
Cu^{+2} metal ions	2.285	2.5 -100
Cd^{+2} metal ions	2.287	5 - 100
Pb^{+2}metal ions	37	4 -100

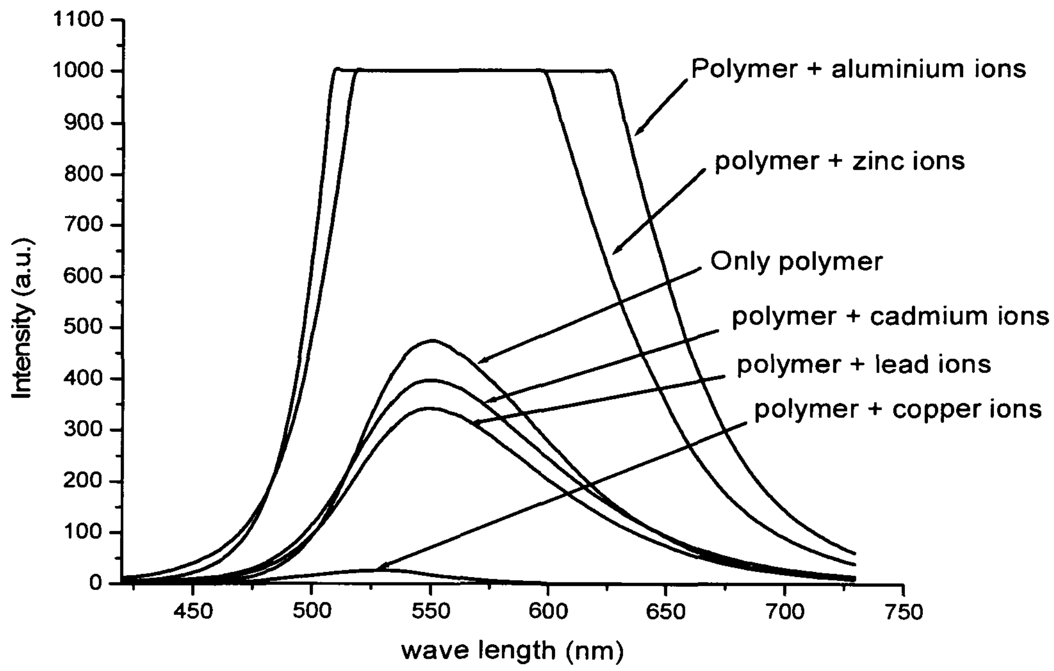


Figure 4.13: Fluorescence of PQTA polymer (2.7×10^{-5} M) in the presence of various metal ions (each 1×10^{-4} M) in THF at excitation wavelength 392 nm.

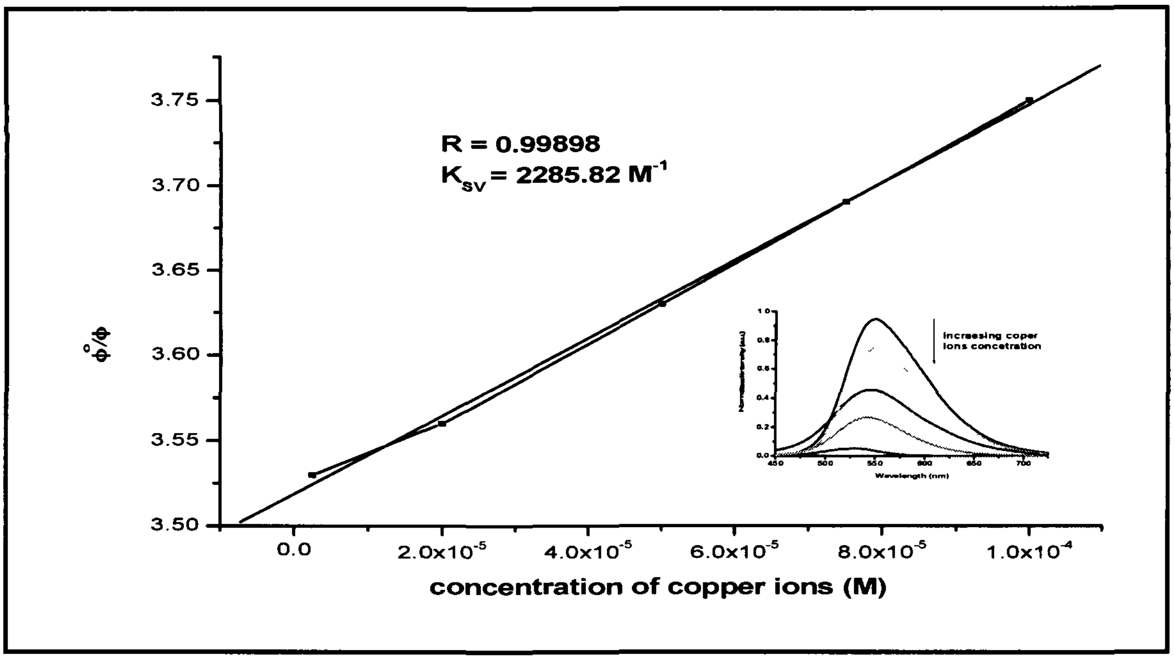


Figure 4.14: Stern - Volmer plot of PQTA polymer (2.7 x 10^{-5} M) in different concentration of copper metal ions (1 x 10^{-4},7.5 x 10^{-5}, 5x 10^{-5}, 2 x 10^{-5}, 2.5 x 10^{-6} M) in THF solution. The inset shows the curve of fluorescence intensity of polymer in THF versus different concentration of copper metal ions excited at 392nm.

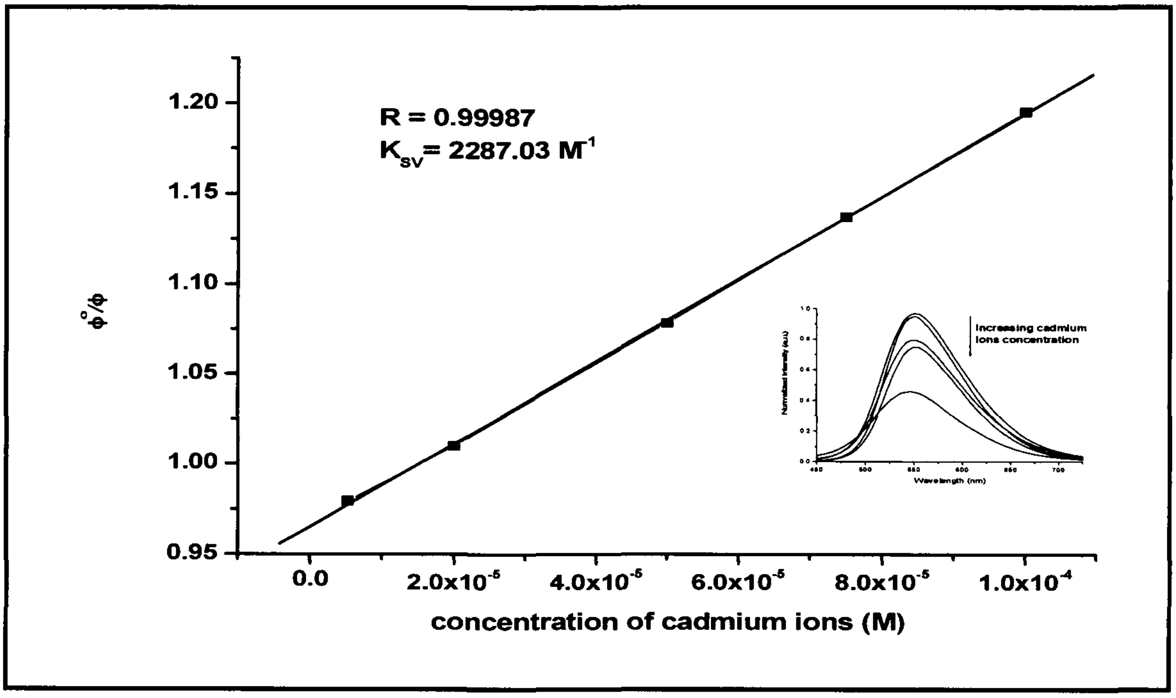


Figure 4.15: Stern - Volmer plot of PQTA polymer (2.7 x 10^{-5} M) in different concentration of cadmium metal ions (1 x 10^{-4}, 7.5 x 10^{-5}, 5x 10^{-5}, 2x 10^{-5}, 5.3 x 10^{-6} M) in THF solution. The inset shows curve of fluorescence intensity of polymer in THF versus various concentration of cadmium metal ions excited at 392nm.

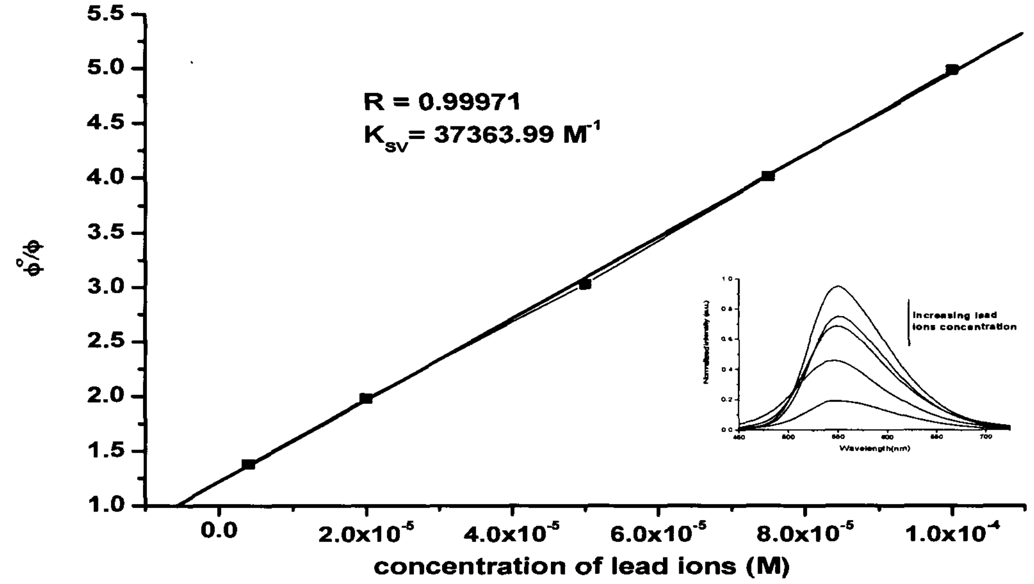


Figure 4.16: Stern – Volmer plot of PQTA polymer (2.7 x 10^{-7} M) in different concentration of lead metal ions (1 x 10^{-4}, 7.5 x 10^{-5}, 5x 10^{-5}, 2 x 10^{-5}, 4 x 10^{-6} M) in THF solution. The inset shows the curve of fluorescence intensity of polymer in THF verses different concentration of lead metal ions excited at 392nm.

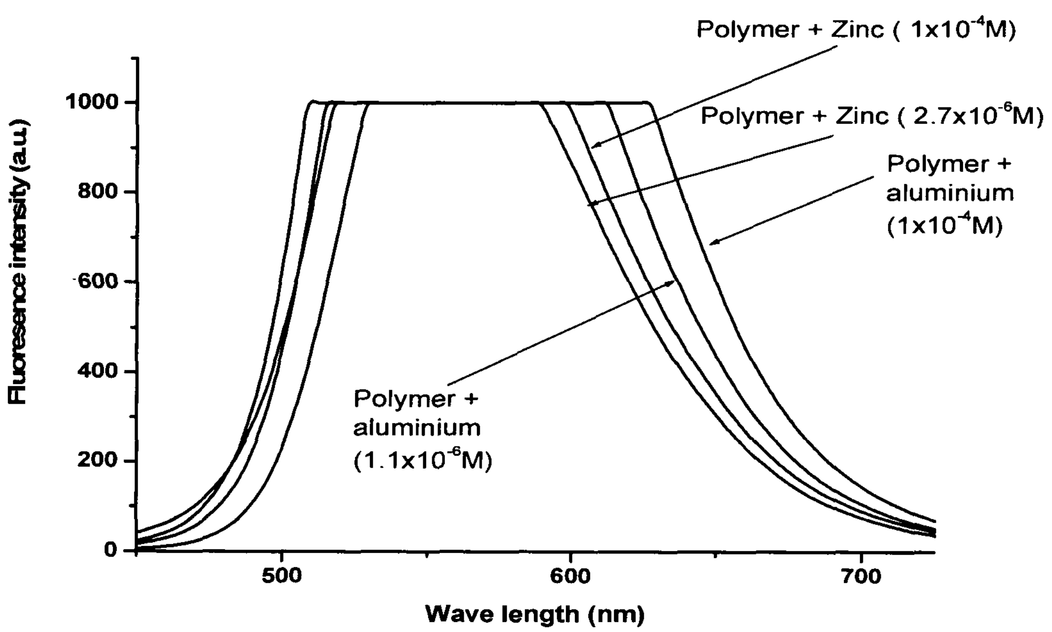


Figure 4.17: Fluorescence of polymer (2.7 x 10^{-5} M) in the presence of aluminium and zinc ions in THF at excitation wavelength 392 nm.

4.3.4 Bio molecules sensing properties of PQTA polymer

Biochemical sensors have emerged as a dynamic technique for qualitative and quantitative analysis of different analytes in clinical, environmental monitoring and food and process control. One approach to nucleotides detection is to use the special properties of conjugated polymers, which can respond to external stimuli, such as biomolecules, with a change in fluorescence spectra. Here, fluorescence properties of polymer have been studied in the presence of nucleotides and protein (l-proline). The polymer shows fluorescence enhancement rather than quenching, upon addition of nucleotides and protein (l-proline) in THF solution (Figure 4.18). The fluorescence is exorbitantly increased and does not depend on concentration (Figure 4.18). The excessive enhancement is explained by H-bonding stabilization [39] of polymer and nucleotides or protein adduct, through which a possible quenching process, the n-π^* transition from the quinoline moiety, is eliminated.

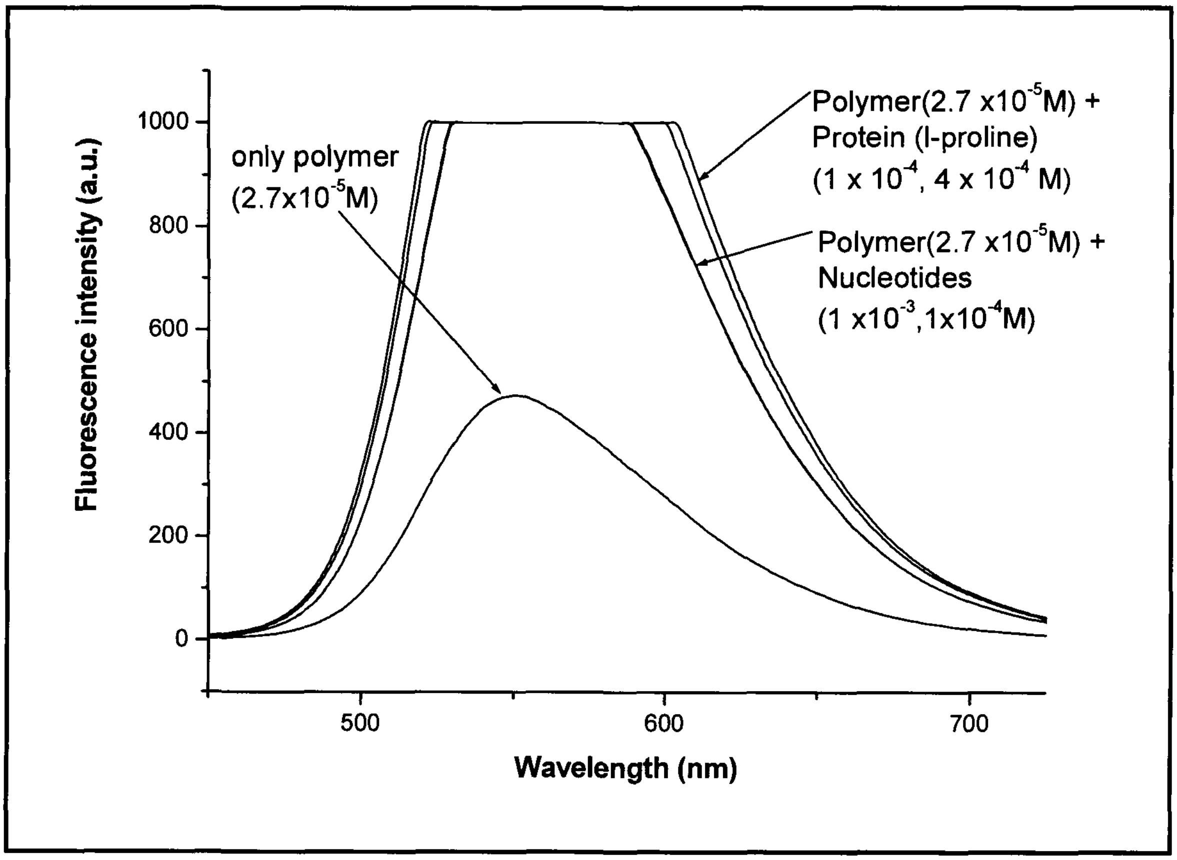


Figure 4.18: Fluorescence of PQTA polymer (2.7 x 10^{-5} M) in the presence of nucleotides (1 x10^{-3}, 1x 10^{-4} M) and protein (l-proline)(1x10^{-4}, 4 x 10^{-4} M) in THF at excitation wavelength 392 nm.

4.4 Conclusion

Only quinolinyl containing polymer PQTA shows fluorescence quenching behaviour in the presence of HCl and other polymers do not show any significant fluorescence quenching the in presence of HCl. The fluorescence quenching of PQTA polymer in acids is due to the protonation of imine nitrogen in quinolinyl group. The PQTA polymer can trace the small concentration of acid and metal ions in solution. The Stern-Volmer quenching coefficient for HCl is calculated and found to be 141 M^{-1}. Moreover quenching depends on concentration of HCl. The detection limit of HCl acid by PQTA polymer is found to be 0.08 -10 mole L^{-1}. The PQTA polymer can be reusable after treatment with alkali for acid detection purpose. The fluorescence of PQTA polymer is quenched by copper, cadmium and lead metal ions and quenching is sensitive to concentrations of metal ions. The Stern-Volmer quenching coefficients are 2.285×10^{3} M^{-1} for Cu^{2+} ions, 2.287×10^{3} M^{-1} for Cd^{2+} ions and 3.7×10^{4} M^{-1} for Pb^{2+} ions. In the case of Cu^{2+} ions, the overall detection range is 2.5×10^{-6} - 100×10^{-6} mole L^{-1}, while for Cd^{2+} ions the overall sensing range is 5×10^{-6} - 100×10^{-6} mole L^{-1}, and for Pb^{2+} ions overall detection range is 4×10^{-6} - 100×10^{-6} mole L^{-1}. The fluorescence of PQTA polymer is exorbitantly increased in the presence of Al^{3+}, Zn^{2+}, nucleotides and protein (l-proline). The PQTA polymer possesses multifacet fluorescence properties which can sense the wide range of compounds from acids to metal ions and from nucleotides to protein.

References

1. G. F. Nordberg, *Ambio, 3* **(1974)** 55.
2. T. R. Sandrin , R. M. Maier, *Environ Health Perspect, 111* **(2003)** 1093.
3. J. F. Verner, H. R. Michael, E. H. Rybicka, B. Je˘drzejczyk, *Appl. Geochem., 11* **(1996)** 11.
4. L. Järup, *Brit. Med. Bull., 68* **(2003)** 167.
5. B. Liu, B. S. Gaylord, S. Wang, G. C. Bazan, *J. Am. Chem. Soc., 125* **(2003)** 6705.
6. K. V. Balakin, V. A. Korshun, I. I. Mikhalev, G. V. Maleev, A. D. Malakhov, I. A. Prokhorenko, A. B. Yu, *Biosens. Bioelectron., 13* **(1998)** 771.
7. K. F. Karlsson , P. Asberg, K. P. R. Nilsson, O. Ingana¨s, *Chem. Mater., 17* **(2005)** 4204.
8. C. Li, M. Numata, M. Takeuchi, S. Shinkai, *Angew. Chem. Int. Ed., 44* **(2005)** 6371.
9. Y. Tang, F. He, M. Yu, F. Feng L. An, H. Sun, S. Wang, Y. Li, D. Zhu, *Macromol. Rapid Commun., 27* **(2006)** 389.
10. S. P. G. Costa, E. Oliveira, C. Lodeiro, M. M. M. Raposo, *Tetrahedron Lett., 49* **(2008)** 5258.
11. H. A. Ho, M. Leclerc, *J. Am. Chem. Soc., 125* **(2003)** 4412.
12. Y.G. Kim, L.A. Samuelson, J. Kumar, S.K. Tripathy, *J. Macromol. Sci. Part A, 39* **(2002)**1127.
13. L. Chen, D. W. McBranch, H.-L. Wang, R. Helgeson, F. Wudl, D. G. Whitten, *Proc. Nat. Acad. Sci., 96* **(1999)** 12287.
14. P. S. Heeger, A. J. Heeger, *Proc. Nat. Acad. Sci., 96* **(1999)**12219.
15. F. He, Y. L. Tang, S. Wang, Y. L. Li, D. B. Zhu, *J. Am. Chem. Soc., 127* **(2005)** 12343.
16. U. Lange, N. V. Roznyatovskayal, V. M. Mirsky, *Anal. Chim. Acta., 6 1 4* **(2008)** 1.
17. X. Song, H.-l. Wang, J. Shi, J.-W. Park, B. I. Swanson, *Chem. Mater., 14* **(2002)** 2342.
18. B. Liu, W.-L. Yu, J. Pei, S.-Y. Liu, Y.-H. Lai, W. Huang, *Macromolecules, 34* **(2001)** 7932.
19. J. Kim, *Pure Appl. Chem., 74* **(2002)** 2031.
20. I. G. Scheblykin, A. Yartsev, T. Pullerits, V. Gulbinas, V. Sundstrm , *J. Phys. Chem. B, 111* **(2007)** 6303.
21. N. Somanathan, S. Radhakrishnan, *Int. J. Mod. Phys. B, 19* **(2005)** 4645.
22. X.Hu, L. Xu, *Polymer, 41* **(2000)** 9147.
23. X. Zhao, X. Hu, L. H. Gan, *Polym. Adv. Technol., 16* **(2005)** 370.
24. J. Guillet, Polymer Photophysics and Photochemistry, Cambridge University Press **(1985)** London.
25. E. L. Cabarcos , S. A. Carter , *Macromolecules, 38* **(2005)** 4409.
26. S. Lee, S. I. Hong, C. Lee, S. B. Rhee, T. J. Kang, *Mol. Cryst. Liq. Cryst., 295* **(1997)** 19.
27. J. Maiti, S. K. Dolui, *J. Lumin., 129* **(2009)** 611.
28. H. Dacres, R. Narayanaswamy, *Talanta, 69* **(2006)** 631.
29. M. G. Baron, R. Narayanaswamy, S. C. Thorpe, *Sens. Actuators B, 34* **(1996)** 511.
30. L. Wang, R.V. Kumar, *Sens. Actuators B, 98* **(2004)** 196.
31. A. V. Samoylov, V. M. Mirsky, Q. Hao, C. Swart, Y. M. Shirshov, O.S. Wolfbeis, *Sens. Actuators B, 106* **(2005)** 369.
32. Y.Itagaki, K. Deki, S-I. Nakashima, Y. Sadaoka, *Sens. Actuators B, 117* **(2006)** 302.

33. J. Jang, J. Bae, *Sens. Actuators B, 122* **(2007)** 7.
34. P. Kalimuthu, S. A. John, *Polymer, 627* **(2008)** 247.
35. W. Liu, J. Tang, Y.Wang, G. Shen, R. Yu, *Fresenius J Anal. Chem,. 362* **(1998)** 387.
36. W. P. Carey, B. S. Jorgensen, *Appl, Spec., 45* **(1991)** 834.
37. L. S. Sapochak, F. E. Benincasa, R. S. Schofield, J. L. Baker, K. K. C. Riccio, D. Fogarty, H. Kohlmann, K. F. Ferris, P. E. Burrows, *J. Am. Chem. Soc., 124* **(2002)** 6119.
38. D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev., 100* **(2000)** 2537.
39. D.-S. Kim, K. H. Ahn, *J. Org. Chem., 73* **(2008)** 6831.

CHAPTER 5

Conclusion and future scope of the present investigation

5.1 Conclusion

Conjugated polymers are attractive materials for optoelectronic applications such as light-emitting diodes, sensors and solar cells. They offer advantages with respect to traditional inorganic semiconductors regarding processability (they require simple techniques such as spin coating, printing) and functionality (modification of the molecules offers enormous variety in functionalization). Rapid progress is being made in the development of polymers for electronic devices. The use of polymer in electronic devices for large scale applications requires high performance, reliability and stability, longer lifetime, good control and reproducibility. A large number of different classes of conjugated polymers have been developed such as poly(N-vinylcarbazole)s, poly(fluorine)s (PFs), poly(p-phenylene vinylenes) (PPVs), and poly(thiophenes) (PTs). Polythiophenes and its derivatives are very unique among other polyconjugated systems due to their solubility, environmental stability, fusibility, processibility. Now-a-days, soluble polythiophene derivatives are of great importance due to their easy processing purpose. The tuneable emissive properties are particularly attractive for lighting and display applications. The wavelength of emission depends on the extent of conjugation, and can be controlled by modification of the chemical structure. This can be achieved by the attachment of functional groups, which alter the electronic structure of the polymer. So, light emission is possible over the entire visible range of the visible spectrum, by "chemical" tuning of the HOMO-LUMO energy gap of the polymer.

The purpose of this thesis is to provide an insight into the synthesis, characterization and electrochemical, photoluminescence and electroluminescent properties of π-conjugated 3-ester substituted polythiophene derivatives for the polymer-based light emitting diode devices.

The findings of the thesis are described below

1. Synthesis and characterization of ester substituted polythiophenes

A series of ester substituted thiophene monomers has been synthesized by esterification reaction. The yield of the monomers is 60-80%. The formation of monomers was confirmed by FTIR, ^{1}H NMR spectroscopy. The polymers have been prepared by the oxidative polymerization using ferric chloride. The polymerization process is slow and yield of the polymer is 42-66%. The polymers show good solubility in THF, $CHCl_3$, DMF, DMAc, and DMSO. The number average molecular weights of polymers are in the range of 3154 to 22260 g / mole. The soluble part of the polymers is found to be oligomer. The Absorption maximum in UV-Vis spectra of the polymers is in the range of 307-392 nm. All the polymers show red shift of absorption maximum with respect to their monomers. Optical band gap of the polymers is found to be 2.1-2.47 eV. XRD analysis reveals that polymers are amorphous in nature. Polymers possess good thermal stability with the onset decomposition temperature around 300-350 °C under nitrogen atmosphere. Thermal stability increases with the increase in molecular weight of polymers. The polymers exhibit a glass transition temperature (Tg) in the range of 63-154°C. It is observed that T_g of the polymers decreases with the increase in length of side chain.

2. Electrochemical, photoluminescence and electroluminescence properties of ester substituted polythiophenes

Cyclic voltammetry study indicates that the oxidation potentials of polymers are high (2.45V) and there is no significant change with substituents. At the same time, change in side chain plays a significant role for altering the reduction potential of polymers. The reduction potential of the polymers is in the range of -0.84V to -2.25 V. It is observed that quinolinyl containing polymer PQTA have the least reduction potential amongst ester substituted polymers due to large molecular weight compared to others. All the polymers seem to be stable under cyclic oxidation and reduction potential (up to 10 cycles). The phenyl and quinolinyl containing polymers have higher band gap and HOMO energy level than alkyl and cyclohexyl derivative polymers. LUMO energy level is same for all the polymers. The electrochemical band gap of the polymers is in the range of 1.57 -2.365 eV and the value is lower than the optical band gap.

The fluorescence emission maximum of the polymers is found to be in the range of 530nm for PPDCHTA to 547 nm for PHTA. The light emission is in the yellow-green region. Stokes shifts of the polymers are in the range of 148 nm for PQTA to 230nm for PPDCHTA. The PL intensity increases with increasing the degree of polymerization. It is found high for PQTA and low for polymer PPDCHTA. It is consistent with their degree of polymerization. The enhanced fluorescence efficiency of polymers is achieved at the cost of their solubility. Here, ester spacer weakens the direct effect of side chain on polythiophene backbone. Also, PL intensity increases with dilution and the limiting value of the concentration is 0.0125 wt % for all polymers except PQTA which is 0.006 wt%. The PL intensities increase with dilution which indicates fluorescence quenching at higher polymer solution concentration. Polymers in solid state show emission band at 553- 564 nm. The fluorescence of polymers in solid state shows red shift in comparison to their solution. The relative fluorescence quantum yield of polymers in THF solution is in the range of 0.237 to 2.481 with respect to Rhodamine B dye. The high fluorescence quantum yield of PQTA polymer is due to the presence of quinoline moiety in the polythiophene backbone.

The polymers show yellowish colour in EL spectra. The turn on voltage of devices is in the range of 5.4V to 7V for current injection. Turn on voltage of POTA is low (5.4 V) and is high (7 V) for PPDPTA. The emission maxima of EL devices based on POTA and PQTA are 536 and 540nm respectively, which are similar to their corresponding photoluminescence maximum. Light emission of the EL device was too weak to be measured for PHTA, PDTA, and PDDTA and no emission was observed for PPDPTA and PPDCHTA. This may be due to the weak film forming capability and low intensity of PL in solid state of oligomer compound. This results in poor interaction of interfaces for charge transport of carrier in LED device.

3. Fluorescence quenching of ester substituted polythiophenes and their application as chemical sensor

Only quinolinyl containing polymer PQTA shows fluorescence quenching behaviour in the presence of HCl and other polymers do not show any significant fluorescence quenching in the presence of HCl. The fluorescence quenching of PQTA polymer in acids is due to the protonation of imine nitrogen in quinolinyl group. The PQTA polymer can trace the small concentration of acid and metal ions in solution. The Stern-Volmer quenching coefficient for HCl is calculated and found to be 141 M^{-1}. Moreover quenching depends on concentration of HCl. The detection limit of HCl acid by PQTA polymer is found to be 0.08 -10 mole L^{-1}. The PQTA polymer can be reusable after treatment with alkali for acid detection purpose. The fluorescence of PQTA polymer is quenched by copper, cadmium and lead metal ions and quenching is sensitive to concentrations of metal ions. The Stern-Volmer quenching coefficients are 2.285×10^{3} M^{-1} for Cu^{2+} ions, 2.287×10^{3} M^{-1} for Cd^{2+} ions and 3.7×10^{4} M^{-1} for Pb^{2+} ions. In the case of Cu^{2+} ions, the overall detection range is 2.5×10^{-6} - 100×10^{-6} mole L^{-1}, while for Cd^{2+} ions the overall sensing range is 5×10^{-6} - 100×10^{-6} mole L^{-1}, and for Pb^{2+} ions overall detection range is 4× 10^{-6} - 100× 10^{-6} mole L^{-1}. The fluorescence of PQTA polymer is exorbitantly increased in the presence of Al^{3+}, Zn^{2+}, nucleotides and protein (l-proline). The PQTA polymer possesses multi facet fluorescence properties which can sense the wide range of compounds from acids to metal ions and from nucleotides to protein.

The same polymer can be utilized in light emitting diode, chemical sensor and other optoelectronic applications by incorporating the appropriate side chain moiety on the conjugated backbone.

5.2 Future scope of the present investigation

1. Theoretical study of band gap for 3-ester substituted polythiophenes.
2. Interaction of 3- ester substituted polythiophenes and quantum dot and its light emitting diode application.
3. To study the actual mechanism of blue shifting emission of PQTA polymer in the presence of specific copper metal ions.
4. To investigate the exorbitantly enhanced fluorescence of PQTA polymer in the presence of Al^{3+} , Zn^{2+}, nucleotides and proteins.

List of publications

Journals

1. J. Maiti and S. K. Dolui, "Synthesis and characterization of π-conjugated poly (thiophene-3-yl-acetic acid 8-quinolinyl ester) and its electrochemical properties", **Journal of Polymer Material 25 (2008) 445-455.**
2. J. Maiti and S. K. Dolui, "Photoluminescence properties of poly (thiophene-3yl-acetic acid 8-quinolinyl ester) in solution and in acid medium", **Journal of Luminescence 129 (2009) 611-614.**
3. A. K. Khan, B.C. Ray, J. Maiti, S.K. Dolui, "Preparation of core-shell latex from co-polymer of styrene-butyl acrylate-methyl methacrylate and their paint properties" , **Pigment and Resin Technology 38 (2009)159-164.**
4. J. Maiti, B. Pokhrel, R. Boruah, S. K. Dolui, "Polythiophene based fluorescence sensors for acids and metal ions" **Sensors and Actuators B Chemical (article in press)**
5. J. Maiti, S.K. Dolui, " Synthesis and haracterization of π- conjugated poly alkyl ester thiophenes and their electroluminescence properties" **(manuscript submitted)**
6. J. Maiti, S. K. Dolui, "Synthesis and characterization of π- conjugated poly (3-pentadecyl cyclohexyl 2-(thiophene -3-yl) acetate and poly (3-pentadecyl phenyl 2-(thiophene -3-yl) acetate and their electroluminescence properties" **(manuscript submitted)**
7. B. Pokhrel, J. Maiti, A. K. Guha, B. Adhikari, S. K. Dolui, "Polythiophene (phenyl azomethine derivatives): electronic structure, synthesis and characterization" **(manuscript submitted)**

Conferences Presentation (Published as Proceeding):

1. J. Maiti, S. K. Dolui, "Synthesis and Characterization of π-conjugated Poly (thiophene-3-yl-acetic acid 8-quinolinyl ester) and its Photoluminescence Properties" Inetrnational Seminar on Frontier in Polymer Science and Technology (POLY-2007) Guwahati, Assam, India, November 1-3, **2007.**

   (Awarded as Dr. S. N. Ghosh memorial best paper presentation)

2. J. Maiti, S. K. Dolui, "Polythiophene based fluorescent sensor for acids and metal ions" 8th International Conference on Advanced Polymers via Macromolecular Engineering Dresden, Germany, October 4 to 7, **2009** (accepted)