DEVELOPMENT OF ELECTROACTIVE POLYMERS AND THEIR APPLICATION IN ELECTROLUMINESCENT DEVICES

A thesis submitted

in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

By

Muhsina Kafiah Huda

Registration No.015 of 2009

Department of Chemical Sciences

Tezpur University

Napaam, Tezpur-784028

Assam, India

December 2010

Dedicated to Abba and Amma………………

DEVELOPMENT OF ELECTROACTIVE POLYMERS AND THEIR APPLICATION IN ELECTROLUMINESCENT DEVICES

Abstract

Background and scope of the present work

A burst of research activity is witnessed in recent years in the area of development of different organic polymers in the field of optoelectronic materials. The display market is a fast growing area, driven by developments in the field of portable electronic devices like cellular phones, digital cameras, etc. Polymer light emitting diode (PLED) technology may become a strong competitor for the liquid crystal display (LCD) technology in the near future. Today, simple PLED displays are already integrated in shavers, car stereos and cellular phones. Although this technology is young compared to the inorganic light emitting devices, mainly based on semiconductor, the quality of PLEDs can compete with them in many cases such as the large area flat panel display, no backlight for the emission, flexible and hence easy processibility, self emission, high resolution, higher scan rate, maximum viewing angle and above all these can be manufactured at lower production costs. In spite of these advantages, improvements are required to achieve the long-term stability of PLED. These polymers are semiconducting in nature with good mechanical properties.

In general, PLEDs are composed of functionally divided multilayers such as hole injection, hole-transporting (HT), emissive, hole-blocking, electron-transporting (ET) layers, and so on. This structure enables the optimal charge balance essential to high electroluminescence (EL) efficiency. In the last decade, many kinds of amorphous molecular semiconductor materials, working as HT materials and ET materials, have been proposed. Efforts were made to develop different polymeric system for the display application to overcome the short comings of inorganic materials as well as the small organic molecules. The special emphasis was given to the solubility and luminescence character. Solubility of a polymer in common organic solvent is dependent on factors like

the average molecular weight, extent of conjugation and the side group characteristics. Another important aspect for a good polymer material for display devices is the surface morphology of the polymer, their glass transition temperature and the stability. In addition to the solubility issue, charge mobility in amorphous organic semiconductors is a crucial property to enhance current *vs.* voltage characteristics of OLEDs, and high mobility leads to lower operation voltage and lower power consumption. Transport of electrons is much more difficult to that of holes in a multilayer device that hampers the recombination and radiation process. The electron mobility in amorphous organic semiconductors is low possibly due to the external perturbations such as oxygen carrier trap. It is needless to say that high electron affinity of molecules is important for electron transport; planar molecules with a large π-electron system are advantageous.

In the last decades a large number of such π-conjugated polymer systems were developed, modified and commercially applied in different display(OLED and PLED), photovoltaic and sensor applications. Poly(p-phenylene vinylene) (PPV), polythiophene(PT), poly(N-vinylcarbazole)s, poly(fluorene)s (PFs), poly 1,3,4-oxadiazoles are some of the examples. Each of the polymers carries some special features with different colour emission properties. Though advantageous in their performance in light emitting properties, the solubility of these polymers is a issue to think about. Modifications are done in conjugated polymers by introducing alkyl or alkoxy side groups, spacer groups in the main chain or the pendant fluorophore in the polymer chain to improve the solubility of the polymers in common organic solvents. The introduction of the side groups also tunes the luminescence and electrochemical behavior of the polymer system; which is in turn very important for a polymer in commercial use for device fabrication and operation. That is why it is important to develop a kind of polymer that fulfills the all possible requirement from solubility to the luminescence and yet very cost effective too. Out of these 1,3,4-oxadiazole containing polymers become very unique and important as it is the most effective electron transporting material with a tailorable wide band gap. The structure of the molecule reveals the electron deficient character of the system and the –C=N bond is very important in determining the band gap of the polymer. The high electron affinity of 1,3,4-oxadiazole is based on the two electron-accepting unit hybridization. The molecule consists of planar ring units only. Therefore, strong electronic interactions among adjacent molecules cause high electron mobility. The fabrication of blue inorganic LED is difficult and expensive as for the blue light emission the active luminescent material requires a HOMO-LUMO energy gap of approximately 2.7-3.0 eV. Since low molecular weight organics dispersed in an inert polymer have a tendency to crystallize at elevated temperature reached during device operation, polymers with oxadizole units (with flexible ether, perfluoralkyl or diphenylsilyl linkages) in the backbone or in side chains can prepared as electron transporting materials to overcome the crystallization and aggregation effect. But the main drawback of the 1,3,4-oxadiazole system is their rigid structure that leads to the solubility problem in common organic solvents like chloroform, THF, methanol, DMAc, DMF, DMSO etc. Polyoxadiazoles with alkyl or alkoxy side chains, oxadiazole as a pendant group or with flexible spacer groups in the main chain were synthesized. But these modifications cause a change in the effective conjugation and steric twisting in the system that again affects the luminescence property of the polymer.

Since wide band gap organic semiconducting materials are potentially applicable to ultraviolet (UV: below the wavelength of 380 nm) light emission devices, surface UV light-emitting devices, which are hardly available using other light-emitting technologies, could open another application field for organic devices. However, there have been only a few reports on UV OLEDs and deep violet OLEDs. Oxadiazoles are well known as good electron transporting materials; they are, by nature, also well known as efficient light emitters for scintillation counters. Moreover, since the oxadiazole ring restricts extensions of π-conjugation beyond the ring, they often emit UV fluorescence. For all of these reasons, oxadiazoless can be used as light-emitting electron transporting materials for UV OLEDs. One reason for the scarcity of reports is that it is difficult to inject both charge carriers (electrons and holes) into wide band gap organic semiconductors. Organic materials are working as emissive layer as well as charge carriers. However the carrier injection is crucial for its performance. That is why it become an utmost important for developing a material that not only soluble in organic solvents but also possess a wide band gap and good electron transporting properties.

Wide band gap blue light emitting polymers play a significant role in the display material as it is generally more difficult to fabricate such LEDs from inorganic semiconductors. Furthermore, full color exhibition and white-light devices need blue light. For blue emission, conjugated polymers need to have a large bandgap and defined optical properties.

The HOMO energy level of the oxadiazole containing polymer is deep and hence the choice of a suitable hole injecting material is very necessary. To overcome this difficulty and to make use of the poly1.3.4-oxadiazoles as blue emitter; doping of inorganic nanoparticles in the polymer system improves the charge recombination and radiation in the visible region. The nanocrystal dopants alone are not good as a charge carrier and it is difficult to achieve any electrical contact due to its smaller size. But with organic polymeric system they can act through the donor-acceptor approach where the wide band gap polymers can act as the donor host for the semiconductor nanoparticles. In such blend systems, efficient energy transfer from host matrix (polymer) to guest (nanoparticles) takes place when the donor and acceptor moieties are in close spatial proximity and have a sufficient spectral overlap. Energy and charge transfer from the polymer to the nanoparticles requires an energy band offset at the organic/inorganic interface.

Considering the above pros and cons of the PLED application of the polymers for the blue light emission and the tunability in their light emitting properties; our work targeted the development of soluble oxadiazole containing polymer and their application in the fabrication of the electroluminescent devices with a low turn on voltage and efficient blue light emission.

Objectives of the present investigation

- Synthesis of soluble poly1,3,4-oxadiazole containing polar end groups and 1,3,4-oxadiazole containing polyurethanes in the main chain via simple chemical polymerization method.
- Characterization of the prepared monomers and polymers by spectroscopic techniques such as UV Visible spectroscopy, FTIR spectroscopy. NMR

spectroscopy, thermal analysis by TGA, DSC etc., elemental analysis, luminescence study by fluorescence analyzer.

- Application of the prepared polymers in electroluminescence devices and evaluation of electroluminescence properties
- Study of the colour tuning and device performance of the metal/poly1,3,4-oxadiazole hybrid materials.

Plan and methods of work

To fulfill the objectives of the present work the following plans of work have been adopted.

- Preparation of the poly1,3,4-oxadiazole containing polar end groups
- Preparation of the 1,3,4-oxadiazole containing polyurethanes
- Characterization of the monomers and polymers by spectroscopic techniques like FTIR, 1H NMR, UV-visible spectroscopy
- Preparation of the meta/polymer hybrid with silver, copper and nickel nanoparticles
- Study of the morphology of the metal/polymer hybrides by SEM, TEM and XRD
- Evaluation of the thermal behavior of the polymers and the metal/polymer hybrides by TGA and DSC analysis
- Cyclic voltammetry study of the polymers for the electrochemical nature of the systems
- Study the photoluminescence properties of polymers and metal/polymer hybrides by fluorescence spectrophotometer.
- Fabrication of LED device using synthesized polymers.
- Evaluation and testing the device performance using the 2 probe sourcemeter
- Evaluation of electroluminescence properties.

THE THESIS

The thesis covers the area of electroactive polymer synthesis, property evaluation and their application in the blue light emitting electroluminescent device application. The present work deals with the synthesis of some poly1,3,4-oxadiazoles containing polar end groups and the polyurethanes having oxadiazole moiety in the main chain; evaluation of their thermal, electrochemical and photoluminescence properties and the application of the polymers for the fabrication of electroluminescent devices and assessment of their device properties. The main highlighting area of the work is put on the synthesis of the soluble electroactive polymer as well as electroluminescent device illuminating in the blue visible region.

The thesis includes five chapters which are briefly described below.

Chapter 1 deals with the general introduction of the electroactive polymers, π conjugated systems, blue light emitting polymers and their application in electroluminescent devices. Different kind of device structure, colour tuning related to the HOMO-LUMO band gap, various synthetic procedures and the device performance of different polymeric systems are also included in this chapter. The objectives of the present investigation and the plan and research methodology of the work of the thesis are included in this chapter.

Chapter 2 deals with the synthesis of the monomer and the polymers; their structural characterization, physical properties, optical properties and the thermal behaviours. We have designed and synthesized the following three sets of 1,3,4-oxadiazole containing polymer.

1. **Poly 1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene** containing polar end groups like $-NO_2$, -Cl,$-CH_3$, -OH (**OXD AR1,-AR2,-AR3,-AR4**)
2. **Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene** containing polar end groups like $-NO_2$, -Cl,$-CH_3$, -OH (**OXD BR1,-BR2,-BR3,-BR4**)
3. **Polyurethanes containing 1,3,4-oxadiazole** in the main chain (**PU1, PU2, PU3, PU4**)

The design of the monomer and polymer and their synthetic procedures are included in this chapter. The products are characterized by spectroscopic methods like FTIR, 1H NMR and UV-visible spectroscopy. Different physical properties like solubility, melting point, inherent viscosity etc of the polymers along with their thermal behaviour and degradation characteristics are reported and discussed thoroughly in this chapter. The weight average molecular weights, number average molecular weights and polydispersity index were determined by the GPC analysis.

Chapter 3 includes the photoluminescence bahaviour, quantum yield of the polymers with respect to anthracene; their electrochemical analysis and the redox properties are discussed. The HOMO-LUMO band gaps of the polymers are calculated using the cyclic voltammetry method and their comparative study with the polymer properties are discussed in this chapter. The chapter concluded with the fabrication of the PLED using the polymers in the device structure like 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. The device properties like electroluminescence and the current-voltage (I-V) properties were evaluated and discussed in this chapter. The wide band gap polymers in the range 2.3-2.6 eV show the intense blue emission with an improved turn on voltage 6-8 V.

In **chapter 4**, the change in the photoluminescence properties on the doping of the copper, silver and the nickel nanoparticles with poly 1,3,4-oxadiazole is reported. The promising characteristic of these hybrid organic –inorganic materials in the OLED application is discussed in this chapter.

Chapter 5 concludes the works discussed in the thesis, remarks and the future prospective of the present study. This chapter comprises of the highlights of the findings, remarks and the further study and development of the polymer systems. The poly 1,3,4-oxadiazoles with the nitro polar end groups and the polyurethanes with the oxadiazoles in the main chain are proved to be the efficient blue light emitting polymer in the electroluminescent device application. The photoluminescence behaviour of the poly 1,3,4-oxadiazoles which reside generally in the UV region were shifted to the longer wavelength on doped with copper, silver and the nickel nanoparticles. The polyoxadiazole containing the metal nanoparticle emits in the intense blue region with a turn on voltage of 2-4V. Therefore it can be concluded that the hybrid polymer-inorganic composites can act as a promising candidate for the OLED technology in the near future.

References

1. Burroughes, J. H. *et al.*, Light-emitting diodes based on conjugated polymers. *Nature* **347,** 539-541(1990).
2. Katz H. E.; Organic molecular solids as thin film transistor semiconductors. *J. Mater. Chem.* **7,** 369-376 (1997).
3. Braun, D.; Heeger, A. J. Visible light emission from semiconducting polymer diodes. *Appl. Phys. Lett.* **58**, 1982-1984 (1991).
4. Shaplov, A. S. *et al*, Novel phosphonated poly(1,3,4-oxadiazole)s: Synthesis in ionic liquid and characterization. *React. Funct. Polym.* **68**, 208-224 (2008).
5. Liou, G. S.; Hsiao, S. H.; Chen, W. C.; Yen, H. J. A new class of high T_g and organosoluble aromatic poly(amine−1,3,4-oxadiazole)s containing donor and acceptor moieties for blue-light-emitting materials. *Macromolecules* **39**, 6036–6045 (2006).
6. Chen Y *et al* A new blue-light emitting polymer: Synthesis and photoinduced electron transfer process. *J. Polym. Sc.: Part A: Polym. Chem.* **46**, 4249–4253 (2008).
7. Ding, L.; Karasz; Frank, E.; Lin, Y.; Pang, Y.; Liao, L.; Photoluminescence and electroluminescence study of violet-blue and green emitting polymers and their blend. *Macromolecules* **36,** 7301-7307 (2003).
8. Perzon, E.; Wang, X.; Admassie, S.; Inganas, O.; Andersson, M. R.; An alternating low band-gap polyfluorene for optoelectronic devices. *Polymer* **47**, 4261-4268 (2006).
9. King S. M.; Hintschich, S. I.; Dai, D.; Rothe, C.; Monkman, A. P. Spiroconjugation-enhanced intramolecular charge-transfer state formation in a polyspirobifluorene homopolymer. *J. Phys. Chem. C.*, **111,** 18759–18764 (2007).

10. Brédas, J.L. *et al*, Excited-state electronic structure of conjugated oligomers and polymers: a quantum-chemical approach to optical phenomena. *Acc. Chem. Res.*, **32,** 267–276 (1999).
11. Shim, H K.; Jin, J. I. Light-emitting characteristics of conjugated polymers. *Adv. Polym. Sc.* **158**, 193-243 (2002).
12. Bott, A. W.; Electrochemistry of Semiconductors. *Current Separations* **19**, 71-75 (2001).
13. Oyston, S. *et al*, New 2,5-diaryl-1,3,4-oxadiazole–fluorene hybrids as electron transporting materials for blended-layer organic light emitting diodes. *J. Mater. Chem.* **15,** 194-203 (2005)
14. Ahn, J. H. *et al.*, Blue organic light emitting devices with improved colour purity and efficiency through blending of poly(9,9-dioctyl-2,7-fluorene) with an electron transporting material. *J. Mater. Chem.* **17**, 2996–3001 (2007).
15. Karttunen, M.; Ruuskanen P.; Pitkänen, V.; Albers, W. M. Electrically conductive metal polymer nanocomposites for electronics applications. *J. Elect. Mater.* **37**, 951-954 (2008).
16. Takele, H. *et al*, Tuning of electrical and structural properties of metal-polymer nanocomposite films prepared by co-evaporation technique. *Appl. Phys. A: Mater. Sc. Proces.* **92**, 2345-2350 (2008).

List of publication

1. M. K. Huda and S. K. Dolui, *Synthesis of Oligomeric Poly(1,3,4- oxadiazole)s containing Polar end groups:Their Photoluminescence and Thermal Behaviour*, J. Polym. Mater. Vol. 26, No. 3, 2009, 251-266
2. M. K. Huda and S. K. Dolui , *Luminescence property of Poly 1,3-bis(phenyl-1,3,4-oxadiazole)s containing polar groups in the main chain*, Journal of Luminescence 130 (2010), 2242-2246
3. M K Huda, S K Dolui,*Blue Light Emitting 1,3,4 Oxadiazole Containing Polyurethane For Electroluminescent Devices, journal of Applied Polymer Science(comm.)*

4. M K Huda, S K Dolui, *Thermal Characteristics and Luminescent Property of Optically Active 1,3,4 Oxadiazole Containing Polyurethane, Iranian Polymer Journal (comm.)*
5. M K Huda, S K Dolui , *Electroluminescence And Cyclic Voltammetric Study Of Blue Light Emitting 1,3,4 Polyoxadiazole Containing Polar End Groups, Polymer Bulletin(comm.)*
6. B Pokhrel, S Konwer, A dutta, M K Huda, B Ghosh, S K Dolui, *Study of photovoltaic performance of host-guest system comprising optically active polyurethane and Rhodamine B dye(comm.)*
7. M K Huda, B Pokhrel, S Konwer, S K Dolui, *Electrochemical determination of the ionization potential and electron affinity of polyurethanes containing oxadiazole moiety (comm.)*
8. M K Huda, A Dutta, S K Dolui, *Photoluminescent Behaviour of Metal Nanoparticle/Polyoxadiazole Hybrid Material for OLED Application(comm..)*

Conference presentation

- M K Huda, S K Dolui, "Synthesis and characterization of soluble poly 1,3,4 Polyoxadiazole, Condensed Matter Days" Vishwabharati, West Bengal, August 29-31,2008
- M K Huda, S K Dolui, "The luminescence study of Lead sulfide nanocrystal-Polyhydrazide/1,3,4 polyoxadiazole composite" MACRO 2009, MARCH 9-11, 2009, Chennai
- M K Huda, S K Dolui, "Luminescence Properties of Polyurethanes Containing 1,3,4-Oxadaizole Chromophore for Electroluminescent Diode Application" ICORFAS 2010, September 22-24, 2010, Annamalai University, Chidambaram, Tamil Nadu

  (Awarded best paper in the conference)

DECLARATION BY THE CANDIDATE

The thesis entitled "***Development of electroactive polymers and their application in electroluminescent devices***" is being submitted to Tezpur University in partial fulfillment 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.

Muhsina Kafiah Huda

Date: 30/12/2010
Place: TEZPUR

Muhsina Kafiah Huda
Department of Chemical Sciences
Tezpur University

TEZPUR UNIVERSITY
(A Central University)
NAPAAM, TEZPUR - 784 028
DISTRICT : SONITPUR, ASSAM, INDIA

Prof. Swapan Kumar Dolui
Department of Chemical Sciences

CERTIFICATE OF THE SUPERVISOR

This is to certify that the thesis entitled" ***Development of electroactive polymers and their application in electroluminescent devices*** " *submitted to the School of Science and Technology, Tezpur University* in partial fulfillment for the award of the degree of Doctor of Philosophy in *Chemical Sciences* is a record of research work carried out by Ms. Muhsina Kafiah Huda under my supervision and guidance.

All helps recieived from various sources have been duly acknowledged.

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

Date: 30.12.10
Place: Tezpur

Prof S. K. Dolui (Supervisor)
School of Science and Technology
Tezpur University

Ph. : 03712 - 267009 Extn : 5052 ● Fax : 03712 - 267 005/006 ● Mobile : 99571 98489 ● Email : dolui@tezu.ernet.in

TEZPUR UNIVERSITY
(A Central University established by an Act of Parliament)
NAPAAM, TEZPUR - 784028
DISTRICT : SONITPUR :: ASSAM :: INDIA

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

Certificate of the External Examiner and ODEC

This is to certify that the thesis entitled "**Development of electroactive polymers and their application in electroluminescent devices**" submitted by **Muhsina Kafiah Huda** to Tezpur University in the Department of **Chemical Sciences** under the school of **Science and Technology** in partial fulfillment of the requirement for the award of the degree of Doctor of Philosophy in **Chemical Sciences** has been examined by us on ______________________ and found to be satisfactory.

Signature of

Principal Supervisor

External Examiner

Date: _________

Preface

Electroactive polymers used in organic light emitting diodes have attracted tremendous attention in the past decade owing to their potential advantages such as outstanding mechanical and optical properties, lower device driving voltages, low-cost manufacturing and amenability to large-area displays. This lead to the breeding of new conjugated polymers with new approaches and novel ideas in the optoelectronics whether it is in light emitting diodes, sensors, photovoltaic devices or the actuators.

Different classes of conjugated polymers are developed till date which includes polypyrrole, polyethylenedioxythiophene, poly(p-phenylene vinylene)s, polyaniline, polyoxadiazoles and polythiophenes. The polymers are mainly used for different coloured light emission that again depends on the band gap and the structural properties. Large band gap blue light emitting organosoluble polymers with good thermostability and processibility are in the high demand now a day. The polyfluorenes and the polyoxadiazoles are the leading materials for their blue light emitting properties.

The processing and fabrication of OLEDs out of these polymers is predicament due to the insolubility of the polymers. A considerable effort had made to develop the conjugated polymers to serve the light emission in the visible region. The present thesis deals with the synthesis of some poly(1,3,4-oxadiazoles) containing polar end groups and the polyurethanes having oxadiazole moiety in the main chain; evaluation of their thermal, electrochemical and photoluminescence properties and the application of the polymers for the fabrication of electroluminescent devices and assessment of their device properties. The thesis also covers the change in the luminescence and the semiconducting behaviour of polyoxadiazoles incorporating with metal nanoparticles. ***Chapter 1*** *deals with the general introduction of the electroactive polymers, π conjugated systems, blue light emitting polymers and their application in electroluminescent devices, different kind of device structure, colour tuning related to the HOMO-LUMO band gap is described.* ***Chapter 2*** *deals* *with the synthesis and the characterization of the monomers and polymers and evaluation of their thermal and optical properties.* **Chapter 3** *includes the photoluminescence bahaviour, quantum yield, electrochemical analysis and the HOMO-LUMO band gaps of the polymers. The chapter concluded with the fabrication of the PLED and assessment of their electroluminescence behaviour and the I-V characteristics. In* **Chapter 4**, *the change in the photoluminescence, electroluminescence and I-V characteristic properties on the incorporation of the copper, silver and the nickel nanoparticles with the polyoxadiazoles are reported.* **Chapter 5** *concludes the works discussed in the thesis, remarks and the future prospective of the present study.*

It is our privilege to contribute a little knowledge in the field of electroactive polymers used in light emitting devices and make some possibility for advance research from our work.

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

Muhsina Kafiah Huda

Muhsina Kafiah Huda

Acknowledgement

First of all I would like to express my sincere gratitude to Prof S.K.Dolui, my supervisorfor his inspiring guidance, endless patience, freedom in work, thought provoking discussions with high inspirational words in the few years of my research work in Tezpur University. it would have not been possible to carry out this work without his timely help, support and encouragement throughtout these years.

I express my profound gratitude and thank to Dr N Karak, Dr. R C Deka and Dr A. J. Thakur; members of my doctoral research committee for their suggestions and fruitful discussions. my sincere gratitude is towards the faculty members of our department for their kind encouragement.

I am thankful to Dr M.N. Kamalasanan and Dr. (Mrs) R. Shrivastava, National Physical Laboratory, New Delhi for allowing me to get the training on LED device fabrication and testing in their laboratory. I am also thankful to Amit, Anjar, Razi, Rakhi, Anju, Priyanka Manoj and Arunandan, research scholars in NPL for their help and support in carrying out the LED fabrication.

I am grateful to Dr N. Sensarma and Mr Samiul Islam, IASST, Guwahati, for providing GPC data. I am also thankful to Mr George, NEHU for the TEM analysis of the samples and IIT Guwahati for providing the NMR data of my samples. I would like to offer my gratitude to Dr C.V.Avadhani, NCL, Pune for his suggestions during my research work. I am thankful to my beloved seniors Tapashi ba, Iliasda, Rajuda, Nandini ba, Rashmi ba, Digantada, Rabiulda, Manashi ba and Sibdas da for their timely help and suggestions.

My research work would not be cpmplete without the help the technical team of Department of Chemical Sciences and Department of Physica, Tezpur University; Dr. B. Gohain, Dr. B. Saikia, Dr. K. Baruah, Mr. N. Dutta, Mr. R. Borah, Mr. S. Phukan, Mr. R. Baruah, Mr. J. Borah and Mr Borah.

I will fall in my words if I not mention the thank and gratitude to my friends Dhiraj, Mridul, Prem and Abhishek for the literature and analysis of the samples

I wish to express my thanks to my beloved labmates Maiti da, Binod da, Anamika ba, Lakhya da, Surajit da, Isha, Amar, Monalisha, Binoy, Chandramika and Pranab for all the help and encouragement to carry out the research work and make the staying in the lab very delightful and comfortable. Thank you my friends for the valuable suggestions and friendship.

I would like to thank my friend during my stay at Tezpur University Nirmala, Jagadish, Shilpi, Nabanita, Swati, Manashi, Madhurya, Soumik, Sanchitaba, Ankur Gogoi, Momiba, Suresh, Bornali, Shreemoyee, Anisha, Kalyanda, Mridula, Biplob, Rashmi, Nibedita, Pinkee, Anggana, Murshid, Harekrishna, Buddhadev, Uday, Suvanshuda, Gautam, Mandakini, Jeenajyoti, Sivaprasad, Lakhi, Subrata, Bijoy, Ankur Guha, Satyajit, Pubaleeba, Bulumoniba, Nabanita, Bimalendu, Kananba for their support and help.

It is privilege to express my gratitude to Mrs. Sutapa Dolui for her motherly care and encouragement.

I thank the Defence Research and Development Organization (DRDO) for funding a project and University Grant Comission(UGC), New Delhi for financial assistance under 'fellowship for meritorious student in science'.

I would like express my love and gratitude to Abba and Amma for their love and faith on me, Mustafizul, Waris and my family members to bear with my countless complaints and encourage me in carrying out my work.

Finally, I would like to thank the authorities of Tezpur Uniuversity for granting me the permission to do this research work.

Muhsina Kafiah Huda

Contents

Chapter 1: Introduction

Chapter 2: Synthesis, characterization and evaluation of thermal and optical properties of 1,3,4-oxadiazole containing polymers

List of Tables

List of Figures

List of Schemes

Abbreviations used in the thesis

EAP	Electroactive polymer
OLED	Organic light emitting diode
CP	Conductive Polymer
PLED	Polymer light emitting diode
LED	*Light emitting diode*
EL	Electroluminescence
HTL	Hole transporting layer
ETL	Electron transporting layer
EML	Emitter layer
LCD	Liquid crystal display
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
PDHF	poly(9,9'di-n-hexyl fluorene)
ITO	Indium tin oxide
PBD	2-(4-Biphenylyl)-5-phenyl-1,3,4-oxadiazole
PDAF	Polyalkylfluorene
PPP	poly(p-phenylene)
PL	Photoluminescence
PT	Polythiophene
PCHMT	Poly(3-cyclohexyl-4-methylthiophene)
Ca	Calcium
Al	Aluminium
Cu	Copper
Ag	Silver
Ni	Nickel
Zn	Zinc
PPy	Polypyridine
PPV	p-phenylenevinylene

QE	Quantum yield
PVK	Polyvinylcarbazole
OXD	Oxadiazole
P-oxd	Polyoxadiazole
MEH-PPV	Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]
PF	Polyfluorene
ETM	Electron transporting material
UV	Ultraviolet
Mg	Magnesium
NIR	Near infra red
PU	Polyurethane
DMF	Dimethylformamide
DMAc	Dimethylacetamide
NMP	N-methylpyrrolidone
THF	Tetrahydrofuran
DMSO	Dimethylsulfoxide
PEDOT:PSS	Poly(ethylene-dioxythiophene)/poly(styrene sulphonic acid)
NPB	N'-diphenyl-N,N'-bis(1-naphthyl)(1,1'-biphenyl)-4,4'diamine
PMMA	Polymethylmethacrylate
PFO	poly(9,9'-dioctylfluorene)
ZnO	Zinc oxide
KBr	Potassium bromide
$Zn(POTPA)_2$	
FTIR	Fourier transform infrared spectroscopy
NMR	Nuclear magnetic resonance
TGA	Thermogravimetric analysis
DSC	Differential scanning calorimetry

TEM	Transmission electron microscope
SEM	Scanning electron microscope
XRD	X-ray diffraction
CV	Cyclic voltammetry
RGB	Red-green-blue
GPC	Gel permeation chromatography
ATPH A	Amine terminated polyhydrazide from terephthaloyl chloride
OXD A	Poly 1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene
OXD AR1	Poly 1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing –NO_2
OXD AR2	Poly 1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing -Cl
OXD AR3	Poly 1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing -CH_3
OXD AR4	Poly 1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing –OH
OXD B	Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene
ATPH B	Amine terminated polyhydrazide from isophthalic acid chloride
OXD B	Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene
OXD BR1	Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing –NO_2
OXD BR2	Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing –Cl
OXD BR3	Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing -CH_3
OXD BR4	Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing –OH
PU1	Polyurethane containing 1,3,4 oxadiazole moiety and

	toluene diisocyanate
PU2	Polyurethane containing 1,3,4 oxadiazole moiety , binaphthol and toluene diisocyanate
PU3	Polyurethane containing 1,3,4 oxadiazole moiety and hexamethylene diisocyanate
PU4	Polyurethane containing 1,3,4 oxadiazole moiety, binaphthol and hexamethylene diisocyanate
T_g	Glass transition temperature
T_m	Melting temperature
T_d	Onset degradation temperature
TDI	Toluene diisocyanate
HMDI	Hexamethylene diisocyanate
λ	Wavelength
φ	Quantum yield
E_g	Band gap
h	Plank's constant
c	Wavelength of light
LiF	Lithium fluoride
I-V	Current-voltage
$LiClO_4$	Lithium perchlorate
NC	Nanocrystal

CHAPTER 1

Introduction

Chapter 1: Introduction

1. Introduction

Light is the source of life. The sustainability of a life on the earth starts with the light and water. The cold earth become adaptable for the life with the light and heat from the sun, the ultimate source of all energy. There are different sources of light energy; direct and indirect. More than sensory energy, sunlight fuels the earth by taking part in the preparation of food. The other forms of light energy are the converted form of mechanical or electrical energy. Yet the 21st century people are more advance in harvesting light in a more smart way by developing 'smart materials' or the 'intelligent material'. Electroactive polymers for light emitting diode application are another breed of intelligent material tailor made to harvest light from the electrical energy.

1.1 Electroactive polymer

Electroactive polymers or more simply EAPs have attracted much attention from engineers and scientists from diverse disciplines. The advancement of the EAPs is found in the area of display application, energy conversion from light to electrical energy, electrochemistry and in actuators etc[1-3].

A material can be defined electroactive if it responds to an electrical stimulation with a reversible variation of one or more physico-chemical properties. The electroactivity of a material can be evaluated in several respects. In relation to the particular applications, definite output variables are taken into account in order to quantify the material response. Owing to the ease of generation and processing of electrical input signals, electrically responsive materials with tailorable functionalities (as electroactive polymers) are considered today as smart materials. For many years, several types of electroactive polymers (EAPs) have been widely investigated for different kinds of applications, including chemical and physical sensors, actuators and a large number of electronic and optoelectronic devices like organic light emitting diodes(OLEDs), electron and ion conductors, photoconductors, batteries, photovoltaic cells, supercapacitors, field-effect transistors, optical memories, photodiodes, electrochromic and photoelectrochromic components and even lasers. The continuous demand for new products requiring novel solutions, unthinkable until a few years ago, is today greatly driving such investigations, in order to replace the conventional electric, electronic and optoelectronic devices with smart plastics capable of offering improved functioning in many niche applications. Electronic/optoelectronic components for portable, flexible or even wearable systems like electroluminescent devices, electrochromic cells, keyboards, displays, sensors and processors used for personal information and monitoring are just some examples of possible fields of application of organic electroactive materials. Such a trend is encouraged not only by already demonstrated and continuously improving tunable active performances of organic materials, but also by the flexibility (compliance) offered by most of the organics, overcoming the typical stiffness of inorganic materials (such as silicon).Moreover, organic materials offer low weight and low cost, combined with a remarkable ease of processing techniques like spin coating, ink-jet printing or casting. This method is considered inexpensive when compared with usual processes required by inorganic materials, such as vacuum vapour deposition[4-10].

There are two major categories of EAPs depending on their mode of activation mechanism; these include *electronic* and *ionic* categories. Electric field or Coulomb forces generally drive electronic EAPs, while the primary driver for ionic EAPs is the mobility or diffusion of ions[1] (**Table 1.1**)

Table 1.1: The leading EAP materials[16-17]

Electronic EAP	**Ionic EAP**
Dielectric EAP	Carbon Nanotubes
Electrostrictive Graft Elastomers	Conductive Polymers
Electrostrictive Paper	Electro Rheological Fluids
Electro-Viscoelastic Elastomers	Ionic Polymer Gels
Ferroelectric Polymers	Ionic Polymer Metallic Composite
Liquid Crystal Elastomers	

Conductive Polymers (CP)

Among the various categories of EAPs, conducting polymers with conjugated double bonds have received great interest because of their wide range of potential applications, including optoelectronic applications like light-emitting diodes, batteries, electrochromic devices, sensors, photovoltaic devices, electromagnetic shielding and corrosion inhibition. Since they combine the chemical and mechanical properties of the polymers with the electronic properties of the metals and semiconductors, these materials are often termed as synthetic metals. CPs actuate via the reversible counter-ion insertion and expulsion that occurs during redox cycling. Significant volume changes occur through oxidation and reduction reactions at corresponding electrodes through exchanges of ions with an electrolyte[11-14].

Conjugated polymers and polymers carrying the heteroaromatic rings with lone pairs of electrons often used as the conducting polymers. Examples for CP are polypyrrole[15], polyethylenedioxythiophene[16], poly(p-phenylene vinylene)s[17], polyaniline[18], polyoxadiazoles[19], polythiophenes[20] etc. These polymers and its derivatives made their use in the fabrication of polymer light emitting diodes (PLEDs)[21], solar cells[22], sensors[23] etc. Light emitting diodes are commercially valuable materials for the display application from television, mobiles to the detectors and signaling equipments used in defence. Some applications reported for these CPs are miniature boxes that have the ability to open and close, micro-robots, surgical tools, surgical robots that assemble other micro-devices[24-61].

1.2 Luminescence

Luminescence is "cold light", light from other sources of energy, which can take place at normal and lower temperatures. In luminescence, some energy source kicks an electron of an atom out of its "ground" (lowest-energy) state into an "excited" (higher-energy) state; then the electron gives back the energy in the form of light so it can fall back to its "ground" state[62-66].

There are several varieties of luminescence, each named according to what the source of energy is, or what the trigger for the luminescence is.

a) **Fluorescence and Photoluminescence** are luminescence where the energy is supplied by electromagnetic radiation (rays such as light); photoluminescence is generally taken to mean luminescence from any electromagnetic radiation, while fluorescence is often used only for luminescence caused by ultraviolet, although it may be used for other photoluminescences also. Fluorescence is seen in fluorescent lights, amusement park and movie special effects, the redness of rubies in sunlight, "day-glow" or "neon" colors, and in emission nebulae seen with telescopes in the night sky. Bleaches enhance their whitening power with a white fluorescent material. Photoluminescence should not be confused with reflection, refraction, or scattering of light, which cause most of the colors to see in daylight or bright artificial lighting. In photoluminescence light is absorbed for a significant time and generally produces light of lower frequency[64, 67-69].

b) **Chemiluminescence** is luminescence where the energy is supplied by chemical reactions. Those glow-in-the-dark plastic tubes sold in amusement parks are examples of chemiluminescence[70].

c) **Bioluminescence** is luminescence caused by chemical reactions in living things; it is a form of chemiluminescence. Fireflies glow by bioluminescence[71].

d) **Electroluminescence** is luminescence caused by electric current. Cathodoluminescence is electroluminescence caused by electron beams; this is how television pictures are formed. Other examples of electroluminescence are neon lights, the auroras, and lightning flashes. This should not be mistaken for what occurs with the ordinary incandescent electric lights, in which the electricity is used to produce heat, and it is the heat that in turn produces light[72-73].

e) **Phosphorescence** is delayed luminescence or "afterglow". When an electron is kicked into a high-energy state, it may get trapped there for some time. In some cases, the electrons escape the trap in time; in other cases they remain trapped until some trigger gets them unstuck. Many glow-in-the-dark products, especially toys for children, involve substances that receive energy from light, and emit the energy again as light later[74].

f) **Triboluminescence** is phosphorescence that is triggered by mechanical action or electroluminescence excited by electricity generated by mechanical action. Some minerals glow when hit or scratched, as you can see by banging two quartz pebbles together in the dark[75].

g) **Thermoluminescence** is a form of luminescence that is exhibited by certain crystalline materials, such as some minerals, when previously absorbed energy from electromagnetic radiation or other ionizing radiation is re-emitted as light upon heating of the material. The phenomenon is distinct from that of black body radiation. This can be used to date buried objects that have been heated in the past, since the ionizing dose received from radioactive elements in the soil or from cosmic rays is proportional to age[76-77].

h) **Optically stimulated luminescence** is phosphorescence triggered by visible light or infrared. In this case red or infrared light is triggered for the release of previously stored energy[78-79].

1.2.1 Band gap of molecule and polymer and the luminescence

The luminescence efficiency and the colour generation are very much important for the display device application for a particular polymer. Higher is the band gap of the emissive layer, lower is the wavelength of that layer. Cyclic voltammogram is the most commonly used instrument to study the electrochemical nature of the polymer, their redox property, stability during the charge generation and the emission process under the applied potential. The oxidation reduction potential or more commonly the doped-undoped state of a polymer and its performance under electric field is much important to determine the lifetime and luminescence efficiency of the polymer[67-69, 80].

1.3 Electroluminescent device

An electroluminescent (LED) device is similar to a laser in which photons are produced by the return of an excited substance to its ground state, but unlike lasers EL devices require much less energy to operate and do not produce coherent light. EL devices include *light emitting diodes*, which produce light when a current is applied to a doped p-n junction of a semiconductor. EL displays (LEDs) can be used to display text, graphics and other computer images. EL is also used in lamps and backlights. Electroluminescent devices can be fabricated using thin films of either organic or inorganic materials. The organic materials may be small molecules or macromolecules with high or low molecular weights; whereas the semiconducting materials of group III-V, organometallic compounds, sulfides of metal nanoparticles are the inorganic compounds used in the device materials. Contemporary studies include the EL devices with inorganic/organic nanocomposite and hybrids for better quality product. The thin film layers contain a bulk semiconductor (or host material for organic EL) and a dopant which defines the visible color emitted. The semiconductor needs to have wide enough bandwidth to allow exit of the light[28, 39, 43, 81-96].

1.3.1 Structure of Organic Light Emitting Diode (OLED)

Commonly OLED devices may be of two types

a) Single layer devices

A simple single layer OLED consists of an emitter material which is sandwiched between a transparent bottom electrode (anode) and a metal electrode (cathode) on top (**Figure 1.1**). Usually an indium tin oxide (ITO) coated glass substrate serves as a transparent anode whereas the cathode normally consists of metals with low work functions (Al, Mg, Ca). The emitter material can either be a polymer or a low molecular weight compound such as tris(8-hydroxyquinolinato)-aluminium (Alq_3). If an external field is applied between the two electrodes, positive and negative charges are injected at the anode and cathode, respectively.

These charges recombine within the emission layer by the formation of localizedt excited states (excitons) which emits light by radiative decay.

But the disadvantage of single layer devices is the unbalanced charge flow through the devices which leads to higher operating voltages and reduced lifetimes. The difference between the amount of positive (holes) and negative (electrons) charge carriers injected into the device is mainly caused by a mismatch between the HOMO and LUMO levels of the emitter material and the Fermi level of the adjacent electrode. Also, holes possess a higher mobility than electrons in many emitter materials which leads to non radiative neutralization of the positive charges at the cathode[97-99].

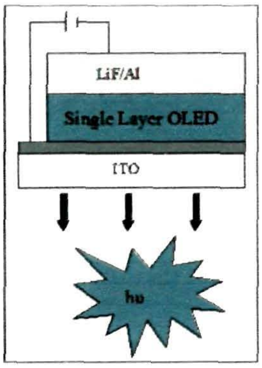


Figure 1.1: Device structure of single layer device

(b) Double layer devices

To circumvent the problem with the single layer devices additional charge-injection layers between the emission layer and the corresponding electrodes is introduced to get the double layer devices (**Figure 1.2**).

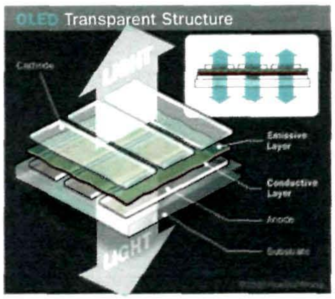


Figure 1.2: Device structure of double layer OLED

The insertion of an electron-conducting/hole-blocking (ECHB) layer effectively inhibits the quenching of holes at the cathode[100-102].

(c) Multilayer devices

The most efficient and compatible device structure for the commercial application is the multilayer devices that consists of the anode/hole transporting layer (HTL)/emitter layer(EML)/electron transporting layer (ETL)/cathode. HTL can transport holes from the anode to (EML) and the electron transporting layer (ETL) is used to transport electrons from the metal cathode to the EML[103-105] **(Figure 1.3)**.

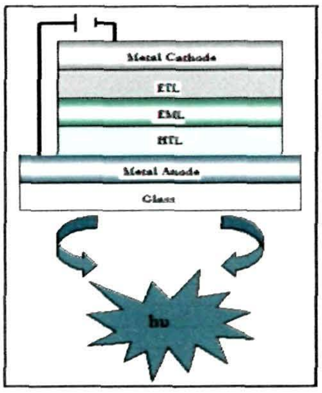


Figure 1.3: Device structure of multilayer OLED

Polymer light emitting diodes (PLEDs) are even more suitable for the display application than OLEDs as they are flexible and are very much suitable for the large area flat panel display. Advantages of PLEDs are given below[106-113]

- A PLED display consists of polymer material manufactured on a substrate of glass or plastic, and does not require additional elements such as backlights, and filters.
- PLED technology is very energy efficient and lends itself to the creation of ultra-thin lighting displays that will operate at lower voltages.

- OLED fabrication needs the vacuum deposition method to coat the anode surface with the organic small molecules; which is a very expensive method. Polymer materials can be spin coated on the anode surface easily.
- The resulting benefits include brighter, clearer displays with viewing angles approaching 180 degrees, simpler construction offering the potential for cheaper, more robust display modules, and ultra-fast response times allowing full colour display even at low temperature.

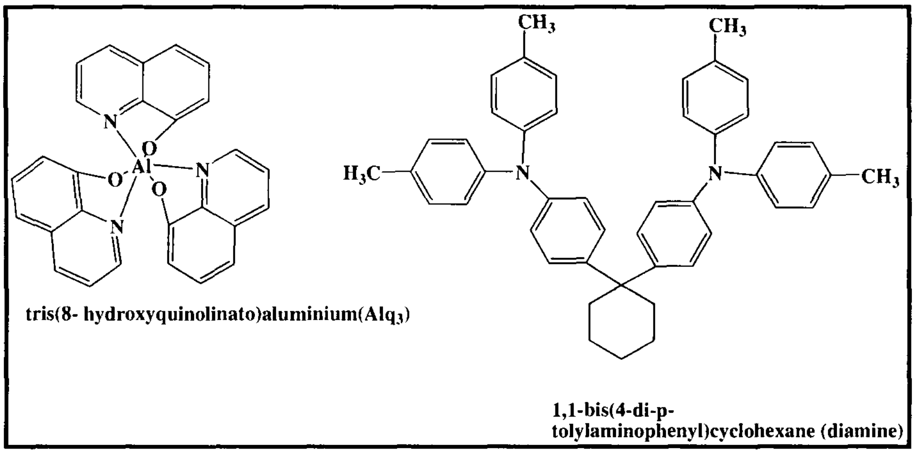
1.3.2 Drawbacks of OLEDs and PLEDs

Regardless of having these qualities, OLEDs and PLEDs have some drawbacks that to be developed in future such as the life time, degradability, colour balance, water resistance and screen burn-in problems. The lifespan of the PLEDs is limited as compared to inorganic LEDs or the LCDs; almost half of their performance time. Besides OLEDs require a colour balance of the pixels emitting the three primary colours; red, blue and green. But the lifespan of the blue light is very short which is creating a colour imbalance in the overall diplay application. Unlike displays with a common light source, the brightness of each OLED pixel fades depending on the content displayed. The varied lifespan of the organic dyes can cause a discrepency between red, green, and blue intensity. This leads to image-persistance, also known as burn-in[114-118].

1.3.3 Scientific Origins

Electroluminescence was first observed in silicon carbide (SiC) by Captain Henry Joseph Round in 1907. Round reported that a yellow light was produced when a current was passed through a silicon carbide detector. Electroluminescence (EL) was observed for the first time in inorganic compounds (ZnS phosphors) as early as 1936 by Destriau. In the mid-1960s, there was a revival of EL research in the United States focused on display applications. Sigmatron Corporation first demonstrated a thin-film EL dot-matrix display in 1965[119-120].

Organic electroluminescence was first discovered by Pope *et al.* in 1963. They observed luminescence when a voltage of about 400 V was applied to an anthracene crystal. However the development of devices based on organic electroluminescence was very slow, because of the high voltage required and the low efficiency. In 1987, Ching W. Tang and Steve Van Slyke developed a novel electroluminescent device at Eastman Kodak Company: this is considered the first organic light-emitting diode. The device was fabricated by vapor deposition using Alq$_3$ and diamine in a double layer structure (**Figure 1.4**). This structure makes the electron and hole recombination effective and the device has a 1% external quantum efficiency, 1.5 lm/W luminous efficiency, and a brightness of more than 1000 cd/m^2 at a driving voltage of about 10 V [121-123].



Figurel.4: First organic electroluminescent material

One of the key disadvantages of LEDs relative to liquid crystal displays (LCDs) was that until 1981 LEDs were not capable of displaying more than one color. Even after 1981, color LEDs was limited to a limited range of colors (red, green, and yellow) until 1993 when a blue phosphor was discovered. Recently, blue, red, and green emitting thin film electroluminescent materials have been developed that offer the potential for long life and full color electroluminescent displays[124-125].

Electroluminescent technologies require low power consumption compared to competing lighting technologies, such as neon or fluorescent lamps. This, together with the thinness of the material, has made EL technology valuable to the advertising industry.

1.4 Chemical Structures and Synthetic Strategies for Light-Emitting Polymers

1.4.1 Requirements for Electroluminescence on a Polymer

Fluorescent conjugated polymers have emerged as an important class of sensory materials for chemical and biochemical targets. This interest has been driven by the ability of conjugated polymers to create large signal amplification relative to small molecule chemosensors due to the delocalization and rapid diffusion of excitons throughout the individual conjugated polymer chains in solution and in thin films.. In photoluminescent compounds generally, the longest wavelength of absorption corresponds to $\pi \rightarrow \pi^*$ excitation. On the other hand, species in which the longest absorption wavelength corresponds to $n \rightarrow \pi^*$ transition (common in molecules containing heteroatoms or heterocyclic aromatic molecules) are seldom fluorescent.

It is observed that the excited singlet state normally has a half-life of $\sim 10^{-8}$ s. If the half-life is $>10^{-8}$ s, intersystem crossing will be favored; a shorter half-life implies rapid deactivation of the molecule by other process. Increasing the extent of conjugation and therefore increasing the mobility of the π electrons often results in an increase in fluorescence intensity. Increasing planarity and rigidity helps to increase fluorescence, as both will also enhance the free mobility of the π electrons and charge transportation. Biphenyl and fluorene possess the same degree of conjugation, but the aromatic rings in the latter compound are held rigidly in a planar configuration, whereas aromatic ring in biphenyl are not[126-128].

The generation of light and colour also depends on the band gap of the polymer HOMO and LUMO energy levels. The electrochemical band gap calculated from the cyclic voltammetry show the colour tuning with the change in their band gaps. Red shifting of light is observed for the high band gap polymer and vice versa129-131.

There are four steps necessary to produce electroluminescence in LEDs:

1. Electrons tunnel from electronic states at the insulator/phosphor interface;
2. Electrons are accelerated to ballistic energies by high fields in the phosphor;
3. The energetic electrons impact-ionize the luminescent center or create electron-hole pairs that lead to the activation of the luminescent center; and
4. The luminescent center relaxes toward the ground state and emits a photon.

1.4.2 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[132-141]:

- 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

Synthesis of conjugated polymer systems for the OLED applications are usually involves electrochemical polymerization and the chemical polymerization method depending on the kind of monomer used and the processibility.

Electrochemical polymerization

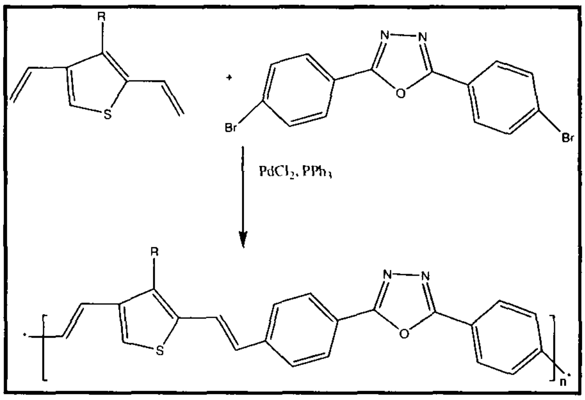
Electrochemical synthesis of conjugated polymers is a novel method in which simultaneous polymerization and doping occur and the polymer is deposited on the electrode surface. Electropolymerisation of monomers in which the oxadiazole ring is adjacent to the thiophene one may be difficult to achieve because of the acceptor character of oxadiazole, which makes the oxidative coupling of thiophene, via the a carbon, more difficult. Therefore, polymers containing thiophene and oxadiazole are prepared by a polycondensation reaction leading to a nonconjugated precursor polymer. Then it is transformed into its conjugated analogue with simultaneous formation of the oxadiazole rings. Moreover, the use of this method inevitably leads to the incorporation of a phenylene rings into the polymer backbone[142-145].

Chemical polymerization

One of the shortcomings of electropolymerization is its limitation in large scale preparation and yielding insoluble materials. Therefore, passionate efforts came into play in developing suitable methods for chemical preparation of conjugated polymers since early 1980's. Chemical polymerization methods for the synthesis of polyoxadiazole and its derivative include Heck Coupling reaction, Suzuki Coupling reaction etc.

Heck coupling reaction to synthesize Oxadiazole derivative (Scheme 1.1)

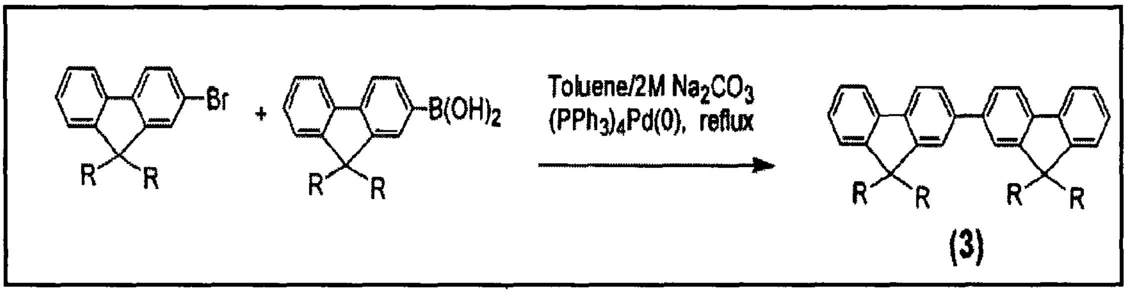
Poly[(2,4-divinyl-3-hexylthiophene)-alt-2,5-bisphenyl-1,3,4-oxadiazole] (P3HTV–OXDwas synthesized by the Heck coupling reaction reacting Poly[(2,4-divinyl-3-hexylthiophene) and 2,5-bisphenyl-1,3,4-oxadiazole as reported by Zheng-Jian Qi and co workers in 2010. [146]



Scheme 1.1: Synthesized Oxadiazole-PPV polymer by Heck Coupling reaction

Suzuki coupling reaction (Scheme 1.2)

This C-C bond formation reaction method used to apply for the synthesis of conjugated systems also. An example shows the alternating copolymers of 9,9-dioctylfluorene and oxadiazole have been prepared by the tetrazole route or the Suzuki coupling reaction. Bis(9,9-dioctylfluorene) (**3**) was prepared by the Suzuki coupling reaction of boronic acid with bromide[147].



Scheme 1.2: Synthesis of fluorene by Suzuki coupling reaction

1.4.3 Characterization Methods for the of luminescent polymers

The chemical structure and the electronic arrangement play an important role in the optical properties of the luminescent polymer. To unveil the structure-property relationship different characterization techniques are employed as discussed in the following sections.

Absorption, photoluminescence and electroluminescence spectroscopy

Generally, the observed transitions in absorption spectroscopy of conjugated polymers are attributed to electronic excitation- emission from π-π^* states and vice versa. Upon electronic excitation of the polymer, a number of photo-physical processes, shown in **Figure 1.5**, may occur: fluorescence, phosphorescence, or radiationless decay. 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[148-151].

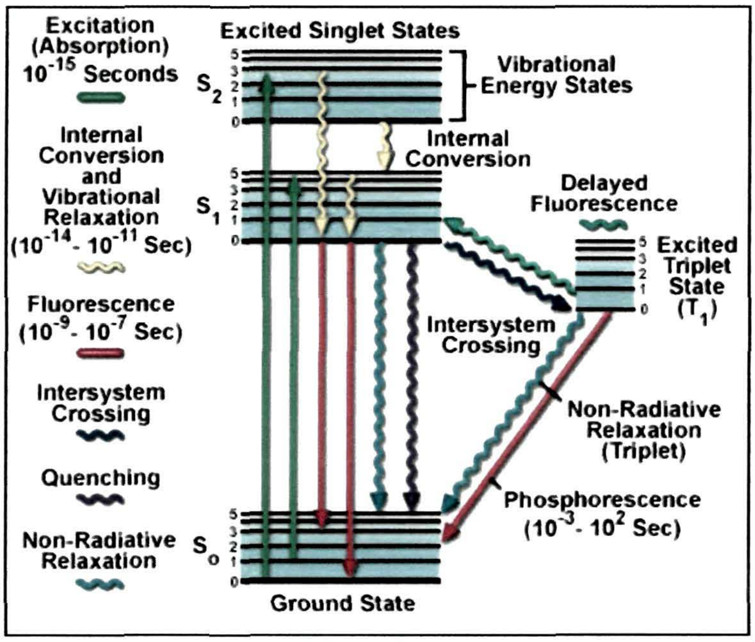


Figure 1.5: Mechanism of fluorescence and phosphorescence

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**[107]

Φ_{PL}= No. of photons emitted/No. of photons absorbed...............(1)

Φ_{PL}=Quantum yield of photoluminescence..

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 (τr) and non-radiative (τnr) decays, as described in **Equation**[151] 2

$$\Phi_{PL} = \tau_r/\tau_r + \tau_{nr} \qquad . \ (2)$$

1.4.4 Working principle of OLED

Electroluminescence (EL) is the generation of light by electrical excitation in fluorescent materials. Light emitting diodes emits light upon electrical excitation. The luminescent materials used in the fabrication of LEDs may be inorganic, organic or polymeric in nature. The materials are deposited as thin film by relatively expensive techniques of sublimation or vapour deposition or spin coating, which are not well suited to fabrication of large area flat panel 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, effortless processing by cheap technologies (spin and blade coating, ink–jet printing), or the ability to tune the emission colour by changing the molecular structure of the emitting material[152,84 89,12].

The process of electroluminescence 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 discharged 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)[88]. 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[34].

Typical pictorial representation of an OLED device is given below in **Figure 1.6.**

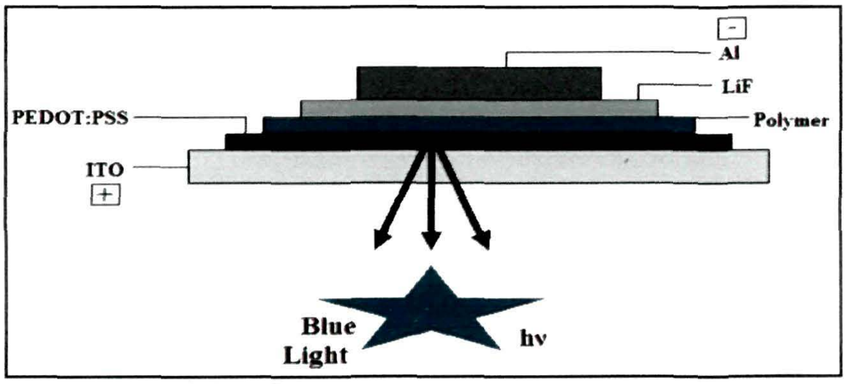


Figure1.6: Fabrication of electroluminescence device

1.4.5 Electrical Conductivity in Polymers

The nature of the electrical conductivity in Semiconducting polymers is a significant tool to investigate the nature and the quality of the polymer for the application as diodes or actuators. Mostly it is found that electrical conductivity varies exponentially with temperature, is a function of time, and may vary with the electrical field[153] i.e.,

$$\sigma = \sigma 0 \exp - E\sigma / kT \text{ ....(3)}$$

Changes in Eσ, the activation energy of conduction, are often observed in the neighborhood of glass-transition temperatures. Since conductivity is made of terms relating to both the number and the mobility of the charge carriers, any prediction regarding the conduction process that does not recognize these dependences is insignificant. As more mobility measurements have been carried out, it has become recognized that the motion of the charge carriers is an activated process. Thus, the simple assumption that polymer can be described in terms similar to those used for crystalline covalent semiconductors[154-155]

The Charge Carriers

Ways of balancing charge injection which have met with notable success are as follows[85, 156-162] (**Figure 1.7**):

(i) A low work function metal, such as calcium, can be used as the cathode to lower the energy barrier to electron injection into the polymer film. The drawback of this strategy is that such metals are highly reactive and are unstable in the atmosphere.

(ii) Multilayer structures can be assembled with an electron transporting hole-blocking (ETHB) layer placed on top of the emissive polymer film (by spin-coating or thermal evaporation) before deposition of the cathode. This approach requires more complex fabrication procedures than those used for single-layer devices

(iii) Electron-deficient segments can be covalently bound to the emissive polymer, either by insertion into the main-chain, as end-capping groups, or as pendant side-groups. The synthesis of these polymers can be very challenging, often requiring multi-step routes and/or specific cross-coupling reactions.

(iv) Electron transport materials can be blended into the emissive polymer prior to deposition. Single-layer devices of this type have the advantage that their manufacture requires only a single spin-coating process.

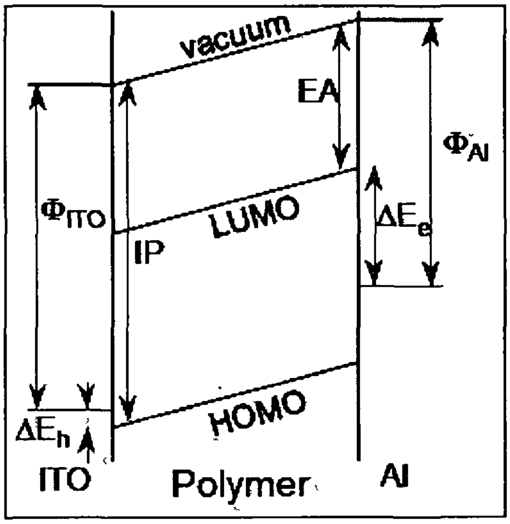


Figure 1.7: Energy level diagram of LED device

1.5 Blue light emitting polymers and polyoxadiazoles

1.5.1 Stipulate to develop the blue light emitting polymer

In the past two decades, organic light-emitting devices (OLEDs) have attracted a great deal of interest because of their potential applications in full-colour flat-panel displays. Polymers with aromatic or heterocyclic units generally absorb light with wavelengths in the range from 300 to 500nm due to π-π* transitions[98, 145-147]. The colour of the electroluminescent emission of π-conjugated polymers depends upon their conjugation length. In particular, short-range conjugations are responsible for blue-shifted emissions, whereas red-shifted colours are ascribable to long-range conjugations. Therefore, as for electrochromic polymers, a high degree of colour tailorability can be achieved by synthesizing electroluminescent polymers with specific conjugation lengths. The excited states of electrons of chromophores (excitons) release energy radiatively as well as nonradiatively on returning to the ground state. The radiative decay of excitons to the ground state can emit visible light. These excitons are also formed when a bias potential is applied to an emissive polymer sandwiched between an anode and a cathode due to the recombination of holes and electrons. The color of light, quantum efficiency of light emission, turn-on voltage and stability of the devices must be optimized for LEDs to be applicable as commercial light emitting devices. As one of the three primary colours, blue emission is important in full-colour displays. The large energy gap hole and electron transporting layers are the beneficial key for confining excitons in the emissive layer and improving the efficiency of the blue OLED. Amongst the variety of EL conjugated polymers, blue-light emission is deemed desirable since it is generally more difficult to fabricate such LEDs from inorganic semiconductors. Furthermore, full color exhibition and white-light devices need blue light. There are very effcient dyes for converting the energy of incident light of a short wavelength to that of a longer one. Blue light can be converted to green or red with proper dyes, which means a blue PLED alone may generate all colors while green or red cannot be converted to blue by the same method[162-168]. For blue emission, conjugated polymers need to have a large bandgap and defined optical properties. The photoluminescence bahaviour of the light emitting polymers can be controlled by two major routes: a)increasing or decreasing the band gap of the polymer by introducing substituents on the polymer backbone that changes the electronic structure of the material and b)reducing the effective conjugation length of the polymer by introducing torsion in the polymer backbone with sterically bulky side chains or by breaking the chain conjugation with non-conjugated monomer during the copolymerization process. Nevertheless, the operating voltages of the blue light emitting materials are generally high because of the mismatch of their lowest unoccupied molecular orbital (LUMO) levels and the work function of the cathode materials. However, improvements in processability, mechanical properties and stability are desirable. Recently, research into new blue EL materials achieved by controlling the effective conjugation has been reported. For example, blue EL polymers have been synthesized by different approaches such as capping a polymer backbone with non-conjugated units, separating the emitting units with non-conjugated spacers as in conjugated nonconjugated block copolymers, inserting meta linkages in the main chain, or imposing steric distortions in the main chain[125].Full color LED displays may be constructed in different ways such as filtering white light for a specific color, applying different bias potentials to LEDs, using efficient dyes to convert colors, or patterning pixels for the three principle colors (blue, green, red) independently. Color filtering of white light is simple but wastes energy due to the generation of unwanted colors. Some light emitting materials produce different colors depending on the operation potential. However, it may not be easy to control the light intensity and the emission color at the same time. There are very efficient dyes for converting the energy of incident light of a short wavelength to that of a longer one. Blue light can be converted to green or red with proper dyes, which means a blue PLED alone may generate all colors while green or red cannot be converted to blue by the same method. Although all three principle colors have been demonstrated in PLEDs, only green and orange PLEDs currently have the abilities to meet requirements for commercial uses. Blue light-emitting polymers for commercial use are still undeveloped, and the red light-emitting polymers must be further improved[169-170]

1.5.2 Fluorophores for blue light emission

The fluorophores for blue color emission consist of chemical structures like phenyl, or fluorene, or heterocycles such as thiophene, pyridine and furan as shown in **Figure 1.8**. These fluorophores are either in the polymer backbone or in the side chain. Multiple substitutions of alkyl, alkoxy or aromatic groups on the fluorophores are adept to enhance interactions in order to change fluorophore planarity for a color-shift of the emission spectrum, to disturb excimer formation and/or to enhance the solubility of the polymers[98.104.145.147171-173]. The first PLED for blue color emission was fabricated in 1991 from polyfluorene[174].

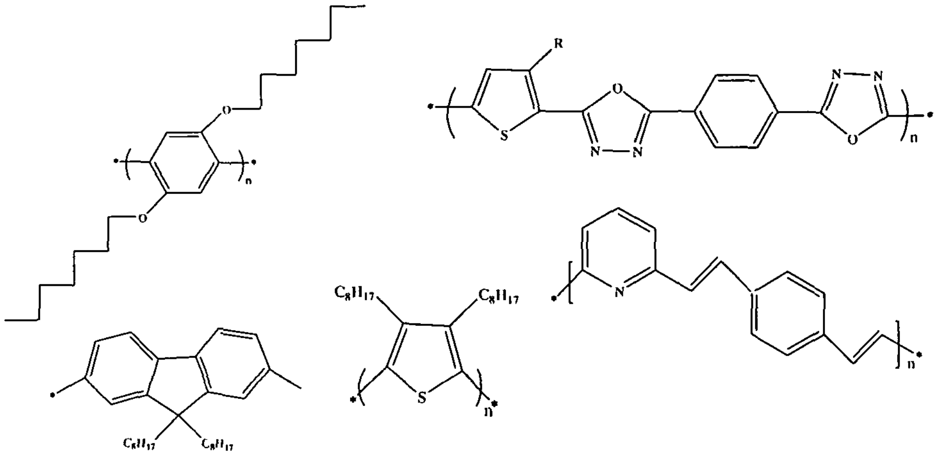


Figure 1.8: Flourophores for the blue light emission

Other active materials for blue LEDs are done mainly on polyalkylfluorene (PDAF) and poly(p-phenylene)s (PPPs)[175-176]. The photoluminescence (PL) spectrum of the polymer gives an emission maximum at 460 nm on photoexcitation at 351 nm. The LED fabricated with PPP emits light with a blue color. The electroluminescence (EL) spectrum shows the emission maximum at 485 nm. PPP makes robust films but its poor solubility *and low QE are critical handicaps for commercial use. Electrochemically* and chemically obtained alkyl derivatives of the PPP polymers show improved quantum efficiency in the

OLED performance. The para and meta linkage in the polymer backbone affect the luminescence efficiency and the device performance of the polymers. Alkoxy substituted PPP polymers show a good bathochromic shift in the visible region and are soluble in organic solvents also[177-181].

Polythiophenes (PTs) occupy a prominent position in polymer electronics because of their unique electronic and optical properties. The band gaps for polythiophenes(PTs) can be controlled over 2 eV covering the full visible spectrum from blue to infrared by introducing steric hindrance via bulky side chain substituents on the thiophene unit. Poly(3-cyclohexyl-4-methylthiophene) (PCHMT) exhibits the widest band gap among the polythiophenes and the PL maximum of a chloroform solution is 460 nm. The LED fabricated with a bilayer of PCHMT as the emitting layer and PBD as an electron transporting layer sandwiched between ITO and Ca gives an external QE of 0.6% and an EL maximum at 460 nm. A polythiophene with a crown ether unit attached to 3 and 4 positions also gives an EL maximum for the LED with a structure of ITO/polymer/Al at 470 nm. The polymer with the crown ether units in the reduced state is stable in air, different from other polythiophenes. It appears that polythiophenes with substituents on 3 and 4 positions of the thiophene unit have a short conjugation length, giving light emission in the blue region. Poly(dioctylthiophene) shows a PL maximum in toluene at 470 nm . The LED with a structure of ITO/ Poly(dioctylthiophene)/In shows a EL maximum the same as that for the PL[16, 182-184].

Polypyridines(PPy) are the class of another blue light emitting polymer commonly soluble in mineral acids gives a PL maximum at 460 nm on photoexcitation at 370 nm. The LED fabricated with PPy spin-coated onto ITO followed by the evaporation of Al has an EL maximum at 497 nm, a blue-green color[173].

Polyoxadiazoles and its derivatives are the class of polymer that gives intense blue light with PL maxima around 450nm. Polyoxadiazoles were discovered in 1960's and developed during the 70's as a promising heat resistant material. The application of the polyoxadiazoles in the display application came into play during the late 1980's where the substitute polyoxadiazole was used as an electron transporting material by C Adachi, T Tsutsui and S Saito[34]. The use of polyoxadiazoles in the display application is in high demand due to its electron deficient system. Therefore the polyoxadiazoles are a good carrier of electron and show high absorption and the emission property. Besides homopolymers, copolymers of PPP, PPV, polyfluorene, polythiophene, polyoxadiazole are the promosing candidates for the blue light emission[185-188]. These includes[46]

i. Copolymers of PPP with phenylene, vinylene or acetylene units in the backbone
ii. Copolymer of fluorene and phenylene unit
iii. Polythiophene copolymerize with phenylene and acetylene unit
iv. Copolymers of polycarbazole and thiophene
v. Copolymers of polyoxadiazole with thiophene and carbazole unit
vi. PPV copolymer with oxadiazole and carbazole unit

Blue light-emitting polymers with isolated fluorophores includes[46]

i. Polymers with alkylene units
ii. Polymers with ether linkages
iii. Polymers with silylene linkages
iv. Polyesters
v. Polyamides, polyurethanes and polyimides
vi. Polymers with blue light emitting pendant groups

1.5.3 Blue light emitting 1,3,4 Oxadiazole containing polymer and electron transporting properties

Drawbacks to 1,3,4-oxadiazole containing polymers are 1) the poor solubility they impart and 2) the lack of thorough understanding as to the specific contribution of oxadiazole units makes to the optical and electronic characteristics of their compounds. Practically, the issue of solubility has been addressed by the addition of flexible side chains, often alkoxy structures of various lengths, to the rigid oxadiazole backbone[46].

Out of the different classes and array of polymers scientists are always engaged in developing wide band gap electron transporting polymers for blue light emission. Many efforts have been made to synthesize polymers with either hole or electron transporting properties or with both properties in one polymer chain in order to confine the excitons away from quenching sites. Polymers may give better results for LED performance if charge transporting polymers are also light emissive with a wider band gap than the main light emitting material to confine the excitons in the emitting layer. Excitons formed in the charge transporting layer may also transfer energy to the fluorophores in the light emitting layer to provide high QE values[46.189-190].

During the OLED operation, the mobility of the injected charges within polymers is rather low compared to inorganic semiconductors. Shortening the recombination time for the two opposite charges in the light emitting layer is required. Most light emitting polymers have either hole transporting or electron transporting characteristics. It is desired that the recombination of charges should occur away from the electrodes in order to reduce exciton quenching at the electrode surfaces. Organic materials dispersed in inert polymer matrices or vaporized in vacuum to form individual layers have been used for charge transport in the fabrication of LEDs. However, LEDs are heated up during their operation often resulting in poor LED performance due to the crystallization of the organics[101, 191].

Most of light emitting polymers with π-conjugations are p-dopable and show a greater tendency for transporting holes than electrons. Charge imbalances in the charge recombination zone are one of the key obstacles for increasing the QE of PLEDs. It has been known that imine nitrogens -C=N with electron-accepting properties are susceptible to chemical and electrochemical reduction, and generate negatively charged carriers in the polymer backbone. Oxadiazoles are deficient in electrons and are capable of n-doping. Pyridine, quinoline, quinoxaline, triazine and bithiazole are all capable of electron transporting properties[46].

Addition of flexible side chains to the oxadiazole polymers to impart solubility

One of the most efficient electron transporting organic materials is PBD of which the oxadiazole unit has a high electron affinity. Since low molecular weight organics dispersed in an inert polymer have a tendency to crystallize at elevated temperature reached during device operation, polymers with oxadizole units in the backbone or in side chains have been utilized as electron transporting materials. An alternating copolymer with a structure of m-(butylphenyl)oxadiazole and p-phenyloxadiazole fluoresces purple-blue (PL maximum near 410 nm) under UV irradiation with a quantum yield of 11%. An LED fabricated with an alternating copolymer of oxadiazole and stilbene sandwiched between ITO and Al possesses an EL maximum at 483 nm. The oxadiazole units confine the conjugation to the stilbene units. The copolymer shows emission in the blue region, and at the same time the oxadiazole units render the electron transporting capabilities. The polymer with a repeating unit of styrylstilbene oxadiazole shows a PL maximum in chloroform at 440 nm while its film shows the emission at 502 nm. A LED with a structure of ITO/OXD-stilbene/PBD/Al exhibits an EL maximum at 470 nm. It has been observed that the PL spectrum red-shifts into the green region when the phenylene units in the polymer are disubstituted by octyloxy groups. Similarly (PVK-Ox) of poly(vinyl carbazole) derivatives preared also show good luminescence and high quantum yield properties. PVK-Ox a good electron-blocking layer. The single layer nature and the use of soluble materials simplify the fabrication of devices by common solution coating techniques. The color of the emitted light can be tuned across the visible spectrum by using appropriate dyes[46. 192-199].

Three vinyl copolymers containing pendant aromatic 1,3,4-oxadiazole derivatives were prepared from their precursor poly(styrene-ran-4-vinylbenzyl chloride). The photoluminescence spectroscopy revealed that the architectures of polymers suppressed aggregate formation in the solid state. The luminance and current efficiency of an electroluminescence device [indium tin oxide/poly(3,4-ethylene dioxythiophene)/MEH-PPV/Al] were improved significantly through blending with the vinyl copolymers. This study proved that copolymers are versatile materials for electron-transport/injection applications. Another new class of emitter molecules having an oxadiazole group as an electron transport unit and a triphenylamine group as a hole transport unit showed strong blue-green fluorescence, ranging from 450 to 490 nm. With the best device using these emitters, the maximum luminance exceeded 19 000 cd/m^2 and a quantum yield of 4% was obtained. The optimum EL cell structure was studied using the bipolar emitters. But the durability performance of the EL device with the emitting material was quite inferior. The time for the luminance to decay to half of the initial luminance was below 1 h. Besides the use of oxadiazole molecules as an electron transporting material (ETM), these materials were useful for an emissive layer (EML). Because the dimethylamine group has hole-transport ability, the molecules have a bipolar transport character and thus offered good recombination sites for hole and electron charge carriers[200-201].

Polyurethanes (PUs) have been widely used in industrial applications due to their better elasticity, flexibility, thermal stability, and excellent chemical resistance. Due to their good solubility in polar aprotic solvents such as DMF, DMAc and NMP and film forming capability; they are the appropriate candidates for study. However the application of the polyurethanes in PLED application has recently been reported. Again due to the metal ion free synthetic pathway for the polyurethanes is advantageous for the PLED application because a low level contamination of the metal ions in polymer can affect the properties to a great extent. As PUs can be synthesized from the condensation of diols and diisocyanates, where no metal containing reagents are used the ionic contamination is minimized. Polyurethane reported for the PLED application (**Figure 1.9**) till date are very few and are mostly used in LCPs where it is found to have good solubility as well as film casting properties. In addition polyurethanes as polar polymers are thought to play an important role in the efficiency of OLEDs because in the past studies it has been reported that the grafting of dipolar molecules on the ITO surface will enhance the device performance[202-204].

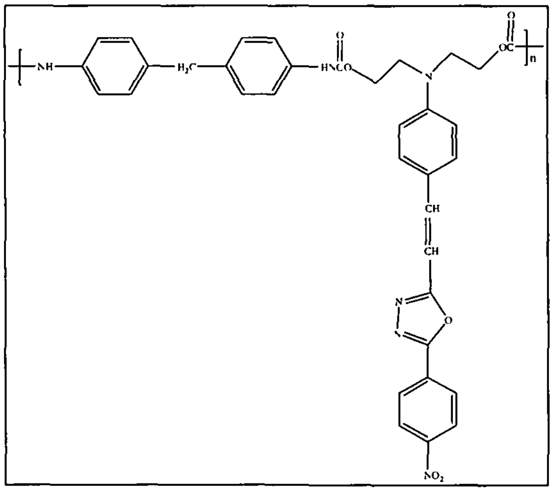


Figure 1.9: Polyurethane containing oxadiazole moiety for OLED application

A novel family of hole-transport polyurethanes (PUs) has been developed. The PUs were prepared from the condensation polymerization of isophorone diisocyanate with (*E,E*)-1,4-bis(2-hydroxystyryl) benzene, an oligo *p*-phenylene-(*E*)-vinylene unit, and various amounts of 2,5-bis(4-hydroxyphenyl)-1,3,4-oxadiazole (OXD), as well as with 4-*tert*-butyl phenol as the terminal group. The PUs demonstrates superior properties on the basis of the improved current injection in the corresponding hole-only device. The OLED device with the OPV-PU interfacial layer inserted in ITO/PEDOT: PSS(20 nm)/PU(30 nm)/R-NPB(10 nm)/Bebq2(20 nm)/Ca(10 nm)/Ag(100 nm) has a dramatic voltage reduction of 2.5 V under the current density of 100 mA/cm^2. When compared to the control device, the current efficiency is improved 2.37 times[205].

Distyrylbenzene derivatives with electron-transporting segments (1,3,4-oxadiazole derivatives) have been reported. In an effort to decrease the electron-injection barrier from the anode electrode, four copoly(aryl ether)s consisting of alternating isolated electron transporting [2,5-diphenyl-1,3,4-oxadiazole the polymers and 5,5 '-diphenyl-2,2'-*p*-(2,5-bishexyloxyphenylene)-bis-1,3,4-oxadiazole and emitting chromophores (1,4-distyryl-2,5-dihexyloxybenzene and 1,4-distyryl-2,5-dihexylbenzene), have been synthesized by the nucleophilic displacement reaction between bisfluoride and bisphenol monomers. Single-layer light-emitting diodes (Al/Polymer/ITO glass) have been fabricated that divulge blue and purple-blue electroluminescence. Moreover, the incorporation of bisoxadiazole units increases the electron affinity and reduces the turn-on electric field better than one oxadiazole unit[201].

Poly(amine-1,3,4-oxadiazole) prepared from the poly amine hydrizide via the cyclization route are readily soluble in many common organic solvents, and could be solution cast into transparent, tough, and flexible films with good mechanical properties. Their photoluminescence spectra in NMP solution and film show maximum bands around 459–461 nm in the blue region. The polymers reveal excellent stability of electrochromic characteristics, changing color from original pale yellowish to blue[206].

Addition of flexible alkoxy and polar substituents to the oxadiazole polymer for colour tuning and solubility (Figure 1.10)

Introduction of electron-deficient 1,3,4-oxadiazole pendant units into poly(p-phenylenevinylene) as a side chain, increase the luminance efficiency by 20 cd/A. These results are attributed to the high electron affinity and the good electron transport of the oxadiazole units, which facilitate electron injection from the Al electrode, and bipolar transport in the active layer. A new series of high brightness and luminance efficient poly(p-phenylenevinylene)(PPV)-based electroluminescent (EL) polymers containing oxadiazole and their corresponding random copolymers with an electron-deficient 1,3,4-oxadiazole unit on the side groups, were synthesized through the Gilch polymerization method. Double-layer LEDs with an ITO/PEDOT/polymer/Al configuration were fabricated by using those polymers. Electrooptical properties and device performance could be adjusted by introducing the Oxa-PPV content in the copolymers. A copolymer with 3-alkylthiopheneoxadiazole and phenyleneoxadiazole units linked alternatingly has a conjugation throughout the molecular backbone without a vinyl unit show improved solubility and luminescence property [46,207-209].

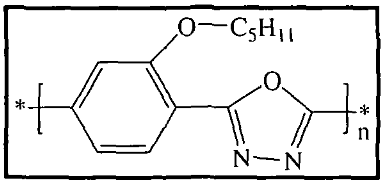


Figure 1.10: Alkoxy substituted oxadiazole containing polymer

Large band gap Polyfluorenes (PFs) have been intensively studied as promising electro-optical polymers for electroluminescence (EL) devices. The major advantages of PFs are their facile solubility and their large band gaps for blue emissions, and the high photo-oxidation stability. Some PF derivatives with electron-transport (*n*-type) moieties have been reported (**Figure 1.11**). Blue-light-emissive fluorene-based polyoxadiazole, an *n*-type polyfluorene derivative, was synthesized by both one-step and two-step methods. Directly polymerized poly[(9,9'-didodecylfluorene-2,7-diyl)-*alt*-(1,3,4-oxadiazole-2,5-diyl)] (PFOx-DP) exhibited a more efficient photoluminescence quantum yield than poly[(9,9'-didodecylfluorene-2,7-diyl)-*alt*-(1,3,4-oxadiazole-2,5-diyl)] (PFOx) prepared via a polyhydrazide precursor. Both polymers, differently prepared, showed similar photoluminescent properties in 1,2-dichloroethane. The electron-deficient property of an oxadiazole group in the polymer backbone resulted in low-lying highest occupied molecular orbital and lowest unoccupied molecular orbital energy levels of -6.29 and -3.26eV, respectively, of the polymer suitable for electron-transport/hole-blocking layers and emissive layers in multilayer electroluminescence devices[210]. 1, 2 Poly(dioctyl fluorene) is known as a highly fluorescent blue light emitting material and oxadiazole containing molecules have widely been used as the electron transporting and hole blocking materials because of its relatively high electron affinity.

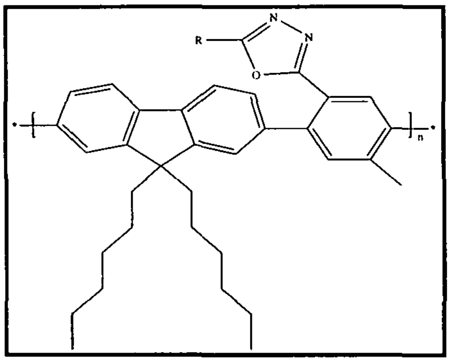


Figure 1.11: Polyfluorene containing oxadiazole moiety

Using (MEH-PPV) as the emissive material with the electron transport (ET) compounds used for electron injection, it seems that electroluminescence originates exclusively from the MEH-PPV material. The external quantum efficiencies of the devices increased with increasing concentration of the ET compound. Hedrick reported the synthesis of some oxadiazole polyethers from 2,5-bis(4-fluorophenyl)-1,3,4-0xadiazoles and various para-substituted bisphenols. Another synthetic aspects of new aromatic polyethers containing oxadiazole units are described. All polyethers are fully soluble in common organic solvents and excellent films are obtained by spin-coating. Strukelj et al. introduced 1,3,4-OXD units into the side chain of PMMA backbone, which improved Tg and when used as electron transporting materials, enhanced the lifetime of devices. A series of novel mesogen-jacketed polymers containing styrene and oxadiazole units with side alkyl groups were incorporated into polymer light-emitting device as the light-emitting layers. All of the polymers have excellent solubility in common organic solvents[46,210-211]

Colour tuning of the oxadiazole based polymers with metal ions, metal complexes and semiconductor nanoparticles

Recently, the phosphorescent polymer light emitting devices (PLEDs) using polymers as hosts and phosphorescent dyes as guests have attracted increasing attention because of their potential applications in large-area displays and backlights. In these guests and hosts systems, most of the phosphorescent dyes-based guests are cyclometalated iridium complexes; and the polymeric hosts arc poly (N-vinylcarbazolc) (PVK), poly(9,9'-dioctylfluorene)(PFO), poly[2-(6'-cyano-6'-methylheptyl)oxy 1,4phenyl], hyperbranched polyfluorene-p-substituted triphenylamine, polyhedral oligomeric silsesquioxane terminated poly(9,9-dioctylfluorene) and poly (9,9'-alkyl-3,6-silafluorcnc). Optoelectronic properties of the oxadiazole-functionalized iridium complex-doped polymer light-emitting devices(PLEDs) are demonstrated with two different polymeric host matrices at the different dopant concentrations. The devices using a blend of poly(9,9-dioctylfluorene)(PFO) and 2-(4biphenyl)-5-(4tert-butylphenyl)-1,3,4oxadizole(PBD) as a host matrix exhibited a maximum luminance efficiency of 11.3cd/A at 1 7.6mA/cm2. In contrast, the devices using a blend of poly(N-vinylcarbazole) (PVK) and PBD as a host matrix reveal only a peak luminance efficiency of 6.5cd/A at 4.1 mA/cm^2. The significantly enhanced electrophosphorescent emissions are observed in the devices with the PFO-PBD blend as a host matrix[46]. This indicates that choice of polymers in the host matrices is crucial to achieve highly efficient phosphoresce. Electroluminescent polymer nanocomposite hybrid from PEDOT:PSS and ZnO was reported by Chang and the coworkers with much improvement in the emissive and the semiconducting properties. Bloom and his coworkers reported the current–voltage characteristics of light-emitting devices containing thin films of poly-dialkoxy-*p*-phenylene vinylene(PPV) incorporated with silicon dioxide nanoparticles. It is demonstrated that the current enhancement of the devices containing composite layers can be modeled by assuming that the effective thickness of the composite layers is about half of their actual thickness. Oxadiazole complexes have electron-transporting ability and high luminous efficiency, but they usually cannot transport holes. To enhance the emission and device performance the concept of bipolar complexes has been introduced. The new oxadiazole complex with bipolar ligand, Zn(POTPA)2,was designed and synthesized, and used as an emitter material in single-layer organic electroluminescent (EL) devices (OLED). The UV absorbance of Zn(POTPA)2 is caused by electron π–π^* transition. $Zn(POTPA)_2$ exhibits strong blue luminescence in solution and film. Compared with triphenylamine and 2,5-diphenyl-1,3,4-oxadiazole, cyclic voltammograms exhibited that Zn(POTPA)2 has bipolar properties, and the optical band gap energy calculated based on the cyclic voltammograms is nearly equal to that deduced from the absorption spectrum. Single-layer device with the structure of ITO/Zn(POTPA)2/Mg:Ag were fabricated and blue electroluminescence was observed with a maximum luminance of 271 cd/m^2 and efficiency of 0.46 cd/A. Oxadiazole derivative carbon nanotube composite was reported to improve the performance of the polymer and its mechanical properties. But not much emphasis was put on the improvement in the luminescent properties and the semiconducting properties of polyoxadiazoles by inorganic nanoparticles. Polyoxadiazoles are UV light emitting polymers with an electron deficient system; hence their properties can be improved by the incorporation of inorganic particles to tune the band gap of the polymer[212-219].

1.6 Objectives and plan of the work

1.6.1 Motivation of the present investigation

The display market is a fast growing area, driven by developments in the field of portable electronic devices like cellular phones, digital cameras, etc. OLED-technology may become a strong competitor for the liquid crystal display (LCD) technology in the near future. Today, simple OLED displays are already integrated in shavers, car stereos and cellular phones. Although this technology is young compared to the inorganic light emitting devices, mainly based on semiconductor, the quality of OLEDs can compete with them in many cases.

The present thesis aims at the development of the 1,3,4-oxadiazole based polymers as an electron transporting layer in the OLEDs for blue light emission. 1,3,4-oxadiazole containing polymers are used as a blue emitter in the display devices as the oxadiazole is electron deficient nature. But the main disadvantages of these polymers lies in the solubility and the processibility due to their rigid structure. Therefore it is a prime requirement for the polymers to be tailor made to get the full benefit as a soluble blue light emitting electron transporting layer for the display device fabrication.

1.6.2 Objective of the present work

- Synthesis of soluble 1.3.4 oxadiazole conatining polymers via simple chemical polymerization method
- Characterization of the prepared monomers and polymers by spectroscopic techniques such as UV Visible spectroscopy, FTIR spectroscopy. NMR spectroscopy, thermal analysis by TGA, DSC etc., elemental analysis, luminescence study by fluorescence analyzer.
- Application of the prepared polymers in electroluminescence devices and evaluation of electroluminescence properties
- Study of the colour tuning and device performance of the polymers doping with metal nanoparticles

1.6.3 Plan of work

To fulfill the objectives of the present work the following plans of work have been adopted.

- Preparation of the 1,3,4 polyoxadiazole containing polar end groups
- Preparation of the 1,3,4 oxadiazole containing polyurethanes
- Characterization of the monomers and polymers by spectroscopic techniques like FTIR, 1H NMR, UV-visible spectroscopy
- Preparation of the metal/polymer hybrid with silver, copper and nickel nanoparticle
- Study of the morphology of the polymer hybrids by TEM and XRD
- Evaluation of the thermal behavior of the polymers and the hybrids by TGA and DSC analysis
- Cyclic voltammetry study of the polymers for the electrochemical nature of the systems
- Study of the photoluminescence properties of polymers and composites by fluorescence spectrophotometer.

- Fabrication of LED device using synthesized polymers.
- Evaluation and testing the device performance using the two probe sourcemeter
- Evaluation of electroluminescence properties.

References

1. Chidsey, C. E. D.; Murray, R. W. Electroactive Polymers and Macromolecular Electronics. *Science* **231**, 25-31(1986).
2. Bar-Cohe, Y. Electro-active polymers: current capabilities and challenges. *Proceedings of the SPIE Smart Structures and Materials Symposium, EAPAD Conference*, San Diego, CA 4695-4702 (2002).
3. Web address: http://www.azom.com/details.asp?ArticleID=885
4. Cohen, Y. B.; Kim, K. J.; Choi, H. R.; Madden, J. D. W. Electroactive polymer materials. *Smart Materials and Structures* **16**, 1-2(2007).
5. Wallace, G. G.; Spinks, G. M.; Kane-Maguire, L. A. P.; Teasdale, P. R. *Conductive electroactive polymers: intelligent materials systems* (CRC Press, 2008).
6. Kim, J. H.; Cheong, B.H.; Lee, H. S. Reflective unit using electroactive polymer and flexible display employing the reflective unit. *US patent No. 7,660, 025 B2*, Feb 9, 2010.
7. S. Middleman and A.K. Hochberg *Process Engineering Analysis in Semiconductor Device Fabrication* (McGraw-Hill, 1993).
8. Xue, F.; Su,Y.; Varahramyan, K. Modified PEDOT-PSS Conducting Polymer as S/D Electrodes for Device Performance Enhancement of P3HT TFTs. *IEEE transactions on electron devices* **52**, 1982-1987(2005).
9. Wang, J. Z.; Zheng,Z. H.; Li, H. W.; Huck, W. T. S.; Sirringhaus, H. Dewetting of conducting polymer inkjet droplets on patterned surfaces. *Nature Materials* **3**, 171–176(2004).
10. Tsao, L.C.; Chang, D.R.; Shih, W. P.; Fan, K. C. Fabrication and characterization of electro-active polymers for flexible tactile sensing array. *Key Engineering Materials* **281**, 391-394(2008).
11. Scrosati, B. *Applications of electroactive polymers* (Springer, 1993).
12. Nalwa, H. S. *Handbook of Advanced Electronic and Photonic Materials and Devices: Conducting polymers* (Elsevier, Vol 8, 2001).
13. Chandrashekhar, P. *Conducting polymers, fundamentals and applications: a practical approach* (Springer, 1999).
14. Heeger, A.J.; Kivelson, S.; Skreiffer, J.R.; Su, W. P. Solitons in conducting polymers. *Rev. Mod. Phys.* **60**, 781–850 (1988).
15. Vishnuvardhan, T. K.; Kulkarni, V. R.; Basavaraja, C.; Raghavendra, S. C. Synthesis, characterization and a.c. conductivity of polypyrrole/Y_2O_3 composites. *Bull. Mater. Sci.* **29**, 77–83(2006).
16. Lee K.-M. *et al* Effects of mesoscopic poly(3,4-ethylenedioxythiophene) films as counter electrodes for dye-sensitized solar cells. *Thin Solid Films* **518**, 1716-1721 (2010).

17. Amrutha, S. R.; Jayakannan, M. Structure control of π-conjugated polymers for enhanced solid-state luminescence: synthesis and liquid crystalline and photophysical properties of new bulky poly(*p*-phenylenevinylene)s and oligo(phenylenevinylene)s bearing tricyclodecane pendants. *Macromolecules* **40**, 2380-2391(2007).
18. Langer,J. J. *et al* Non-linear optical effects (SRS) in nanostructured polyaniline LED. *J. Mater. Chem.* **20**, 3859-3862(2010).
19. Kim, T. H.; Kim, H. J.; Kwak, C. G.; Park, W. H.; Lee, T. S. Aromatic oxadiazole-based conjugated polymers with excited-state intramolecular proton transfer: their synthesis and sensing ability for explosive nitroaromatic compounds. *J. Polym. Sci.: Part A: Polym. Chem.* **44**, 2059–2068 (2006).
20. Xu, Y.; Berger, P. R. High electric-field effects on short-channel polythiophene polymer field-effect transistors. *J. Appl. Phys.* **95**, 1497-1501 (2004).
21. Huang, B. *et al* Synthesis and properties of new poly(terfluorene) derivatives containing spirobifluorene and electron transport groups for stable blue electroluminescence. *J. Polym. Sci.: Part A: Polym. Chem.* **43**, 4517–4529 (2005).
22. Winder, C.; Muhlbacher, D.; Neugebauer, H.; Sariciftci, N. S.; Brabec, C. Polymer solar cells and infrared light emitting diodes: dual function low bandgap polymer. *Mol. Cryst. Liq. Cryst.* **385**, [213]/93–[220]/100 (2002).
23. Mayr, T. et al Light harvesting as a simple and versatile way to enhance brightness of luminescent sensors. *Anal. Chem.* **81**, 6541–6545 (2009).
24. Gustafsson, G. *et al* Flexible light-emitting diodes made from soluble conducting polymers. A. J. *Nature* **357**, 477-479 (1992).
25. Baeriswyl,D.; Campbell, D. K.; Mazumdar, S. *Conjugated conducting polymers* (Springer-Verlag, Berlin, 1992).
26. Cacialli, F. *et al* Recent developments in the controlled synthesis and manipulation of electroactive organic polymers. *Phil. Trans. R. Soc. Lond.* A. **355**, 707-714(1997).
27. Hide, F.; D´ıaz-Garc´ıa, M. A.; Schwartz, B. J.; Heeger, A. J. New developments in the photonic applications of conjugated polymers. *Acct. Chem.Res.* **30**, 430-436(1997).
28. Kalinowski, J. Electroluminescence in organics. *J. Phys. D: Appl. Phys.* **32**, R179–R250 (1999).
29. Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W.S. Progress with Light-Emitting Polymers. *Adv Mater.* **12**, 1737–1750(2000).
30. Gross, M. *et al* Improving the performance of doped p-conjugated polymers for use in organic light-emitting diodes. *Nature* **405**, 661-665 (2000).
31. Baldo, M. A.; Thompson, M. E.; Forrest, S. R. High-efficiency fluorescent organic light-emitting devices using a phosphorescent sensitizer. *Nature* **403**, 750-753(2000).

32. Friend, R. H. Conjugated polymers. New materials for optoelectronic devices. *Pure Appl. Chem.* **73**, 425–430 (2001).
33. MacDiarmid, A. G. Synthetic metals: a novel role for organic polymers (nobel lecture) *Angew. Chem. Int. Ed.* **40**, 2581 - 2590 (2001).
34. Akcelrud, L. Electroluminescent polymers. *Prog. Polym. Sci.* **28**, 875–962 (2003).
35. Yanga, N.; Chang, C. S.; Suh, D. H. Synthesis and optically acid-sensory properties of novel polyoxadiazole derivatives. *Polymer* **44**, 2143–2148 (2003).
36. Erokhin, V.; Berzina, T.; Camorani, P.; Fontana, M. P. Conducting polymer-solid electrolyte fibrillar composite material for adaptive networks. *Soft Matter.* **2**, 870–874 (2006).
37. Shao, Y.; Bazan, G. C. Heeger, A. J. Long-lifetime polymer light-emitting electrochemical cells. *Adv. Mater.* **19**, 365–370(2007)
38. Kalinowski, J. Optical materials for organic light-emitting devices. *Opt. Mater.* **30**, 792-799 (2008).
39. Bradley, D. D. C. Conjugated polymer electroluminescence. *Synth. Met,* **54**, 401-415 (1993).
40. Baigent, D. R. *et al* Light-emitting diodes fabricated with conjugated polymers-recent progress *Synth. Met.***67**, 3-10(1994).
41. Neher, D. Substituted Rigid Rod-Like Polymers—Building Blocks for Photonic Devices. *Adv. Mater.* **7**, 691-702(1995).
42. Segura, J. L. The chemistry of electroluminescent organic materials. *Acta Polym.* **49**, 319-344(1998).
43. Friend, R. H. *et al* Electroluminescence in conjugated polymers. *Nature* **397**, 121-128(1999).
44. Grell, M.; Bradley, D. D. C. Polarized luminescence from oriented molecular materials. *Adv. Mater.* **11**, 895-905(1999).
45. Heeger, P. S.; Heeger, A. J. Making sense of polymer-based biosensors. *Proc. Nat. Aca. Sci. USA* **96**, 12219-12221(1999).
46. Kim,D. Y.; Cho, H. N.; Kim, C. Y. Blue light emitting polymers. *Prog. Polym.Sci.* **25**, 1089-1139(2000).
47. Friend, R. H. Conjugated polymers-New materials for optoelectronic devices. *Pure Appl. Chem.* **73**, 425- 430(2001).
48. Dai, L.; Winkler, B.; Dong, L.; Tong, L.; Mau, A. W. H. Conjugated polymers for light-emitting applications. *Adv. Mater.* **13**, 915-925(2001).
49. Leclerc, M. Polyfluorenes: Twenty years of progress. *J. Polym. Sci. Part A: Polym. Chem.* **39**, 2867-2873(2001).
50. Heeger,A. J. Semiconducting and metallic polymers: the fourth generation of polymeric materials (Nobel lecture). *Angew. Chem. Int. Ed.* **40**, 2591-2611(2001).

51. Qui, Y.; Duan, L.; Wang, L. Flexible organic light-emitting diodes with poly-3, 4-ethylenedioxythiophene as transparent anode. *Chin. Sci. Bull.* **47**, 1979-1982 (2002)
52. Scherf, U.; List, E. J. W. Semiconducting polyfluorenes—towards reliable structure–property relationships. *Adv. Mater.* **14**, 477-487(2002).
53. Schwartz, B. J. Conjugated polymers as molecular materials: how chain conformation and film morphology influence energy transfer and interchain interactions. *Annu. Rev. Phys. Chem.* **54**, 141-172(2003).
54. Grazulevicius, J. V.; Strohriegl, P.; Pielichowski, J.; Pielichowski, K. Carbazole-containing polymers: synthesis, properties and applications. *Prog. Polym. Sci.* **28**, 1297-1353(2003).
55. Misra, A. *et al* Blue electroluminescence in organic semiconductors. *Ind. J. Pure Appl. Phys.***42**, 793-805(2004).
56. Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. Electron transport materials for organic light-emitting diodes. *Chem. Mater.* **16**, 4556-4573(2004).
57. Singh,T. B.; Sariciftci,N. S. Progress in plastic electronics devices. *Annu. Rev. Mater. Res.***36**, 199-203(2006).
58. Thomas III, S. W.; Joly,G. D.; Swager,T. M. Chemical sensors based on amplifying fluorescent conjugated polymers. *Chem. Rev.* **107**, 1339-1386(2007).
59. Yang, X.; Loos,T. Toward high-performance polymer solar cells: the importance of morphology control. *Macromolecules* **40**, 1353-1362(2007).
60. Lutz, J. F.; Borner, H. G. Modern trends in polymer bioconjugates design. *Prog. Polym. Sci.* **33**, 1-39(2008).
61. Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. Synthesis of light-emitting conjugated polymers for applications in electroluminescent devices. *Chem.Rev.* **109**, 897-1091(2009).
62. George, G. A.Characterization of solid polymers by luminescence techniques. *Pure & Appl. Chem.* **57**, 945-954 (1985).
63. Chen,S.-H.; Hwang,S.-W.; Chen, Y. Photoluminescent and electrochemical properties of novel copoly(aryl ether)s with isolated fluorophores. *J. Polym. Sci.: Part A: Polym. Chem.* **42**, 883–893 (2004)
64. Ronda, C. *Luminescence: from theory to applications* (Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2008).
65. Chen, X.; Mutasim, Z.; Price, J.; Feist, J. P.; Heyes, A. L.; Seefeldt, S. Industrial sensor TBCs: studies on temperature detection and durability. *Inter. J. Appl. Ceram. Technol.* **2**, 414-421(2005).
66. Heyes, A. L.; Seefeldt, S.; Feist, J. P. Two-colour thermometry for surface temperature measurement. *Opt. Las. Technol.* **38**, 257-265(2005).
67. Franck, J.; Dymond, E. G. Elementary processes of photochemical reactions. *Transactions of the Faraday Society.* **21**,536–542(1926).

68. Condon, E. A Theory of intensity distribution in band systems (Meeting abstract). *Phys. Rev.* **27**, 640-656(1926).

69. Condon, E. A theory of intensity distribution in band systems. *Phys. Rev.* **28**, 1182–1201(1926).

70. Web address: https://docs.google.com/View?id=dfk4gz7_1tbc3vqhs

71. Hastings, J.W. Biological diversity, chemical mechanisms, and the evolutionary origins of bioluminescent systems. *J. Mol. Evol.* **19**, 309–21(1983).

72. Kafafi, Z. Organic electroluminescence. (Taylor and Francis, 2005)

73. Pudzich, R.; Fuhrmann-Lieker, T.; Salbeck, J. Spiro compounds for organic electroluminescence and related applications. *Adv Polym Sci* **199**, 83–142(2006).

74. Baldo, M.; Segal, M. Phosphorescence as a probe of exciton formation and energy transfer in organic light emitting diodes. *Phys. Stat. Sol.* **201**, 1205–1214 (2004)

75. Martín Gil Jesús and Martín Gil Francisco J. "Triboluminescence of new uranyl salts", *Journal of Chemical Education.* **55**, 340-347(1978).

76. Keizar, K.Z.; Forrest, B. M.; Rink, W. J. Natural residual thermoluminescence as a method of analysis of sand transport along the coast of the St. Joseph Peninsula, Florida,. *J. coast. Res.* **24**, 500 - 507(2008).

77. Webaddress:http://www.mnsu.edu/emuseum/archaeology/dating/thermoluminescence.html

78. Web address:http://www.glassner.com/andrew/cg/research/fluphos/fluphos.htm

79. Yacobi, B. G.; Holt, D. B. *Cathodoluminescence Microscopy of Inorganic Solids.*(New York, Plenum 1990)

80. Parish, C. M.; Russell, P. E. Scanning cathodoluminescence microscopy. *Adv. Imag. Electr. Phys.***147**, 1-49 (2007)

81. Sampietro, M.; Sotgiu, R. Electrical characteristics of light-emitting electrochemical cells based on a wide bandgap polymer. *Phys. Rev. B.* **61**, 266-271 (2000).

82. Blom, P.W.M.; Jong, M.J.M.D. Device operation of polymer light emitting diode. *Philips. J. Res.* **51**, 479-494 (1998).

83. Tang, C. W.; Slyke, S. A. V. Organic electroluminescent diodes. *Appl. Phys. Lett.* **51**, 913-915 (1987)

84. Burroughes, J. H. *et al* Light-emitting diodes on conjugated polymers. *Nature* **347**, 539-541(1990).

85. Enemchukwu, N. O. Synthesis and photoluminescence characterization of polymeric materials for organic light-emitting devices (OLEDs). *MURJ reprts* **12**, 55-60(2005)

86. Hu, Y.; Zhang, Y. Gao, J. Strong electroluminescence from polymer films with heavily quenched photoluminescence. *Adv. Mater.* **18**, 2880–2883(2006).

87. Pichler, K. Conjugated polymer electroluminescence: technical aspects from basic devices to commercial products. *Phil. Trans. R. Soc. Lond. A.* **355**, 829-842(1997).

88. Baldo, M. A. *et al* Highly efficient phosphorescent emission from organic electroluminescent devices. *Nature* **395**, 151-154(1998).

89. Yasufuku, S. Electroconductive polymers and their applications in Japan. *IEEE Electrical Insulation Magazine(feature article)***17**, 14-24(2001)

90. Doi, S. Light emitting polymers-development of electroluminescent polymers. *Chemistry and Chemical Industry* **50**, 179-182 (1997)

91. Forrest,S.; Burrows,P.; Thompson, M. The dawn of organic electronics. *IEEE Spectrum* **37**, 29-34 (2000).

92. Hellemans, A. Polymer matrix augurs flexible displays. *IEEE Spectrum* **37**, 18-22 (2000).

93. Osaka, T.; Momma,T. Electroactive polymer materials for rechargeable lithium battery cathode. *Kobunshi High Polymers* **44**, 64-67 (1995).

94. Blom, P. W. M.; Schoo, H. F. M.; Matters, M. Electrical characterization of electroluminescent polymer/nanoparticle composite devices. *Appl. Phys. Lett.* **73**, 3914-3916 (1998).

95. Sellinger, A. Self assembly of organic- inorganic nanocomposite thin film for use in hybrid organic light emitting devices (HLED). US Patent No 6861091 B2, Mar 1 (2005).

96. Holder,E.; Tessler, N; Rogach, A. L. Hybrid nanocomposite materials with organic and inorganic components for opto-electronic devices. *J. Mater. Chem.* **18**, 1064–1078(2008).

97. Holmes, R. J. and Forresta, S. R. Blue organic electrophosphorescence using exothermic host–guest energy transfer. *Appl. Phys. Lett.* **82**, 2422-2424 (2003).

98. Wang, P *et al* Single layer light-emitting diodes from copolymers Comprised of mesogen-jacketed polymer Containing oxadiazole units and PVK. *J. Polym. Sci.: Part A: Polym. Chem.* **46**, 1843–1851 (2008).

99. Tayyan, A. A. E.; El-Agez, T. M.; Abdel-Latif, M. S. Electroluminescence from single layer poly(n-vinylcarbazole) films doped with new emitter molecules. *Chin. J. Phys.* **46** ,153-162 (2008)

100. Pommerehne, J. *et al* Efficient two layer LEDs on a polymer blend basis. *Adv. Mater.* **7,** 551-554 (1995)

101. Kim, J. S. et al J. Indium–tin oxide treatments for single- and double-layer polymeric light-emitting diodes: the relation between the anode physical, chemical, and morphological properties and the device performance. *Appl. Phys.* **84**, 6859-6872 (1998).

102. Khramtchenkov, D. V.; Bassler, H.; Arkhipov, V. I.; A model of electroluminescence in organic double layer light emitting diodes. *J. Appl. Phys*. **79**, 9283–9290(1996).

103. Bradeley, D. Electroluminescent polymers: materials, physics and device engineering. *Curr. Opi. Sol. Stat. Mater. Sci.* **1**,789-797 (1996).

104. Buchwald, E. *et al* Enhanced efficiency of polymer light emitting diodes utilizing oxadiazole polymers. *Adv. Mater.* **7**, 839-842 (1995).

105. Pei, Q.; Yang, Y. 1,3,4-oxadiazole-containing polymers as electron-injection and blue electroluminescent materials in polymer light-emitting diodes. *Chem. Mater.* **7**, 1568- 1572 (1995).

106. Mitschke, U.; Baeuerle, P. The electroluminescence of organic materials. *J. Mater. Chem.* **10**, 1471-1507 (2000).

107. Kraft, A.; Grimsdale, A. C.; Holmes, A. B. Electroluminescent conjugated polymers—seeing polymers in a new light. *Angew. Chem., Int. Ed.* **37**, 402-428 (1998).

108. Cao, Y.; Treacy, G.M.; Smith, P.; Heeger, A.J.; Solution-cast films of polyaniline: optical-quality transparent electrodes. *Appl Phys Lett.* **60**, 2711–2713 (1992).

109. Cacialli, F. Organic semiconductors for the new millennium. *Phil Trans R Soc Lond Ser A—Math Phys Engng Sci.* **358**, 173–192 (2000).

110. Segura, J.L. The chemistry of electroluminescent organic materials. *Acta Polym.* **49**, 319–344 (1998).

111. Leventis, N.; Huang, L.-Y. Electroluminescent polymers. *Polym News* **20**, 307–313 (1995)

112. Conwell, E.M.; Stolka, M.; Miller, M.R. Electroluminescent materials, devices and large-screen displays. *Inter. Soc. Opt. Engineer. (SPIE) Proceedings,San Jose, CA*. (1993).

113. Kippelen, B.; Bradley, D. Polymer photonic devices. *IV.International Society for Optical Engineering (SPIE) Proceedings,* San Jose CA. 3281 (1998).

114. Adachi, C.; Nagai, K.; Tamoto, N. Molecular design of hole transport materials for obtaining high durability in organic electroluminescent diodes. *Appl. Phys. Lett.* **66**, 2679-2681 (1995).

115. Han, E.-M., Do, L.-M., Niidome, Y., and Fujihira, M. Observation of crystallization of vapor-deposited TPD films by AFM and FFM. *Chem. Lett.* **23**, 969-972 (1994).

116. Fujihira, M.; Do, L.-M.; Koike, A.; Han, E.-M. Determination of the conduction-band discontinuities of $In_{0.5}Ga_{0.5}P/In_{1-x}Ga_xAs_{1-y}P_y$ by capacitance–voltage analysis. *Appl. Phys. Lett.* **68**, 1787-1789 (1996).

117. Burrows, P. *et al* Reliability and degradation of organic light emitting devices. *Appl. Phys. Lett.* **65**, 2922-2924 (1994).
118. Liu,G.; Kerr, J. B.; Johnson,S. Dark spot formation relative to ITO surface roughness for polyfluorene devices. *Synth. Met.* **144**, 1-6 (2004).
119. Lang,W.; Steiner, P.; Kozlowski, F. Porous silicon electroluminescent devices. *J. Lumin.* **57**, 341-349 (1993).
120. Johnstone, B. *We Were Burning: Japanese Entrepreneurs and the Forging of the Electronic Age* (New York: Basic Books, 1999)
121. Hashimoto, Y.; Senoo, A.; Toshida, Y.; Ueno, K. Luminescent device .US Patent 6586119(1998).
122. Helfrich, W.; Schneider, W.G. Recombination radiation in anthracene crystals. *Phys. Rev. Lett*; **14**, 229-231(1965).
123. Tang, C.W.; Van, S. S.A. Organic electroluminescent diodes. *Appl Phys Lett*; **51**, 913–1005 (1987).
124. Tang, C. Brightness on display. *SPIE newsletter* (online article) DOI: 10.1117/2.5200102.0003.
125. Clery, D. Polymer technology—after years in the dark, electric plastic finally shines. *Science* **263**, 1700–1702 (1994).
126. Brutting, W. *Physics of organic semiconductors* (Wiley-VCH, 2005 - Technology & Engineering).
127. Trager, F. *Springer handbook of lasers and optics* (Springer,2007)
128. Holder, E.; Langeveld, B.M.W.; Shubert, U.S. *Adv. Mater.* **17**, 1109-1121 (2005)
129. Misra, A. *et al* Electrochemicaland optical studies of conjugated polymers for three primary colours. *Ind. J. Pure. Appl. Phys.* **43**, 921-925 (2005).
130. Zhang, H. *et al* Selective tuning of the HOMO–LUMO gap of carbazole-based donor–acceptor–donor compounds toward different emission colors. *Eur. J. Org. Chem.* 1681–1687 (2010).
131. Kaya, I. Synthesis, Characterization, Conductivity, Band Gap, and Thermal Analysis of Poly-[(2-mercaptophenyl)iminomethyl]-2-naphthol and Its Polymer–Metal Complexes. *J. Inorg. Organometal. Polym. Mater.* **20**, 369-379 (2010).
132. Mita, I.; Stepto, R. F. T.; Suter, U. W. Basic classification and definitions of polymerization reactions. *Pure &Appl. Chem.* **66**, 2483-2486 (1994).
133. Odian, G.G. *Principles of polymerization* (John Wiley and Sons, 2004).
134. Mark, J.E. *Physical properties of polymer handbook* (Springer 2007)
135. Jones, T.T.; Malville H.W. The photochemical polymerization of methyl vinul ketone vapour. *Proc. R. Soc. Lond. A.* **187**, 19-36(1946).

136. Grubbs, R.H.; Chang, S. Recent advances in olefin metathesis and its application inorganic synthesis. *Tetrahedron* **54**, 4413-4450 (1998)

137. Miyata, M.; Noma, F.; Okanishi, K.; Tsutsumi, H.; Takemoto, K. Inclusion polymerization of diene and diacetylene monomers in deoxycholic acid and apocholic acid canals. **5**, 249-252 (1998).

138. Morales, P. *et al* Polyethylene Obtained by Plasma Polymerization of Hexene. *Macromolecular Symposia* **283**, 13-17 (2009).

139. Wall, L. A.; Fetters, L. J.; Straus, S. Polymerization and pyrolysis of poly-1,2-dihydronaphthalene. *J. Polym. Sci. Part B: Polym. Lett.* **5**,721-733 (1967).

140. Gu, C.; Fei, T.; Yao, L.; Lv, Y.; Lu, D.; Ma; Y. Multilayer polymer stacking by in situ electrochemical polymerization for color-stable white electroluminescence. *Adv. Mater.* (2010) DOI: 10.1002/adma.201003027

141. Tamura, K.; Maeda, K.; Yashima, E. Chemical modification of a luminescent poly(phenylenevinylene)-amylose composite. *Macromolecules* **41**, 5065-5069 (2008).

142. Nateghi, M.R.; Mosslemin, M.H.; Hadjimohammadi, H. Electrochemical preparation and characterization of poly(3,3′-diaminobenzidine): A functionalized polymer. *React. & Funct. Polym.* **64**, 103–109(2005).

143. Borole, D.D.; Kapadi, U.R.; Mahulikar, P.P.; Hundiwale, D.G. Electrochemical synthesis and characterization of conducting copolymer:Poly(o-aniline-co-o-toluidine). Mater. Lett. **60**, 2447–2452 (2006).

144. Bard, A. J.; Faulkner, L.R. *Electrochemical methods: fundamentals and applications* (John Wiley & Sons, 2000)

145. Fisyuk, A. S.; Demadrille, R.; Querner, C.; Zagorska, M.; Bleuse, J.; Pron, A. Mixed alkylthiophene-based heterocyclic polymers containing oxadiazole units *via* electrochemical polymerisation: spectroscopic, electrochemical and spectroelectrochemical properties. *New J. Chem.* **29**, 707-713(2005)

146. Qi, Z.-J. *et al* Novel 2,4-divinyl-3-alkylthiophene/1,3,4-oxadiazole alternating conjugated copolymer synthesized by the heck coupling method: synthesis, characterization, and electronic and optical properties. J. Appl. Polym. Sci. **116**, 1392–1399 (2010)

147. Ding, J.; Day, M.; Robertson, G.; Roovers, J. Synthesis and characterization of alternating copolymers of fluorene and oxadiazole. *Macromolecules* **35**, 3474-3483 (2002)

148. Kalsi, P.S. *Spectroscopy of organic compounds* (New Age International Publication, sixth edition, 2006)

149. Banwell, C. N.; McCash, E.M. *Fundamentals of molecular spectroscopy* (Tata McGraw Hill Publishing Company Ltd. Fourth edition, 2001).

150. Guillet, J. *Photophysics and Photochemistr* (Cambrige University Press, London, 1985).

151. Lakowitz, J. R. *Principles of Fluorescence Spectroscopy* (Kluwer Academic, New York, 2nd edition, 1999).
152. Burin, A. L.; Ratner, M. A. Effects on the luminescence yield of organic light emitting diodes. *J. Chem. Phys.* **109**, 6092-6102(1998).
153. Y. K. ; Godovsky *Thermal and Electrical Conductivity of Polymer Materials*(Springer-verlag, 1995)
154. Kawakami, S. *et al* Dependence of electroluminescent properties on cathode metals in PVCz double-layered organic EL devices. *Thin Solid Films* **363**, 17-20(2000)
155. Brown, T. M.; Friend, R. H. Electronic line-up in light-emitting diodes with alkali-halide metal cathodes. *J. Appl. Phys.* **93**, 6159-6171 (2003)
156. Choong,V. *et al* Dramatic photoluminescence quenching of phenylene vinylene oligomer thin films upon submonolayer Ca deposition. *Appl. Phys. Lett.* **69**, 1492-1494 (1996).
157. Choong,V.-E. *et al* Effects of Al, Ag, and Ca on luminescence of organic materials *J. Vac. Sci. Technol. A* **15**, 1745-1749 (1997).
158. Park,Y.; Choong, V. E.; Hsieh, B. R.; Tang, C. W.; Gao, Y. Gap-state induced photoluminescence quenching of phenylene vinylene oligomer and its recovery by oxidation. *Phys. Rev.Lett.* **78**, 3955-3958 (1997).
159. Stoessel, M. *et al J. Appl. Phys.* **87**, 4467 (2000).
160. Kido, J.; Matsumoto, T. *Appl. Phys. Lett.* **73**, 2866 (1998).
161. Parthasarathy, G.; Shen, C.; Kahn, A.; Forrest, S. R. *J. Appl. Phys.* **89**,4986 (2001).
162. Huang, B. *et al* Synthesis and properties of new poly(terfluorene) derivatives containing spirobifluorene and electron transport groups for stable blue electroluminescence. *J. Polym. Sci.: Part A: Polym. Chem.* **43**, 4517–4529 (2005).
163. Zheng,M.; Ding,L.; Rel, E. E. G.; Lahti,P. M.; Karasz,F. E. Oxadiazole containing conjugated-nonconjugated blue and blue-green light emitting copolymers. *Macromolecules* **34**, 4124-4129 (2001).
164. Wang, P. *et al* Blue light-emitting diodes from mesogen-jacketed polymers containing oxadiazole units. *Polymer* **48**, 5889-5895(2007)
165. Yu, W.-L.; Cao, Y.; Pei, J.; Huang, W.; Heeger, A. J. Blue polymer light-emitting diodes from poly(9,9-dihexylfluorene-alt-co-2,5-didecyloxy-para-phenylene). *Appl. Phys. Lett.* **75**, 3270-3272 (1999)
166. Yang, I.; Sokolik; *F.* E. Earasz A soluble blue-light-emitting polymer. *Macromolecules* **26**, 1188-1190(1993)

167. Shen, J. Y. High Tg blue emitting materials for electroluminescent devices. J. Mater. Chem. **15**, 2455–2463(2005).

168. Ding, L.; Karasz, F. E.; Lin, Y.; Pang, Y.; Liao, L. Photoluminescence and electroluminescence study of violet-blue and green emitting polymers and their blend. *Macromolecules* **36**, 7301-7307 (2003)

169. Kim, Y. H.; Jung, M. S.; Yoon,D.K.; Jee, M. G.; Jung, H. T.A solution processible semiconducting polymer interlayer for blue light-emitting diodes. *Nanotechnology* **18**, 175608(1-6) (2007).

170. Lu, P. *et al* A wide-bandgap semiconducting polymer for ultraviolet and blue light emitting diodes. Macromol. Chem. Phys. **204**, 2274–2280 (2003)

171. Panin, G. N.; Kang, T. W.; Lee, H. Light emission from the polythiophene derivative/ITO structure under electron beam excitation. Physica E: low-dimensional systems and nanostructures **21**, 1074-1078 (2004).

172. Hwu, J. R. Chuang, K.-S.; Chuang, S. H.; Tsay, S.-C. New benzo[b]furans as electroluminescent materials for emitting blue light. Org. Lett. **7**, 1545-1548 (2005).

173. Zheng, J. Y.; Feng, X. M.; Bai, W. B.; Qin, J. G.; Zhan, C. M. Soluble blue light emitting pyridine-containing polymers prepared by oxidative-coupling copolymerization. *Europ. Polym. J.* **41**, 2770-2775 (2005).

174. Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. Blue electroluminescent diodes utilizing poly(alkylfluorene). *Jpn J Appl Phys* **30**, L1941-1943(1991).

175. Grem,G.; Leditzky, G.; Ullrich, B.; Leising, G. Realization of a blue-light-emitting device using poly(*p*-phenylene). *Adv. Mater.* **4**, 36-37(1992).

176. Komaba, S.; Amano, A.; Osaka, T. Electroluminescence properties of electropolymerized poly(para-phenylene) films by means of electrochemical oxidation and reduction. *J. Electroana.l Chem.* **430**, 97-02(1997).

177. Vahlenkamp, T.; Wegner, G.; Poly(2,5-dialkoxy-p-phenylene)s-synthesis and properties. *Macromol. Chem. Phys.* **195**, 1933-1952(1994).

178. Fukuda, M.; Sawada, K.; Yoshino, K.; Synthesis of fusible and soluble conducting polyfluorene derivatives and their characteristics. *J. Polym. Sci. Part A: Polm. Chem.* **31**, 2465-2471(1997).

179. Cho, H.N.; Kim, D.Y.; Kim, J.K.; Kim. C.Y. Control of band gaps of conjugated polymers by copolymerization. *Synth. Met.* **91**, 293-296(1997).

180. Mori, T.; Strzelec, K.; Sato, H. Synthesis of charge transporting polymer containing TPD units using Friedel–Crafts reaction. *Synth. Met.* **126**, 165-171 (2002).

181. Conway, N. M.; Mckiernan, M. J.; Tierney, B. Light-emitting Device and Materials Therefor. US Patent Application 2010/0276674.

182. Andersson, M.R. *et al* Synthesis of poly(alkylthiophenes)for light-emitting diodes. Synth. Met. **71**, 2183-2184(1995).

183. Miyazaki, Y.; Yamamoto, T. Poly(thiophene-2,5-diyl) having crown ethereal subunit. Preparation, stable n-doped state and light emitting diode. *Chem. Lett.* 41-44(1994).

184. Gill, R.E.; Malliaras, G.G.; Wildeman, J.; Hadziioannou, G. Tuning of photo- and electroluminescence in alkylated polythiophenes with well-defined regioregularity. *Adv. Mater.* **6**,132-135(1994).

185. Sava, I.; Bruma, M.; Szesztay, M.; Muller, P. Poly(1,3,4-oxadiazole-amide-ester)s and thin films made from them. High Perform. Polym. **17**, 263-275(2005).

186. Bruma, M.; Damaceanu, M. D.; Muller, P. Comparative Study of Polyimides Containing Oxadiazole and Ether Groups. *High Perform. Polym.* doi: 10.1177/0954008309339202.

187. Hsiao, S. H.; Huang, Y. H. Synthesis and properties of novel aromatic poly(1,3,4-oxadiazole)s and poly(amide-1,3,4-oxadiazole)s having ortho-phenylenedioxy units. *High Perform. Polym.* **16**, 21-37 (2004).

188. Sung, H.-H.; Lin, H.-C. Novel alternating fluorene-based conjugated polymers containing oxadiazole pendants with various terminal groups. *Macromolecules* **37**, 7945-7954(2004).

189. Brown, S.M. *et al* Spectral emission properties of some blue emitting diodes. *Ancient TL* **17**, 1-4 (1999).

190. Lee, J.-H.; Woo, H.-S.; Kim, T.W.; Park, J.-W. Blue organic light-emitting diodes with carbazole-based small molecules. *Opt. Mater.* **21**, 225–229(2002).

191. Chun-Jun, L. *et al* Polymer Light-Emitting Diode Using Conductive Polymer as the Anode Layer. *Chin. Phys. Lett.* **27**, 097801(1-5) (2010).

192. Burmen, M.; Pernus, F.; Likar, B. LED light sources: a survey of quality-affecting factors and methods for their assessment. *Meas. Sci. Technol.* **19**, 122002 (1-15) (2008).

193. Zhang, B. *et al* High-performance all-polymer white-light-emitting diodes using polyfluorene containing phosphonate groups as an efficient electron-injection layer. *Adv. Funct. Mater.* **20**, 2951–2957(2010).

194. Garten, F. *et al* Blue light emitting diodes based on a partially conjugated Si-containing PPV-copolymer in a multilayer conjuguration. *Synth. Met.* **85**,1253-1254(1997).

195. Pohl, A.; Breadas, J-L. Influence of silicon atoms on the p-conjugation in electroluminescent polymers. *Int. J. Quantum Chem.* **63**, 437-440(1997).

196. Kim, K-D.; Park, J-S.; Kim, H.K.; Lee, T.B.; Blue electroluminescence from novel silicon-containing poly(cyanoterephthalylidene)copolymers. *Macromolecules* **31**, 7267-7272(1998).

197. Wang, S.; Hua, W.; Zhang, F.; Wang, Y. Synthesis and electroluminescent properties of heterocycle-containing poly(p-phenylenevinylene) derivatives. *Synth. Met.* **99,** 249-252(1999).

198. Peng, Z.; Bao, Z.; Galvin, M. Oxadiazole-containing conjugated polymers for light-emitting diodes. *Adv. Mater.* **10,** 680-684(1998).

199. Mikroyannidis, J. A. Luminescent monomer and poly(methacrylate) containing 1,3,4-oxadiazole and stilbene units: synthesis and optical properties. *Macromol. Chem. Phys.* **205**, 1893–1903(2004)

200. Wang, G. *et al* Novel Bipolar Conjugated Polymer Containing Both Triphenylamine and Oxadizole Units. *Chin. Chem. Lett.* **13**, 422– 425 (2002).

201. Yeh, K.-M.; Chen, Y. Vinyl copolymers containing pendant 1,4-distyrylbenzene and 1,3,4-oxadiazole chromophores: preparation and optoelectronic properties. J. Polym. Sci.: Part A: Polym. Chem. **44**, 5362–5377 (2006).

202. Lin, K.-R. *et al* New hole-transport polyurethanes applied to polymer light-emitting diodes. *Europ. Polym. J.* **43**, 4279–4288(2007).

203. Ku, C.-H.; Kuo, C.-H.; Leung, M.-K; Hsieh, K.-H. Carbazole–oxadiazole containing polyurethanes as phosphorescent host for organic light emitting diodes. *Euro. Polym. J.* **45,** 1545–1553(2009).

204. Ku, C.-H. *et al* PLED devices containing triphenylamine-derived polyurethanes as hole-transporting layers exhibit high current efficiencies. *J. Mater. Chem.* **18**, 1296–1301(2008).

205. Kuo, C.-H. *et al* High-performance hole-transport polyurethanes for light-emitting diodes applications. *Chem. Mater.* **18**, 4121-4129(2006).

206. Liou, G.-S.; Hsiao,S.-H.; Chen,W.-C.; Yen,H.-J. A new class of high *T*g and organosoluble aromatic poly(amine-1,3,4-oxadiazole)s containing donor and acceptor moieties for blue-light-emitting materials, *Macromolecules* **39**, 6036-6045 (2006).

207. Boltona, O.; Kim, J. Design principles to tune the optical properties of 1,3,4-oxadiazolecontaining molecules. *J. Mater. Chem.* **17**, 1981–1988(2007).

208. Udayakumar, D.; Adhikari, A. V. Synthesis and characterization of fluorescent poly(oxadiazole)s containing 3,4-dialkoxythiophenes. *Opt. Mater.* **29,** 1710–1718 (2007).

209. Gillo, M. *et al* Alkoxy-substituted poly(*p*-phenylene 1,3,4-oxadiazole)s:synthesis, chemical characterization and electro-optical properties. *Chem. Mater.* **14,** 1539-1547 (2002).

210. Hedrick, J. L.; Twieg, **R.** Poly(aryl ether oxadiazoles). *Macromolecules* **25,** 2021-2025(1992).

211. Strukelj, M.; Papadimitrakopoulos, F.; Miller, T. M.; Rothberg, L. J. Design and application of electron-transporting organic materials. *Science* **267**, 1969-1972 (1995).

212. Chang, C.; Tsao, F.; Pan, C.; Chi, G. Electroluminescence from ZnO nanowire/polymer composite p-n junction. *Appl. Phys. Lett.* **88**, 173503-1-173503-3 (2006).

213. Tsukazaki, A. et al Blue Light-Emitting Diode Based On Zno. Japan. J. Appl. Phys. **44**, L 643–L 645(2005).

214. Tan, Z.; Zhang, F.; Zhu,T.; Xu, J. Bright and color-saturated emission from blue light-emitting diodes based on solution-processed colloidal nanocrystal quantum dots. *Nano Lett.* **7**, 3803-07(2007)

215. Fogg, D. E. *et al* Fabrication of quantum dot-polymer composites: semiconductor nanoclusters in dual-function polymer matrices with electron-transporting and cluster-passivating properties. *Macromolecules* **30**, 8433-8439 (1997).

216. Rathorea, K. S. *et al* Structural and optical charcterization of chemically synthesized Zns nanoparticles. *Chalcogenide Lett.* **5**, 105 – 110(2008).

217. Postolek, K. M.; Bogdal, D. Polymer nanocomposites for electro-optics: perspectives on processing technologies, material characterization and future application. *Polymer Characterization Adv. Polym. Sci.* **230**, 221-282(2010).

218. Lee, D *et al* Electroluminescent polymer nanocomposite material, method of manufacturing the same and organic light emitting display apparatus having the same. US Patent 2009/7491451.

219. Lo, M. Y.; Ueno, K.; Tanabe, H.; Sellinger, A. Silsesquioxane-based nanocomposite dendrimers with photo-luminescent and charge transport properties. *The Chemical Record.* **6**, 157–168 (2006).

220. Gong, X. *et al* High-Efficiency Polymer-Based Electrophosphorescent Devices. *Adv. Mater.* **14,** 581–585 (2002).

CHAPTER 2

Synthesis and characterization of 1,3,4-oxadiazole containing polymers

Chapter 2: Synthesis and characterization of 1,3,4-Oxadiazole containing polymers

2.1 Introduction

Poly(1,3,4-oxadiazole), polythiophene, polypyrimidine, polyaniline, polypyrrole etc. are some of the conjugated polymers carrying heteroaromatic systems are now a day very important for the materials used in the organic light emitting diode application. Amongst them, poly(1,3,4-oxadiazole) take out the cream of the pie as they are the most efficient electron transporting material and yet a very promising candidate for the emission of light in the blue region with a good intensity[1-5].

Poly(1,3,4-oxadiazole)s are synthesized by the polycodensation of hydrazides and acid chlorides followed by the cyclodehydration of the product. The electrochemical polymerization method is not suitable for the synthesis of the 1,3,4-oxadiazole containing polymers[6-7].

One of the key challenges in developing high-performance OLEDs is the design and synthesis of readily processible and thermally robust emissive and charge transport materials with improved multifunctional properties. OLEDs are double charge injection devices, requiring the simultaneous supply of both electrons and holes to the electroluminescent (EL) material sandwiched between two electrodes. The substituents on the conjugated polymeric systems have profound effect in their luminescence efficieny. Substituents which enhance π electron mobility will normally increase the fluorescence. Thus the substituents having positive mesomeric effect will enhance the luminescence property of the polymers. Apart from the fully conjugated systems, the side group participation is also an important criterion for the solubility and colour tuning in the display application.

Considering these factors in developing materials for the electroluminescent devices a considerable effort has been made to synthesize soluble and efficient electron transporting blue light emitting materials. Three electron deficient systems of 1,3,4-oxadiazole based polymers have been synthesized.

Chapter 2: Synthesis and characterization of 1,3,4-Oxadiazole containing polymers

The synthesis of the monomer and the polymers; their structural characterization, physical properties, optical properties and the thermal behaviours are discussed in this chapter. We have synthesized the following three sets of 1,3,4-oxadiazole containing polymer.

1. **Poly-1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene** containing polar end groups like $-NO_2$, -Cl,$-CH_3$, -OH (**OXD AR1,-AR2,-AR3,-AR4**)
2. **Poly-1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene** containing polar end groups like $-NO_2$, -Cl,$-CH_3$, -OH (**OXD BR1,-BR2,-BR3,-BR4**)
3. **Polyurethanes containing 1,3,4 oxadiazole** in the main chain(**PU1, PU2, PU3, PU4**)

All the polymers were synthesized by the polycondensation method. The first two sets of polymers includes the low temperature polycondensation of aromatic dihydrazides of terephthalic acid and the isophthalic acid with their corresponding acid chlorides followed by the thermal cyclization of the polyhydrazide formed. Polyurethanes containing the oxadiazole moiety were prepared by the condensation of 2,5 bis(4 hydroxyphenyl)1,3,4 oxadiazole with diisocyanatess. The synthesized polymers were characterized by 1H NMR, FTIR, UV-Vis, fluorescence and GPC analysis. Thermal properties of polymers were studied by TGA and DSC technique.

2.2 Materials

Terephthaloyl chloride, isophthalic acid, hydrazine monohydrate, potassium carbonate, para nitro benzoic acid, 4-hydroxy benzoic acid, para toluene acid chloride, para chloro benzoic acid, lithium chloride, β-naphthol, ferric chloride, 2,4,toluene diisocyanate, hexamethylene diisocyanate, BF_3, sodium bicarbonate (Merck Ltd., Mumbai) were of analytical grade and used as received. N-methyl -2-pyrrolidone (NMP) was purified by distillation under reduced pressure over basic alumina and stored over 4 Å molecular sieves. Methanol was super dried by Mg/I_2 and Pyridine was dried by refluxed with potassium hydroxide and subsequently distilled. Diethyl ether was purified by calcium chloride and then treating the solvent with sodium and then distilled to get absolute diethyl ether. DMF and DMAc were distilled under reduced pressure to remove the impurity.

2.3 Instrumentation

2.3.1 UV- Visible spectrophotometer

UV-Visible (UV-Vis) spectrophotometer provides the information about structure and stability of the materials in solution. Different kinds of electronic excitation may occur in organic molecules by absorbing the energies available in the UV-Vis region causing different types of electronic transitions within the molecule like n-π*, π-π* and n-σ*; thus providing the information regarding the structure, formulation, and stability of the materials in solution. Both solids and liquid samples can be analyzed. The intensity of the absorption is proportional to the number, type and location of colour absorbing structures in the molecule. 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. UV-Visible spectra were recorded on a Shimadzu UV-2500 UV-VIS Spectrophotometer using dimethylacetamide (DMAc) and N-methyl pyrrolidone (NMP) solvent[5-6].

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. The 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[5].

2.3.3 Nuclear magnetic resonance spectrometer (1H 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 signals of NMR spectra. It is a very selective technique, distinguishing among many atoms within a molecules or collection of molecules of the same type 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. 1H NMR spectra were obtained on a Bruker DMX-400 MHz with deuterated DMSO having TMS as internal standard[5-7].

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, GPC410, Water, USA. Flow rate was 1ml /min. Polymers were dissolved in THF solvent. Molecular weights were determined on the basis of polystyrene standards[7].

2.3.5 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) reveals the thermal characteristics of polymers including degradation temperature, absorbed moisture content, the percentage of oligomer in polymer etc[12]. It determines the weight loss with respect to temperature. Thermogravimetric analysis (TGA) was conducted on a Shimadzu TG50 thermogravimetric analyzer with a heating rate of $10^{o}C$/min under a nitrogen atmosphere and temperature range at 30- $700^{o}C$.

2.3.6 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is used widely for polymers. Glass transition temperature (Tg), melting temperature (Tm) and purity of polymers can be determined from DSC curve. 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 Shimadzu DSC-60 with a heating rate of 10°C/ min under a nitrogen atmosphere and temperature range at -30- 300°C [7-8].

2.3.7 Inherent viscosity

The inherent viscosity (η_{inh}) was determined using an Ubbelohde suspended level viscometer in NMP at 30 ± 0.1°C with 0.5 gm/dL polymer solution. It gives the information regarding the formation of the polymer. The inherent viscosity can be determined from the ratio of the natural logarithm of the *relative viscosity*, η_r, to the mass concentration of the polymer, *c*, i.e.

$$\eta_{inh} = \eta \ln = (\ln \eta_r)/ c$$

where η_r is the relative viscosity expressed as the ratio of the viscosity of the solution, η, to the viscosity of the solvent[9], η_s, i.e. $\eta_r = \eta/\eta_s$.

2.4 Experimental

2.4.1 Synthesis of Poly-1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing polar end groups like $-NO_2$, $-Cl$,$-CH_3$, $-OH$ (OXD AR1,-AR2,-AR3,-AR4)

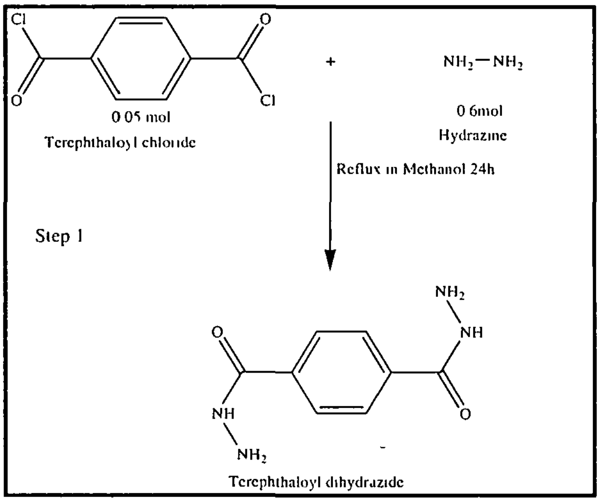
Synthesis of the monomer, Dihydrazide (Step 1)

Terephthaloyl chloride 1A, 10.22g (0.05 mol) was dissolved in 20mL methanol in a 100mL two necked round bottom flask and excess *hydrazine monohydrate*, 30mL (0.6mol) solution in 10mL methanol was added dropwise to the solution from a dropping funnel with the constant stirring. The reaction mixture was refluxed for about 24h and the product was precipitated from the mixture. After cooling to the room temperature, the precipitate was filtered, washed thoroughly with water and recrystallized from methanol and dried completely to give a white solid (**Scheme 2.1**).

(Yield 87%, mp 290°C).

FTIR(KBr disc cm^{-1}) 3211(-NH asymm), 3029(-NH symm.), 2941, 1716(-C=O str), 1600(-NH bend), 1469, 1266, 1172.

1H-NMR δ (400MHz, $DMSO-d_6$) ppm(400MHz): 8. 17(s, 4Ar-H), 8.15(s, 1H), 2.1(s, 2H)



Scheme 2.1: Synthesis of terephthaloyl dihydrazide

Synthesis of the polymer, amine terminated polyhydrazide(ATPH A)*Step 2*

The synthesis of the polyhydrazides involves two processes viz *high temperature phosphorylation* technique and *low temperature solution polycondensation* process. First process involves the condensation of dihydrazide with a dicarboxylic acid in presence of triphenyl phosphite or diphenylphosphite in an amide solvent and inorganic co-solvent like lithium chloride and catalyst (pyridine) at a very high temperature around 130-200°C under nitrogen atmosphere. The second process involves the condensation of dihydrazide with the diacid chloride of the aromatic acid in an amide solvent in presence of inorganic co-solvent and catalyst at low temperature (0-5°C) and then precipitated out in distilled water or methanol. Here we have synthesized the *terephthaloyl chloride* based *poly (amine-hydrazides)* via low temperature polycondensation process[10-12].

In a 100mL two necked round bottom flask a solution of 14g(0.07 mol) *Terephthalic dihydrazide* in 10mL NMP was added to a solution of *Terephthaloyl chloride* 10g(0.05g) in 10mL NMP (1.2:1 mol ratio) with the constant stirring at 0-5°C. 1-2 mL dry pyridine and LiCI (0.85%) was added to the mixture. The reaction mixture was stirred for different time intervals starting from 12hr to 72h at room temperature 30°C. After 8 hrs of the reaction 5mL NMP and 0.2g LiCl were added to enhance the solubility of the product formed and to get a clear solution. After the completion of the reaction visualized by the viscous opaque brown liquid, the mixture was poured in water with stirring to get a white precipitate of the polyhydrazide. The product was washed thoroughly with water and again reprecipitated to get a pure polymer. The product was dried in vacuum at about 70°C (**Scheme 2.2**).

(Yield 48-54 %, degradation temperature above 300°C).

FTIR(KBr disc cm-1) 3195(-NH str), 3027(w, -NH str), 2921, 2853, 1598, 1566, 1272, 1114, 867, 829, 782.

1H-NMR δ (400MHz, DMSO-d_6) ppm (400MHz): 8.1(s,lH), 7.9(s, 4Ar-H), 2.1(s,2 H)

***Synthesis of poly(1,3,4-oxadiazole)s (OXDA) from ATPH A* (Step 3)**

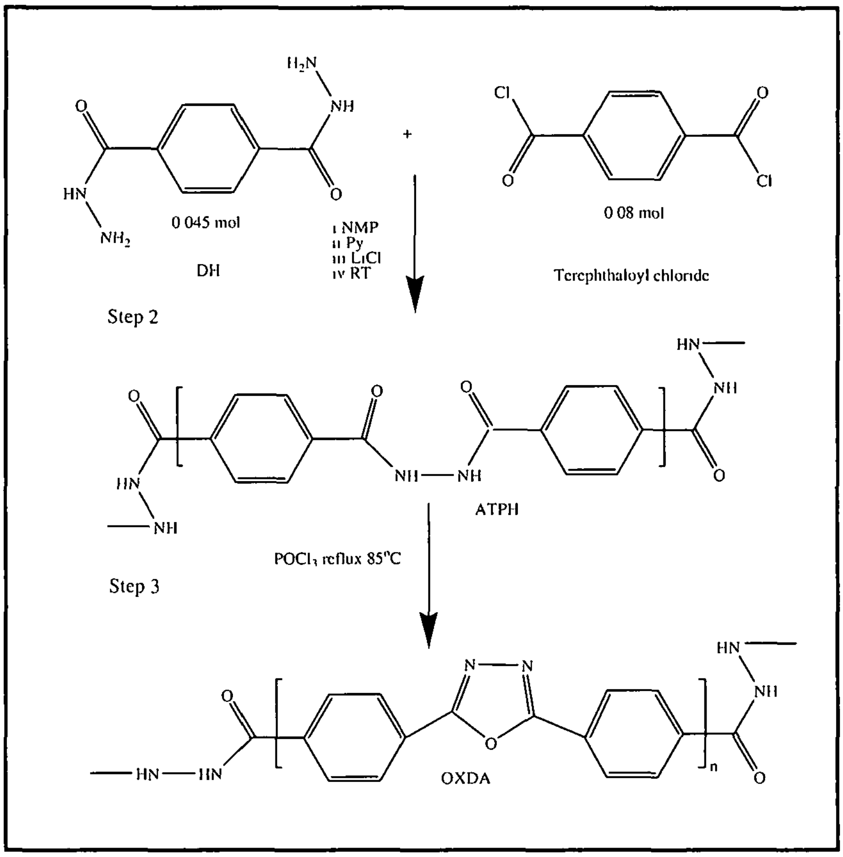
The synthesis of the polyoxadiazole was accomplished by both chemically and by thermal cyclodehydration reaction from the polyhydrazides. The thermal cyclization technique involves the heating of the polyhydrazides in vacuum; the cyclization temperature is optimized from the thermal analysis of the polyhydrazides.

In a 100mL two necked round bottom flask, the prepared 0.2 g ATPH A was added into 30mL phosphorous oxychloride and stirred for about 8h at room temperature and then refluxed for 24h. After cooling to the room temperature 30°C the mixture was poured in crushed ice, the precipitate was filtered, washed thoroughly with water and dried completely to get a light brown coloured solid (**Scheme 2.2**).

(yield 63%, degradation temperature>325°C).

The thermal cyclodehydration of the polymers was done by the thermal heating of the polyhydrazides in vacuum at 300-350°c in a steel vacuum reactor (**Scheme 2.2**).

(Yield 52%, degradation temperature >325°C).



Scheme 2.2: Synthesis of ATPH A and OXD A

FTIR (KBr disc cm^{-1}) 3187, 2985, 2622, 1716, 1669, 1600, 1469, 1274, 1172, 1037, 979, 866, 717, 651.

1H-NMR δ (400MHz, DMSO-d_6) ppm(400MHz): δ 8.4(s Ar-2H), 1.17(d, 2H), 7.9(s,Ar-2H), 7.6(t, Ar-2H), 2.3(s, 1H)

Synthesis of the ATPH A containing polar end groups (Step 4)

Synthesis of the polyhydrazide incorporating polar group -NO_2 from methyl 4-nitro benzoate

A solution of 1 g ATPH A in NMP was added to a solution of ~2.1 g (optimized from adding different percent concentrations) of *methyl 4-nitrobenzoate (synthesized from 4-nitrobenzoic acid)* in 10 mL NMP in a 100 mL round bottom flask with the constant stirring under nitrogen. 1-2 mL dry Pyridine was added and the reaction was carried out for 24 hr at 80°C. The mixture was precipitated in water to get a white powder, filtered and washed thoroughly with water and purified by reprecipitating from NMP.

FTIR (KBr disc cm^{-1}) 3201, 3027, 2922, 2833, 1598, 1537, 1566, 1356, 1272, 1114, 867, 829

Synthesis of the polyhydrazide incorporating polar group -OH from methyl 4-hydroxybenzoate

Similarly polyhydrazide incorporating polar group –OH was synthesized from ~2g of *methyl 4 hydroxybenzoate (synthesized from 4-hydroxybenzoic acid)*

FTIR (KBr disc cm^{-1}) 3449, 2925, 1727, 1678, 1417, 1282, 1116, 754

Synthesis of the polyhydrazide incorporating polar group -Cl from methyl 4-chlorobenzoate

Similarly polyhydrazide incorporating polar group – Cl was synthesized from ~2g of *methyl* 4- *chlorobenzoate (synthesized from 4-chlorobenzoic acid)*

FTIR (KBr disc cm^{-1}) 3222, 1682, 1280, 1108, 933, 741, 725

Synthesis of the polyhydrazide incorporating polar group -CH_3 from p-toluic acid chloride

Similarly polyhydrazide incorporating polar group - CH_3 was synthesized from ~2g of *p-toluic acid chloride* at room temperature for 24 hr.

FTIR (KBr disc cm^{-1}) 3422, 1676, 1417, 1284, 1182, 1112,956,755

Synthesis of poly(1,3,4-oxadiazole)s bearing polar groups

In a 100mL two necked round bottom flask, 2 g of each of the prepared ATPH A incorporating polar group was added into 30mL phosphorous oxychloride in different batches and stirred for about 8h at room temperature initially and then refluxed for another 24h. After cooling to the room temperature the mixture was poured in crushed ice, the precipitate was filtered, washed thoroughly with water and dried completely to get a light brown coloured solid (**Scheme 2.3**).

(Yield 50-55%).

The FTIR spectral data of the polyoxadiazoles bearing polar end groups are summarized in **Table** 2.2. Summary of the codes and composition of the synthesized **Poly-1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene** containing polar end groups are listed below(**Table 2.1**).

Table 2.1: Codes and composition of the poly-1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing polar end groups

CODES	COMPOSITION
ATPH A	Amine terminated polyhydrazide from terephthaloyl chloride
OXD A	Poly 1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene
OXD AR1	Poly 1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing $-NO_2$
OXD AR2	Poly 1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing -Cl
OXD AR3	Poly 1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing $-CH_3$
OXD AR4	Poly 1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing -OH

2.4.2 Synthesis of Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing polar end groups like $-NO_2$, -Cl,$-CH_3$, -OH (OXD BR1,-BR2,-BR3,-BR4)

Synthesis of the monomer, Synthesis of Isophthalic dihydrazide from Isophthalic acid chloride

Step 1 Preparation of *isophthalic acid chloride*

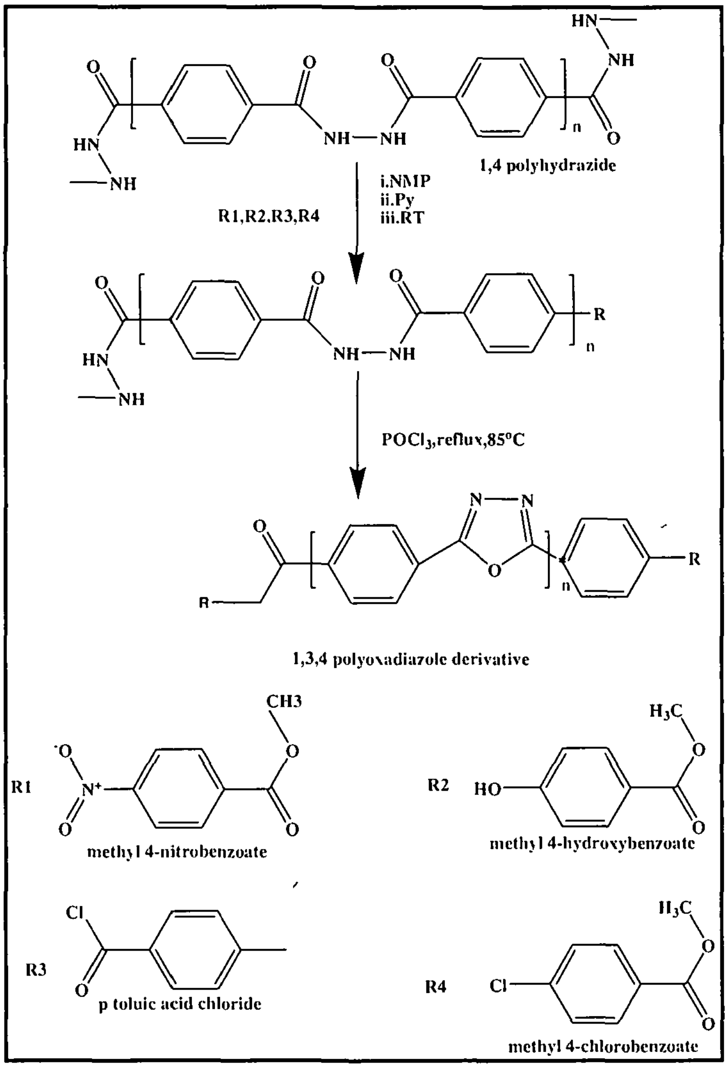
15g (0.09 mol) isophthalic acid was treated with 15 mL(~0.1 mol) oxaloyl chloride in a 100mL round bottom flask fitted with a reflux condenser and a dean n sterk apparatus at 70°C temperature. 1mL DMF was added as catalyst. After 5 hr 10 mL of toluene was added to the mixture and refluxed for another 5 hr at 120 °C. The excess oxaloyl chloride will be treated in toluene in the azeotropic distillation process and removed completely. The product was dried and kept in dessicator for further reactions.
(Yield 62%) (**Figure 2.4**)
FTIR (KBr disc cm^{-1}) 3106(w –CH str), 1705(s, C=O str), 1610(low frequency band due to the overtone of –CH bending mode at 829), [1508, 1416] (C=C str), 829, 725(s, -CH bend)

Step 2 Preparation of *Isophthalic dihydrazide*

9g(0.05 mol) isophthalic acid chloride was dissolved in 20mL methanol in a 100mL two necked round bottom flask and excess hydrazine monohydrate (30mL) solution in methanol(10mL)was added drop wise to the solution from a dropping funnel with constant stirring. The reaction mixture was refluxed for about 24h. After cooling to the room temperature, the product precipitated from the mixture, filtered, washed with water thoroughly and dried completely to give a white solid. (Yield 80%, mp215°C). (**Scheme 2.4**)

FTIR (KBr disc cm^{-1}) 3428 (-NH asymm),3079(-NH symm),1688(C=O),1616(-NH bend),1420(C=C ring str),1294(-C-N str),1161(-C-N str), 925(C=C-H bend),727(s, -CH bend)

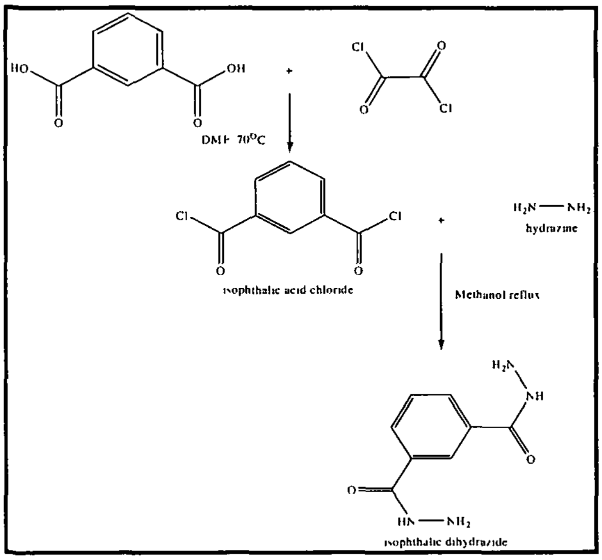
^{1}H-NMR δ (400MHz, DMSO-d_6) ppm (400MHz): δ 8.4(s, Ar-H), 8.14(q, 1H), 7.6(q, Ar-H), 2.1(s, 2H)



Scheme 2.3: Synthesis of **Poly 1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene** containing polar end groups $-NO_2$, $-Cl$,$-CH_3$, $-OH$ (**OXD AR1,-AR2,-AR3,-AR4)**

Table 2.2: FTIR spectral data of Poly 1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing polar end groups

Code	**Wave number(cm^{-1})**						
	-N-H symm.	-N-H Asymm.	-C=O Symm.	=C-O-C= Str.	-C-N Str.	-C=N Str.	-C-O-C bend.
OXD AR1	3429	3302	1682	1287	732,1426 (end group $-C-NO_2$)	1575, 1112	941
OXD AR2	3445 (broad)	3221 (w)	1727 (w)	1282	755	1573, 1114	955
OXD AR3	3223 (w)		1680 (w)	1280	744, 727(w, for -C-Cl)	1571, 1108	932
OXD AR4	3422,		1676	1282	755, 2930(weak -CH),1417(-CH asymm.)	1573, 1111	956



Scheme 2.4: Synthesis of Isophthalic dihydrazide

Synthesis of the polymer

Synthesis of Amine Terminated Polyhydrazide (ATPH B)

In a 100mL two necked round bottom flask a solution of isophthalic dihydrazide (0.045mol) in 10mL NMP was added a solution of isophthaloyl chloride (0.05mol) in 10mL NMP with the constant stirring at 0-5 °C. 1-2 mL dry pyridine and LiCl(0.85%) was added to the mixture(**Scheme 2.5**). The reaction mixture was kept stirring at room temperature (30°C). After 8 hrs of the reaction 5mL NMP and 0.2g LiCl was added to enhance the solubility of the product. After the completion of the reaction visualized by the viscous opaque brown liquid after 50 hr, the mixture was poured into water with stirring, filtered and washed thoroughly with water and again reprecipitated from NMP to get a pure polymer. The product was dried in vacuum at about 70°C.
(Yield 46 %, mp 320°C).
FTIR (KBr disc cm^{-1}) 3285(bonded secondary -NH), 3046(-CH), 2375(primary -NH), 1622(-C=O), 1610(-NH bend), 1525(υ C=C), 1311, 1104,[991, 922] (C=C-H bend), 824,829,689, 622(υ -C-H).
^{1}H-NMR δ (400MHz, DMSO-d_6) ppm (400MHz): δ 8.4(s, Ar-H), 8.14(q, 1H), 7.9(d, Ar-H), 7.6(t, Ar-H), 2.1(s, 2H)

1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene (OXD B) from ATPH B(Scheme 2.5)

Polyoxadiazoles was synthesized by chemically as well as by thermal cyclodehydration reaction of the polyhydrazides.

In a 100mL two necked round bottom flask, the prepared 2g ATPH B was added into 30mL phosphorous oxychloride and stirred for about 8h at room temperature and then refluxed for 24h. After cooling to the room temperature the mixture was poured in crushed ice, the precipitate was filtered, washed thoroughly with water and completely dried in vacuum to get a light brown coloured solid. (yield 63%,mp>325 °C).

The thermal cyclodehydration of the polymers was done by heating ATPH B in vacuum at 300-350 °C in a steel vacuum reactor. (Yield 52%, mp>325 °C).

FTIR (KBr disc cm^{-1}) 3399, 3079, 2996, 1716, 1669, 1600, 1469, 1274, 1172, 1037, 979, 866, 717, 651.

^{1}H-NMR δ (400MHz, DMSO-d_6) ppm(400MHz): ^{1}H-NMR δ (DMSO-d_6) ppm (400MHz): δ 8.14(s, 1H), 7.8(t,Ar-H), 7.5(d, Ar-H), 7.35(t, Ar-H), 2.1(s, 2H).

Synthesis of the polyhydrazide incorporating polar groups –NO_2, -OH,-Cl, -CH_3 from methyl 4-nitrobenzoate, methyl 4-hydroxybenzoate, methyl 4- chlorobenzoate, p-toluene acid chloride

In **Scheme 2.6** a solution of *isophthalic acid chloride* based 1g ATPH B in NMP was added to a solution of ~2g (optimized from adding different percent concentrations) of *methyl 4-nitrobenzoate, methyl 4- chlorobenzoate, p-toluene acid chloride and methyl 4-hydroxybenzoate* in 10 mL NMP in a 100 mL round bottom flask with constant stirring under nitrogen in four different batches. 1-2 mL dry pyridine was added and the reaction was carried out for 24 hr at 80 °C. The mixture was precipitated in water, filtered and washed thoroughly with water and purified by reprecipitating from NMP.

FTIR(KBr disc cm^{-1})of OXD BR1 (-NO_2 end group) 3201,3027, 2922,2833, 1598,1537,[1566, 1356](w, Ar N=O str), 1272, 1114,867,829

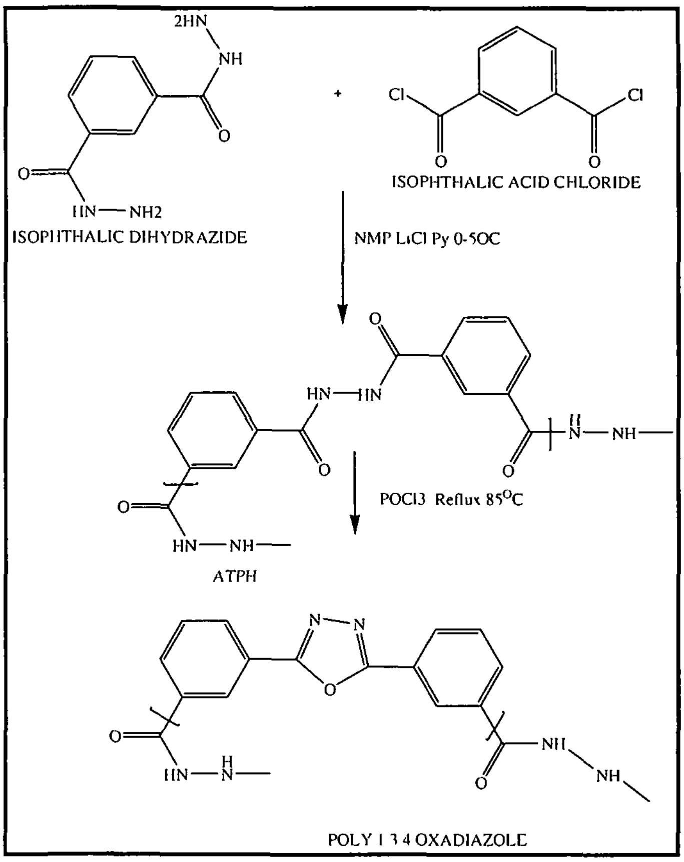
FTIR(KBr disc cm^{-1}) OXD BR2 (-Cl end group) 3222, 2887, 1682,1280, 1108,933,741,725

FTIR(KBr disc cm^{-1}) OXD BR3 (-CH_3 end group)3422, 1676, 1417,1284, 1182, 1112, 956, 755

FTIR(KBr disc cm^{-1}) OXD BR4 (-OH end group)3449,2925, 1727,1678, 1417,1282, 1116, 754

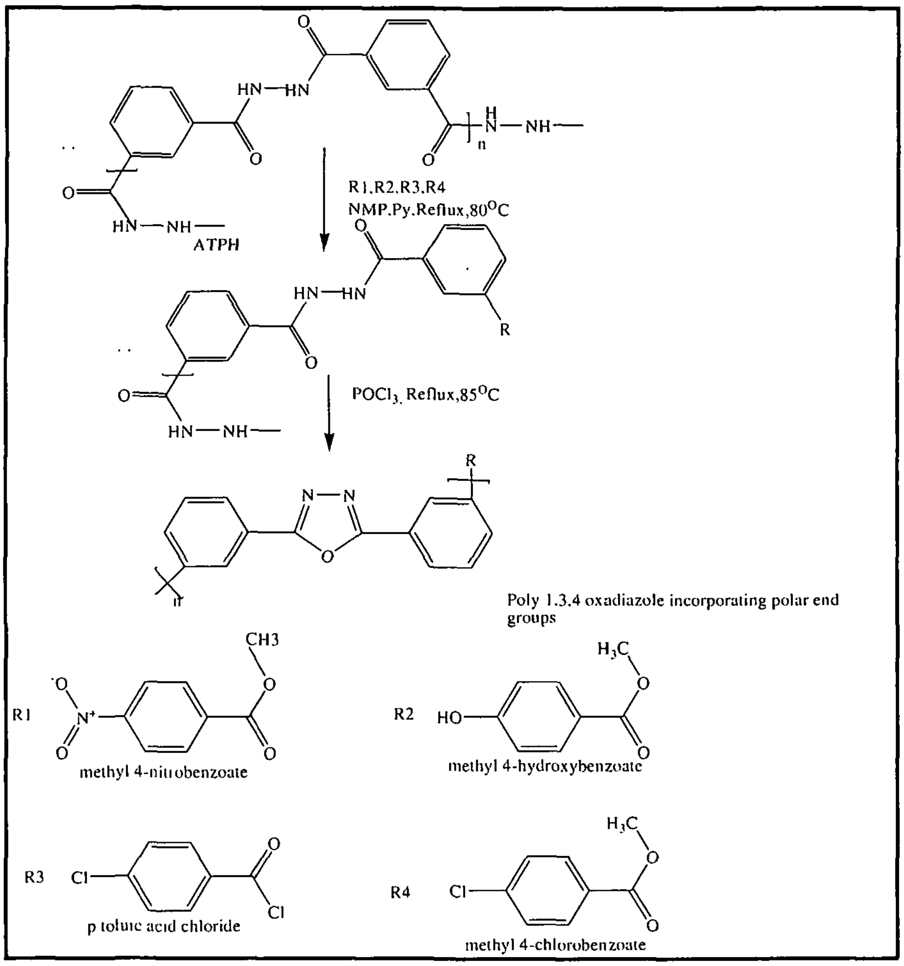
Synthesis of 1,3-Bis(phenyl-1,3,4-oxadiazolyl)phenylene bearing polar groups

In a 100mL round bottom flask, 2 g of each of the prepared poly (amine-hydrazide) incorporating polar group was added into 30mL phosphorous oxychloride and stirred for about 8h at room temperature and then refluxed for 24h. After cooling to the room temperature



Scheme 2.5: Synthesis of ATPH B and OXD B

The mixture was poured in crushed ice, the precipitate was filtered, washed thoroughly with water and dried completely to get a light brown coloured solid.(yield 48%).



Scheme 2.6: Synthesis of Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene incorporating polar end groups

Table 2.3 describes the codes and the composition of the Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing polymers with polar end groups in the main chain and the FTIR spectral data for these polymers are listed in **Table 2.4.**

Table 2.3: Codes and composition of Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing polymers with polar end groups

CODES	COMPOSITION
OXD B	Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene
ATPH B	Amine terminated polyhydrazide from isophthalic acid chloride
OXD B	Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene
OXD BR1	Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing –NO_2
OXD BR2	Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing –Cl
OXD BR3	Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing -CH_3
OXD BR4	Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing –OH

Table 2.4: FTIR spectral data of Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene with polar end groups

FTIR spectral data of the Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene incorporated with polar end groups							
Code	**Wave number(cm^{-1})**						
	-N-H Symm.	**-N-H Asymm**	**-C=O Symm**	**-C=N Str.**	**-C-N Str.**	**-C-O-C Str.**	**-C-O-C Bend.**
OXD B	3399	3079	1716	1274	717	1172	979
OXD BR1	3201	3027	1598	1272	829, 1356(C-NO_2)	1114	867
OXD BR2	3222		1682	1280	741, 725 (w, -C-Cl)	1108	933
OXD BR3	3422		1676	1284	755, 1417(-CH asymm.)	1182	956
OXD BR4	3449	2925	1727	1282	754	1116	956

2.4.3 Polyurethane containing 1,3,4 oxadiazole moiety

Design of Polymer

The polyurethanes synthesized contains the following segments as basic components

1. Segments having electron deficient 1,3,4 oxadiazole moiety i.e. the hole transporting unit; *2,5 bis(4 hydroxyphenyl)1,3,4 oxadiazole (OXD-diol)* (monomer A)
2. Binaphthol component to provide aromatic hard segments; *binaphthol* (monomer B), toluene diisocyanate (TDI) and hexamethylene diisocyanate(HMDI) as diisocyanate source

The incorporation of the monomer A and B to the polyurethane was achieved by the condensation of the monomers with commercially available TDI and HMDI in Toluene in different proportions so that the resultant polymer should meet the solubility and film casting properties.

The first set of the two polymers were synthesized from the condensation of the 2,5 bis(4 hydroxyphenyl)1,3,4 oxadiazole(monomer A) and TDI or HMDI at 70-75°C in 1.5:1, 1.3:1, 1.1:1 ratios. Out of these only the polymers synthesized in 1.3:1 ratio were adopted for study depending on their good solubility behavior.

The second set of polyurethanes was prepared by the condensation of 2,5 bis(4 hydroxyphenyl)1,3,4 oxadiazole(monomer A) and binaphthol (monomer B) together with TDI and HMDI. Concentration of monomer A and B were varied and optimized from the solubility and the UV –visible spectra in solution keeping the isocyanate feed constant. The concentration of A and B were taken in 2:1, 1.5:1, 1.3:1, 1.1:1 and 1:1 ratios but the polymers synthesized in the ratio 1.5:1 keeping the isocyanate feed constant as 1 molar concentration meeting required solubility and UV-vis absorption. This ratio was adopted in the present work as the absorption due to π- π^* interaction at 280-360 nm was found maximum in this concentration. The solubility can also be controlled in this feed ratio of both the diols. The maximum absorption at this concentration can be assigned as the interaction of the oxadiazole and the binaphthol component.

*Synthesis of Monomer A (***Scheme 2.7***)*

Synthesis of the 4-hydroxy methyl benzoate

10g (0.067 mol) of 4 hydroxy benzoic acid was mixed with 70ml of boron trifluoride-methanol complex (14% w/v) and refluxed in a 200mL round bottom flask for 8 hrs. The reaction mixture was cooled and $NaHCO_3$ solution in excess (500mL) was added in a beaker with constant stirring. The organic layer was separated from ether in a separatory funnel and dried over magnesium sulphate. The product was isolated by the distillation of the organic layer[13].

Yield (6.1 g, 61%) mp 115°C

FTIR(KBr disc cm^{-1}): 3419(O-H), 1681(C=O), 1608, 1513, 1433, 1279, 1232, 1165, 952, 850, 769

1H-NMR δ (400MHz,DMSO-d_6): 7.6(d,2H), 6.7(d,2H), 4.3(s,2H)(amine proton peak merged with solvent peak at 2.4)

Synthesis of 4-hydroxy benzohydrazide

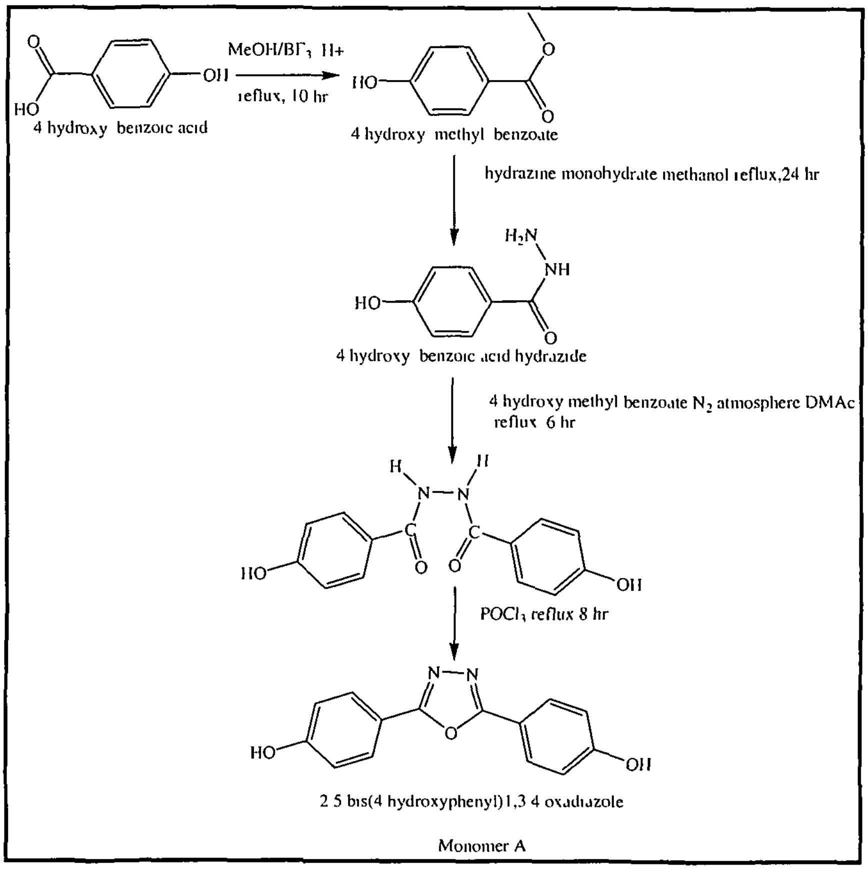
A mixture of hydrazine monohydrate in methanol solution was added slowly dropwise to the mixture of 5 g of *4-hydroxy methyl benzoate* (0.03 mol) in dry methanol with constant stirring. The pale yellow solution was then refluxed for 12 hr and cooled. the product was distilled from the organic solution..

Yield (3.7g, 74%) mp 257°C

FTIR(KBr disc cm^{-1}): 3411,3206,1682,1608,1511,1433,1279,1232,1168,950,850,768

Synthesis of 2,5 bis(4 hydroxyphenyl)hydrazide diol and 2,5 bis(4 hydroxyphenyl)1,3,4 oxadiazole(OXD-diol)

An equimolar mixture (1:1molar ratio) of *4-hydroxy benzohydrazide* and *4-hydroxy methyl benzoate* solution in DMAc and in presence of 1ml pyridine at room temperature. The solution changes colour to a light brown liquid and then poured in water with constant stirring. The precipitate was filtered, washed for several times with water and dried. The dried hydrazide was dissolved in phosphorous oxychloride and refluxed for 18 hr at 80°C. The resultant product was precipitated in crushed ice-methanol mixture, filtered and dried in vacuum.



Scheme 2.7: Synthesis of 2,5 bis (4 hydroxy phenyl)1,3,4 oxadiazole, ***OXD-diol*** (Monomer A)

Yield (49.3%) mp 333°C

FTIR(KBr disc cm^{-1}): ϋ =3408,3206,1682,1608,1511,1433,1279,1232,1168,950,850,768

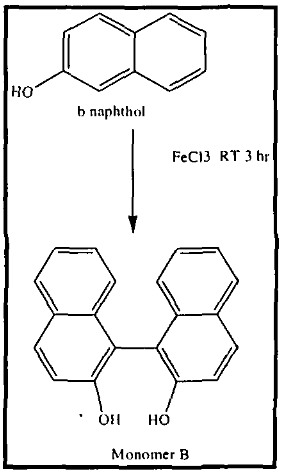
1H NMR (400MHz, DMSO-d_6): υ 7.8(d, 2H), 6.8(s,2H), 3.7(s, 1H)

Synthesis of Monomer B, binaphthol (Binol) **(Scheme 2.8)**

In a 500ml three necked round bottom flask, provided with a dropping funnel, a sealed stirrer and a reflux condenser, 3gm (0.02 mol) of 2-naphthol was taken in 200ml of water and heated to the boiling point. To the boiling liquid containing liquid 2-naphthol, 15 ml aqueous solution of 4.5gm $FeCl_3$ (0.02 mol) was added slowly. Soon the oily drops of 2-naphthol disappeared and the product separated out in flakes. The mixture is boiled for 1hr and hot suspension was filtered and washed with hot water. The product was dried in vacuum and recrystallised from toluene[14]. Yield (89%), m.p.218°C.

FTIR (KBr disc cm^{-1}): ϋ = 3484, 3400, 3047, 2361, 1617, 1596, 1511,1465, 1379, 1320, 1214, 1173, 1143, 979,957, 822,749, 668,572

^{1}H NMR (400 MHz, $CDCl_3$-d_6): 5.2(s, 3H), 7.05(d, 4H), 7.2(m, 11H), 8(q, 7H)



Scheme 2.8: Synthesis of binaphthol, ***Binol*** (Monomer B)

Synthesis of the polymers (Polyurethanes)

Synthesis of Polyurethane PU1 **(Scheme 2.9)**

In a 100 mL three necked round bottom flask 1.5g (0.01 mol) Monomer A (***OXD-diol***) was purged with nitrogen gas for 15 min. To this 2 mL DMF and 0.76 mol equivalent 2,4toluene diisocyanate was added dropwise with constant stirring (**Scheme 2.9**). The reaction mixture was heated to 75°C and maintained for 3 hr. The viscous solution was then cooled to the ambient temperature and poured into the cold water with stirring. The resulting precipitate was filtered and washed several times with hot water. Further, it was dissolved in 3ml DMF and re-precipitated by pouring into 20mL methanol to remove the unreacted monomer, low molecular weight dimer, trimer and so on. The resulting product was filtered and dried in vacuum.

Yield 47%. m.p. 310-316°C

FTIR (KBr disc cm^{-1}): 3285(N-H), 1680(C=O), 1613(C=C), [1540,1274](N=O),1208, 1013, 811, 749

^1H NMR (400 MHz, DMSO-d_6): 8.0(s, 1H), 7.6(d, 1H), 7.4(d, 1H), 6.9(d, 1H), 2.1(s, 3H)

Synthesis of Polyurethane PU3 **(Scheme 2.10)**

In a 100 mL three necked round bottom flask containing 1.5g (0.01mol) Monomer A, ***OXD-diol*** and purged with nitrogen gas for 10 min. Then 3g (0.01mol) Monomer B, ***Binol*** was added slowly with stirring followed by 2 mL DMF and 1.5 mol equivalent 2,4 toluene diisocyanate was added dropwise. The reaction mixture was heated to 75°C and maintained for 3 hr. The viscous solution was then cooled to the ambient temperature and poured into the cold water with stirring. The resulting precipitate was filtered and washed several times with hot water. Further, it was dissolved in 3ml DMF and re-precipitated by pouring into 20mL methanol to remove the monomer, low molecular weight dimer, trimer and so on. The resulting product was filtered and dried in vacuum.

Yield 49%. m.p. 254-289°C

FTIR (KBr disc cm^{-1}): 3289, 1640, 1593, 1527,1268, 1213, 1016,857,812,676,585

^{1}H NMR (400 MHz, DMSO-d_6): 8(d, 1H), 7.6(q, 2H), 7.5(q, 51H), 2.1(s, 1H)

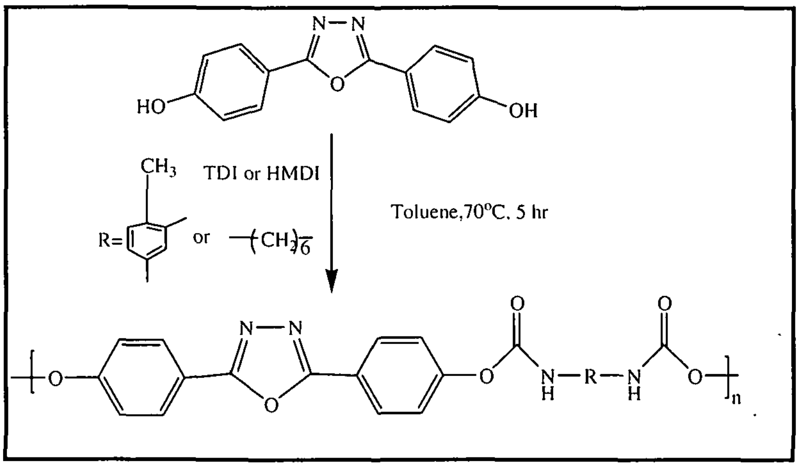
A similar procedure was followed for the synthesis of polyurethanes PU2 and PU4 with HMDI as isocyanate source with the same ratio. The spectral and the analytical data for these polymers are given below.

For PU2:

Yield.46% m.p.313-321°C

FTIR (KBr disc cm^{-1}): 3698, 3276, 1640, 1616, 1507, 1272, 1210, 813, 752, 680

^{1}H NMR (400 MHz, DMSO-d_6): 7.9(d, 2H), 7.3(d, 2H), 7.2(sexlet,2H), 7.1(d,2H), 3 (t,74H), 2.9(d, 2H), 1.9(q,4H)



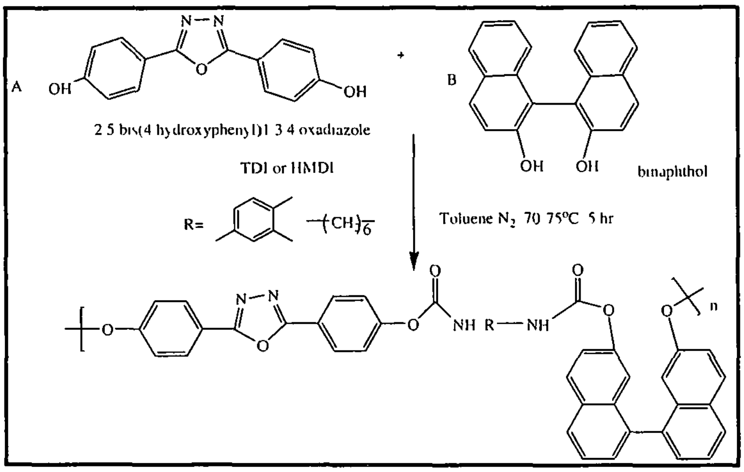
Scheme 2.9: Synthesis of PU1 and PU4

For PU4:

Yield 47% mp 254-286°C

FTIR (KBr disc cm^{-1}): 3776, 3700, 3296, 1671, 1606,1541,1268,1214, 1032, 815,751,680

^{1}H NMR (400 MHz, DMSO-d_6): 8(m, 2H), 7.6(m,2H),7.2(m,4H), 6.8(q,2H), 2.9(q,3H), 3.1(m, 73H), 1.6(d, 2H),1.3(d,2H).



Scheme 2.10: Synthesis of PU2 and PU3

The codes and the composition of the polyurethane polymers and the FTIR spectral data are listed in **Table 2.5 and Table 2.6** respectively.

Table 2.5: Codes and composition of polyurethanes

CODES	COMPOSITION	Monomer
PU1	Polyurethane containing 1,3,4 oxadiazole moiety and toluene diisocyanate	2,5 bis(4 hydroxyphenyl)1,3,4 oxadiazole)
PU2	Polyurethane containing 1,3,4 oxadiazole moiety , binaphthol and toluene diisocyanate	2,5 bis(4 hydroxyphenyl)1,3,4 oxadiazole)
PU3	Polyurethane containing 1,3,4 oxadiazole moiety and hexamethylene diisocyanate	2,5 bis(4 hydroxyphenyl)1,3,4 oxadiazole and Binaphthol
PU4	Polyurethane containing 1,3,4 oxadiazole moiety, binaphthol and hexamethylene diisocyanate	2,5 bis(4 hydroxyphenyl)1,3,4 oxadiazole and Binaphthol

Table 2.6: FTIR spectral data of the polyurethanes

FTIR spectral data of the polyurethanes containing 1,3,4-oxadiazole							
Code	**Wave number(cm^{-1})**						
	-N-H Symm.	**-C=C- Str.**	**-C=O Symm.**	**-C=N Str.**	**-C-N Str.**	**-C-O-C Str.**	**-C-O-C Bend.**
PU1	3285	1613	1680	1208	749	1013	811
PU2	3276	1616	1640	1210	752	1026	813
PU3	3289	1593	1640	1213	812	1016	857
PU4	3296	1606	1671	1214	815	1032	751

2.5 RESULTS AND DISCUSSIONS

2.5.1 Spectroscopic analysis

FTIR analysis of monomer and the polymers

The formation of the dihydrazide from terephthaloyl chloride (**Scheme 2.2**) was confirmed by the appearance of the -NH stretching frequency at 3211 and 3029 cm^{-1} in FTIR for asymmetric and symmetric vibrations of the secondary amine. The broad absorption at these positions confirms the formation of hydrazide functionality. The appearance of a weak stretching band near 1537 cm^{-1} is due to –NH deformation vibration. The polyhydrazide formation involves the decreasing of the intensity of the secondary amine stretching and the C-N stretching 1172 to 1114 cm^{-1}. The formation of the polyoxadiazole from the polyhydrazide is confirmed by the decreasing of the intensity of the stretching frequency of the -NH stretching at 3400-3500 cm^{-1} and -C=O stretching at 1690-1720 cm^{-1} and appearance of a band near 1574 cm^{-1} for -C=N(for oxadiazole ring) stretching in FTIR analysis. In addition to that, =C—O—C=stretching was observed 1110 and 945 cm^{-1} for the oxadiazole polymers which is primarily absent in polyhydrazides. **OXDAR1** shows stretching at 1575 cm^{-1} for -C=N, 1112 and 941 cm^{-1} stretching for =C—O—C= and a characteristic str. for nitro group around 1356 cm^{-1}. Similarly **OXD AR2** shows C=N str at 1573 cm^{-1}, 1114 and 955 cm^{-1} for =C-O-C= str and the stretching band at the fingerprint region at ~ 750-765 cm^{-1} and the shifting of the C=O stretching band 1722 cm^{-1}due to the end chloro group. **OXD AR3** shows C=N str at 1571 cm^{-1}, 1108 and 932 cm^{-1} for =C-O-C= str and a weak stretching band nearly at 3000cm^{-1}due to the end methyl group. **OXD AR4** show C=N str at 1573 cm^{-1}, 1111 and 956 cm^{-1} for =C-O-C= str. The hydroxyl group terminated polymers were confirmed by the broadening of the NH stretching due to the overlapping of the -OH stretching (**Scheme 2.3**).

Depending on meta acid chloride (isophthaloyl chloride) and para acid chloride (terephthaloyl chloride) as starting material, cyclodehydration produced meta-polymers (OXD B) and para-polymers(OXD A), respectively. These materials behave in a slight different manner in the FTIR spetcra. The FTIR spectral data for both the sets of polymers show the same trend of change in absorption intensities and positions in the formation of polyoxadiazoles from their respective polyhydrazides[15-16].

The variation in the carbonyl stretching frequency in the meta- linked polymer is slightly in the lower field as compared to the para-linked polymer. Thus the shifting in the –NH stretching around 3300cm^{-1} and –NH wagging around 750 cm^{-1} is also due to the same reason. The –NH stretching for the meta polymers OXDB and the polar end group containing meta polymers OXDBR1, OXDBR2, OXDBR3 and OXDBR4 have –NH stretching in 3399, 3201, 3222, 3422 and 3449 cm^{-1}. The carbonyl group stretching frequency at 1622 cm^{-1}, the -C=C- group stretching at 1525cm^{-1} and the –C=C-H stretchings at 991 and 922 cm^{-1} in the meta polyhydrazides are more intense than para polymers. The broadening of the –NH stretching frequencies in the meta polymer is also due to the hydrogen bonding which is low in the para polymers[16,17]. The characteristic intense low frequency band near the carbonyl stretching at 1598-1676 cm^{-1} for all the 1,3,4-oxadiazole containing meta polymers is due to the overtone of –CH bending mode at 829cm^{-1}.

The polyurethanes containing oxadiazole moiety show the N–H stretching at 3285, 3276, 3289 and 3296 cm^{-1} for PU1, PU2, PU3 and PU4 which are broad, suggesting that the urethane linkages experience hydrogen bonding (**Scheme 2.9** and **Scheme 2.10**). The -NCO absorption band disappears near 2265cm^{-1} and the appearance of the –C=O stretching at 1680, 1640, 1640, 1671 $cm^{-1}$and -C-O-C- stretching at 1013, 1026, 1016, 1032 cm^{-1} respectively indicate the formation of the polyurethane in the reaction. The low intensity frequencies around 1600cm^{-1} in all the polyurethane polymers may be assigned as the –NH bending characteristic to the urethane bond formation.

1H NMR analysis

The formation of the dihydrazides was confirmed from the 1H NMR spectra in **Figure 2.1** at 400MHz where the peaks for the primary and secondary amine protons found at δ 2.1 and δ 8.15. The aromatic protons resonate at δ 8.17.

Polyhydrazide ATPH A (**Figure 2.2**) shows the increasing of intensity in the same peak positions due to the increase in the concentration of the amine proton with the formation of the polymer. The aromatic protons resonate at 7.9 ppm, amine protons at 8.1 and 2.1 ppm.

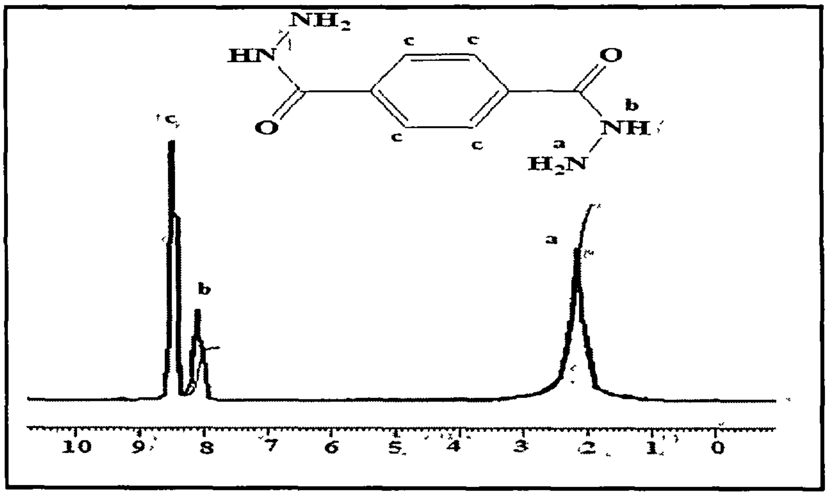


Figure 2.1: 1H NMR spectra of 1,4 terephthaloyl dihydrazide

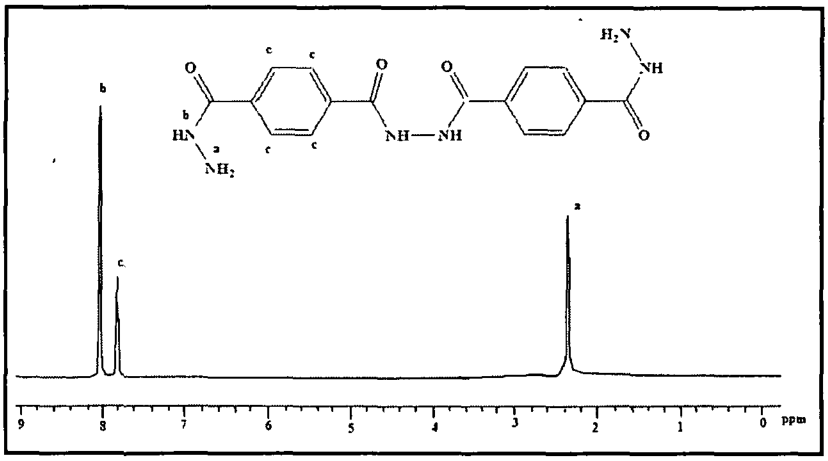


Figure 2.2: 1H NMR spectra of ATPH A

Similarly the shifting of the 1H NMR peaks and splitting of the peaks (doublet) at δ 7.9 to 8 for the protons for benzene ring due to the formation of oxadiazole ring in **Figure 2.3**. The decreasing in intensity of the peaks near at δ 2.3 for the hydrazide protons primary amine (-NH-NH-) is due to the cyclization of the hydrazide linkage. The ratio of the integration of the respective protons matches with the proposed structure of the compound. All the 1H NMR spectra was recorded in a 400 MHz NMR spectrophotometer. Similarly the various polar group containing polymers were confirmed by 1H NMR.

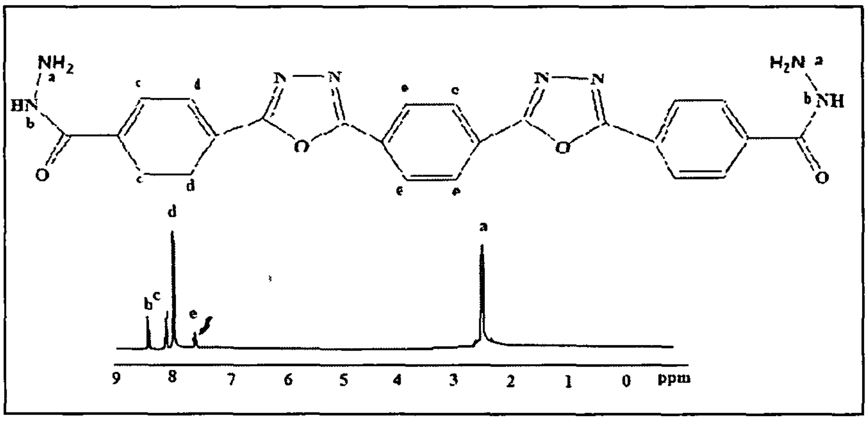


Figure 2.3: 1H NMR of OXD A

1H NMR spectra of the meta-polymers can be explained below. The aromatic proton of the isophthalic dihydrazide (**Figure 2.4**) resonate at 7.62, 8.2 and 8.5 ppm due to the shieldng-deshielding effect of the neighbouring amide protons in 1,3-positions. The amide protons and NH_2 protons resonate at 8.0 and 2.1 ppm respectively.

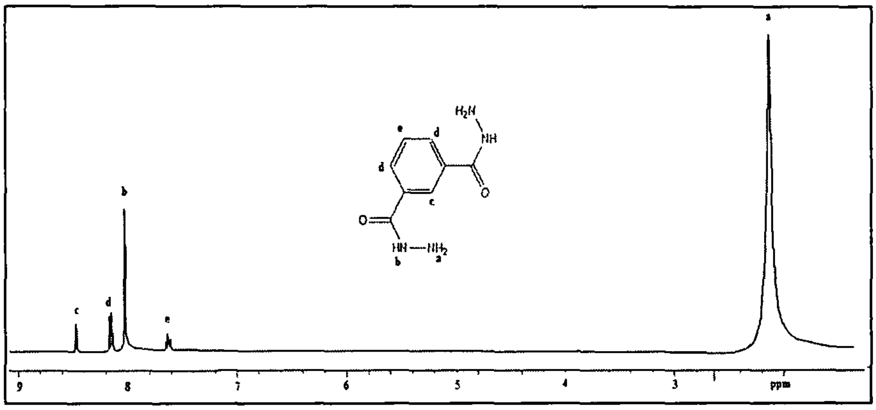


Figure 2.4: 1H NMR of isophthalic dihydrazide

Figure 2.5 represents the 1H NMR spectra of the isophthalic polyhydrazide. the lowering intensity of the NH_2 protons at 2.1 ppm indicates the formation of the polyhydrazide system. The formation of oxadiazole ring is confirmed by the more lowering in intensity of the amide protons at 8.2 ppm and the aromatic protons are deshielded to 7.6, 7.9 and 8.4 ppm (**Figure 2.6**). This is due to the absence of the neighboring protons in the aromatic system.

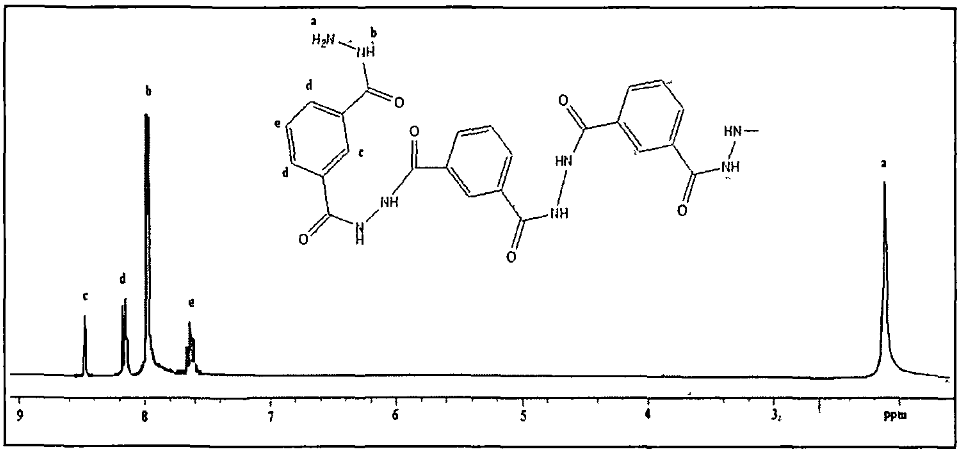


Figure 2.5: 1H NMR of ATPH B

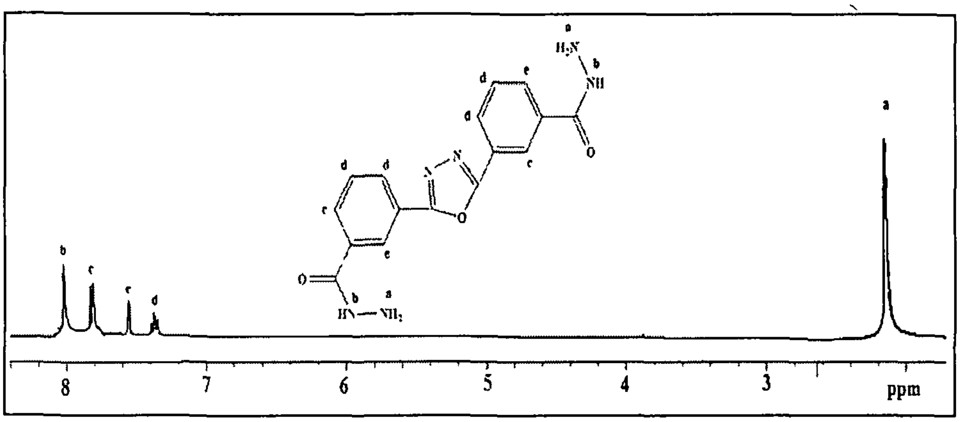


Figure 2.6: 1H NMR of OXD B

1H NMR spectra of the polyurethane (**Figure 2.7-2.20**) show the signal broadening due to formation. The protons resonating at 8.0 ppm are assigned to the -CONH protons, indicating the formation of the urethane linkage. The more deshielded protons of the aromatic ring resonates at 7.6-6.9 ppm correspond to the protons near the oxadiazole moiety.

In **Figure 2.7**, the aromatic protons resonate at 7.6, 7.4 and 6.9 ppm. The methyl proton resonates at 2.1 ppm and the amine proton resonates at 2.6 ppm.

Figure 2.7: 1H NMR spectra of PU1

PU2 can be confirmed by the appearance of -CONH protons at 8.0 ppm from the urethane linkage and the methyl protons at 2.2 ppm (**Figure 2.8**). The more deshielded aromatic protons from the binol rings near 6.9-7.9 ppm conclude the formation of the polymer of the proposed structure.

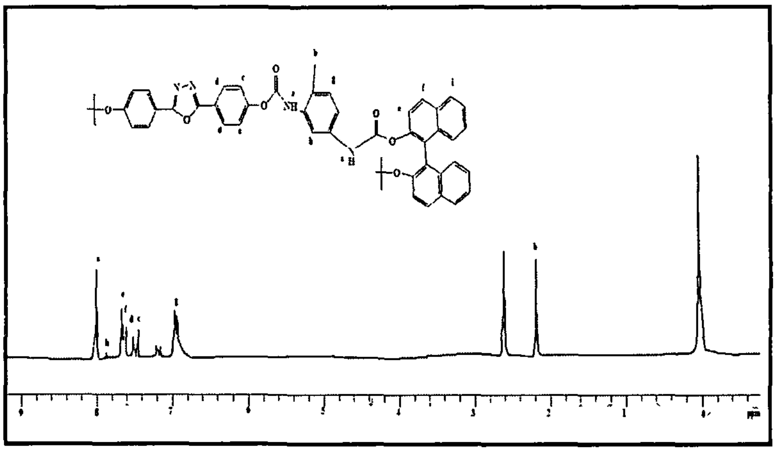


Figure 2.8: 1H NMR spectra of PU2

The formation of PU3 polymer can be confirmed (**Figure 2.9**) by the urethane proton signal at 8.0 ppm and characteristic signals for the $-CH_2$ protons aroud 2-3 ppm for the HMDI confirms the formation of the polymer.

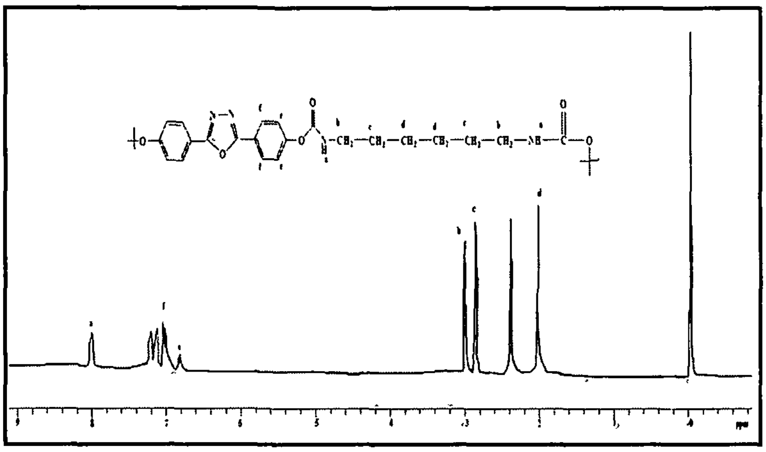


Figure 2.9: 1H NMR spectra of PU3

The -CONH proton signal at 8.0 ppm, and the shifting of the aromatic protons in the NMR spectra confirmed the formation of the PU4 polymer (**Figure 2.10**). The characteristic $-CH_2$ protons around 2-3 ppm is due to the HMDI used.

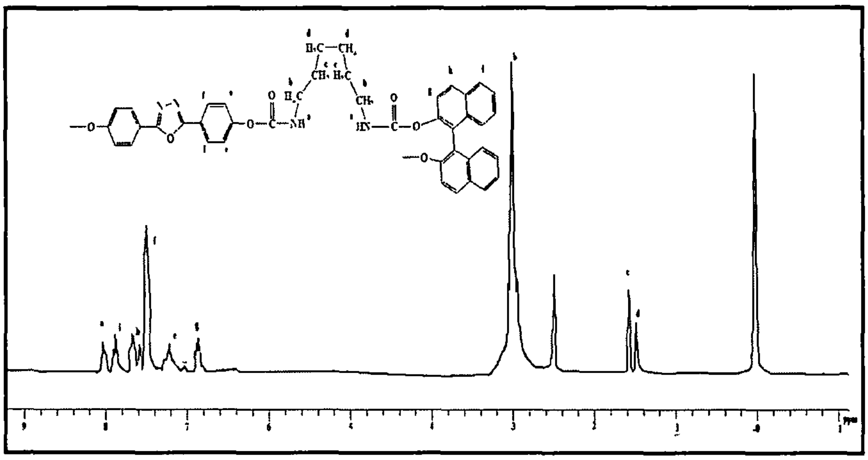


Figure 2.10: 1H NMR spectra of PU4

2.5.2 Molecular weight of polymers

Molecular weight of polymers was measured by gel permeation chromatography (GPC) technique in THF solution using polystyrene standard. Average molecular weights of the polymers in THF are shown in **Table 2.7**. GPC curve of the polymers are explained in the **Figures 2.11-2.17**. The polymers are partly soluble in THF (only 10-15%) solvent and hence the GPC analysis was performed with the soluble part only. The oligomeric polyoxadiazole derivatives resulted with the number average molecular weight (Mn) range from 2650-3400g/mol with polydispersity index (PDI) of 1.11-1.42. by changining the stoichiometry of the reaction we had intentionally prepared low molecular weight polymer to serve our purpose of soluble polymers with 1,3,4-oxadiazole moiety. The number-average molecular weights of the polyurethanes carrying the oxadiazole moiety are in the range of 4158-4617g/mol with polydispersity indexes in the range of 1.06-1.12. The weight average molecular weights of polymers have been found in the range 3789-4130 g/mol. The results show that THF soluble part of polymers is of low molecular weight[18-21].

Table 2.7: Average molecular weight of polymers

Polymer	**Number average molecular weight ¯Mn (g/mol)**	**Weight average molecular weight ¯Mw (g/mol)**	**Polydispersity index ¯Mw/¯Mn (PDI)**
OXD AR1	2425	2621	1.12
OXD AR2	-	-	-
OXD AR3	3174	3758	1.18
OXD AR4	-	-	-
OXD BR1	-	-	-
OXD BR2	2119	2538	1.19
OXD BR3	-	-	-
OXD BR4	-	-	-
PU1	4158	3712	1.12
PU2	4357	4013	1.08
PU3	4617	4163	1.10
PU4	4410	4130	1.06

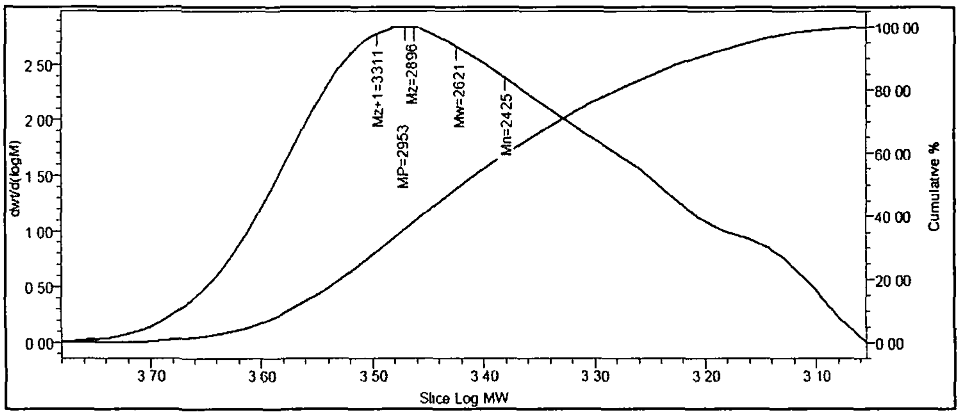


Figure 2.11: GPC result of OXD AR1

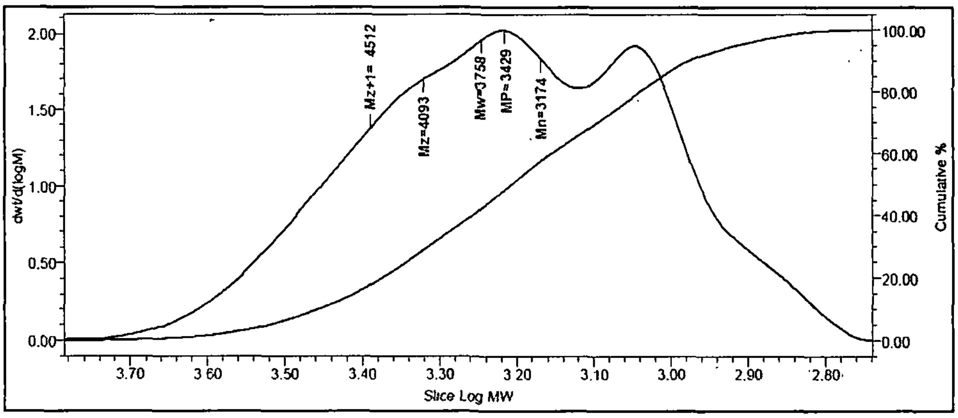


Figure 2.12: GPC result of OXD AR3

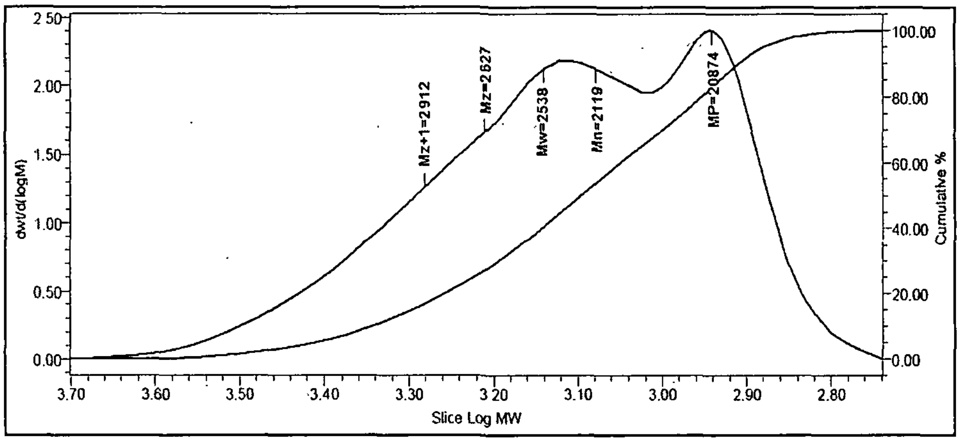


Figure 2.13: GPC result of OXD BR2

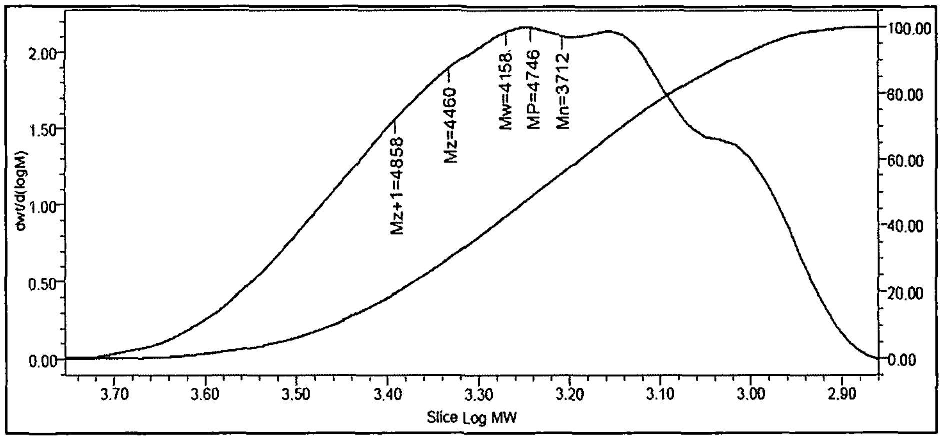


Figure 2.14: GPC results of PU1

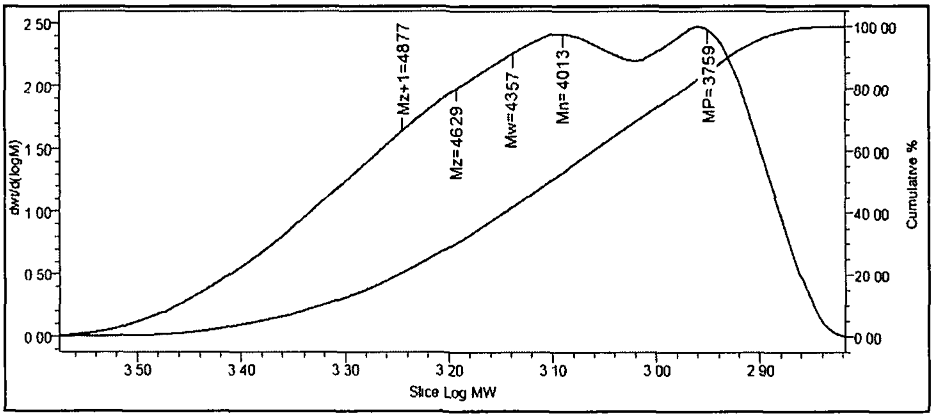


Figure 2.15: GPC results of PU2

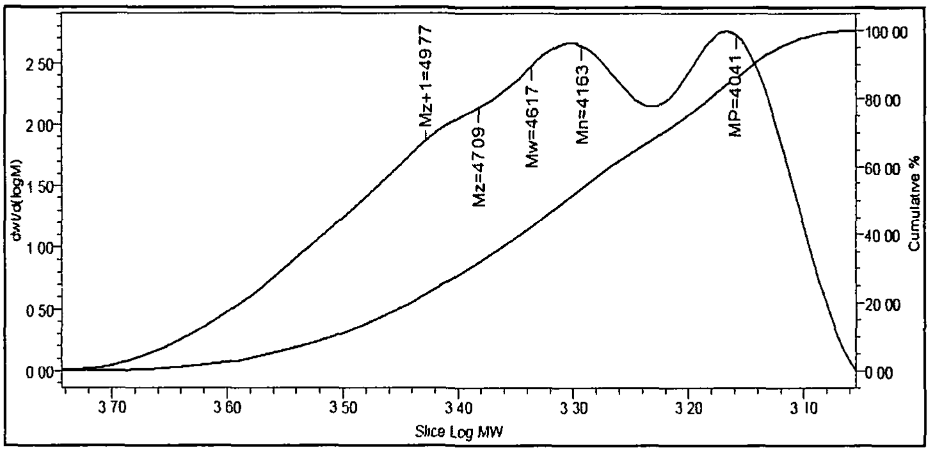


Figure 2.16: GPC result of PU3

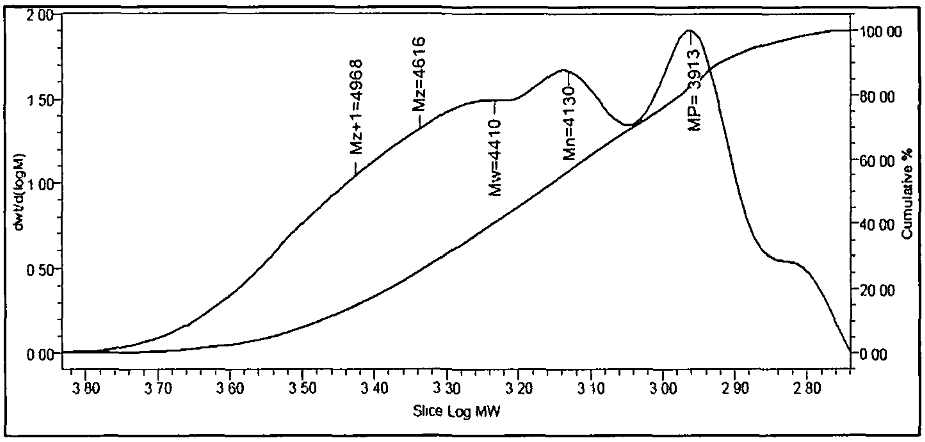


Figure 2.17: GPC result of PU4

2.5.3 Solubility and film forming character of the polymers

Solubility in organic solvents particularly in moderately high boiling solvents is an important factor for the processibility of the electroactive polymers for the device fabrication. Not only is that, for the characterization of the polymer solubility and the void free film formation an important criteria. The polymers are soluble in NMP, DMF, DMAc and DMSO and partly soluble in THF. The solubility of the polymers in different solvents is given below in **Table 2.7**. The poly(1,3,4 oxadiazole)s and the derivatives are soluble in high boiling solvents like DMF, DMAc, NMP etc. and insoluble in low boiling organic solvents like water, methanol, ethanol etc and partially soluble in THF. The solubility of the polymer synthesized is dependent on the time of the reaction for the formation of polyhydrazide and the corresponding polyoxadiazoles. The longer the time taken to complete the polymerization, the solubility gradually decreases in common organic solvents due to formation of the higher molecular weight polymer.

The percent solubility of the polymers in different solvents is shown in **Table2.8**. The fraction of polymers soluble in THF is 10-15 %. 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.

Polymers were cast into films on glass substrate from their respective solutions (0.5%) in NMP. The films are even and thin as desired. Polyoxadiazoles with the nitro, hydroxy and the chloro end groups OXD AR1, OXDAR2, OXDAR3, OXDBR1, OXDBR2, OXDBR3 and the polyurethanes PU1, PU2, PU3 and PU4 form fine films. Therefore these polymers can be investigated for the further study as good film formation from the polymers is one of the criteria for the OLED fabrication[20].

2.5.4 Inherent Viscosity analysis

The inherent viscosity of the polymers (**Table 2.8**) at room temperature in NMP solution was calculated. The inherent viscosity of the polymers in DMAc at room temperature ranges between 0.45-0.6 dl/g. there was no significant change in viscosity was marked with the change in the polar groups in polyoxadiazole polymers. The polyurethanes are low molecular weight compound, moderately viscous and are significant for the typical polyurethane polymer resins[22].

Table 2.8: Percent solubility and inherent viscosity of the polymer

Polymer	Solvents and % solubility										Inherent viscosity at room temperature, 30°C (dL/g)
	Acetone	**Water**	**Chloroform**	**Methanol**	**THF**	**DMF**	**DMAc**	**DMSO**	**NMP**	**Conc. H_2SO_4**	
OXD A	--	--	--	--	-+ 10-15	++ 60-70	++ 60-70	++ 30-40	++ 80-90	++ 95-	0.43
OXD AR1	--	--	--	--	-+ 10-15	++ 60-70	++ 60-70	++ 30-40	++ 80-90	++ 95-	0.45
OXD AR2	--	--	--	--	-+ 10-15	++ 60-70	++ 60-70	++ 30-40	++ 80-90	++ 95-	0.45
OXD AR3	--	--	--	--	-+ 10-15	++ 60-70	++ 60-70	++ 30-40	++ 80-90	++ 95-	0.41
OXD AR4	--	--	--	--	-+ 10-15	++ 60-70	++ 60-70	++ 30-40	++ 80-90	++ 95-	0.43
OXD B	--	--	--	--	-+ 10-15	++ 60-70	++ 60-70	++ 30-40	++ 80-90	++ 95-	0.46
OXD BR1	--	--	--	--	-+ 10-15	++ 60-70	++ 60-70	++ 30-40	++ 80-90	++ 95-	0.45
OXD BR2	--	--	--	--	-+ 10-15	++ 60-70	++ 60-70	++ 30-40	++ 80-90	++ 95-	0.45
OXD BR3	--	--	--	--	-+ 10-15	++ 60-70	++ 60-70	++ 30-40	++ 80-90	++ 95-	0.43
OXD BR4	--	--	--	--	-+ 10-15	++ 60-70	++ 60-70	++ 30-40	++ 80-90	++ 95-	0.43
PU1	--	--	--	--	-+ 10-15	++ 40-50	++ 60	++ 60	++ 90	++ 95-	0.49
PU2	--	--	--	--	-+ 10-15	++ 40-50	++ 60	++ 60	++ 90	++ 95-	0.45
PU3	--	--	--	--	-+ 10-15	++ 40-50	++ 60	++ 60	++ 90	++ 95-	0.51
PU4	--	--	--	--	-+ 10-15	++ 40-50	++ 60	++ 60	++ 90	++ 95-	0.52

--Insoluble; -+partly soluble; ++soluble

2.5.5 Thermal analysis

Thermogravimetric analysis

Thermal properties of the polymers have been investigated by thermogravimetric analysis (TGA) under nitrogen atmosphere. The TGA curve of polymers is shown in **Figure 2.18-2.20** and weight losses at different temperatures and initial degradation temperature are shown in **Table 2.9**.

The series of the polymers exhibit gratifying thermal stability. In the TGA curve the first weight loss around 10% corresponds to weight associated with moisture or solvent present in the sample. The onset thermal degradation of the polymers are found in the range of 278-362°C (**Table 2.9**). The order of thermal stability is OXDAR4< OXDAR3< OXDA< OXDAR2< OXDAR1 (**Figure 2.18**). The presence of hydroxyl and methyl group in OXDAR4 and OXDAR3 have resulted decrease in degradation temperature of the polymers. The oxadiazole moiety in all the polymers plays a vital role in imparting the thermal stability to the polymers. It can be concluded that oxadiazole containing polymers are more or less stable to be used as light emitting layer in OLED devices.

The meta linked polymers also show the degradation behaviour in a similar fashion (**Figure 2.19**). The meta polymers start degrading at a lower temperature compared to the para-polymers. The cyclized polymers are showing the stability upto 278°C because of their compact rigid structure. OXD BR1, OXD BR2, OXD BR3 and OXD BR4 show initial weight loss at 350, 300, 280 and 290°C respectively (**Table 2.9**). The order of thermal stability of the meta linked polymers are OXD BR3< OXDBR4< OXD B< OXD BR2< OXD BR1. The degradation behaviour of these polymers can be explained similarly as the para linked polymers[23-24].

The TGA thermogram of polyurethanes shows two step degradation in **Figure 2.20** and start around 200°C. Polyurethanes containing TDI backbone (**PU1** and **PU3**) showed better thermal stability than those of polyurethanes containing HMDI backbone (**PU2** and **PU4**). The order of thermal stability of these polymers is PU2<PU1<PU4<PU3. This is attributed to smaller chain length, which increases the rigidity of TDI backbone compared to HMDI. At higher temperature, polyurethanes containing TDI backbone exhibited higher value, reflecting the increased thermal stability among the polyurethanes studied[25]. Thermal decomposition temperatures (*Td*) were measured at the loss of 5 wt%.

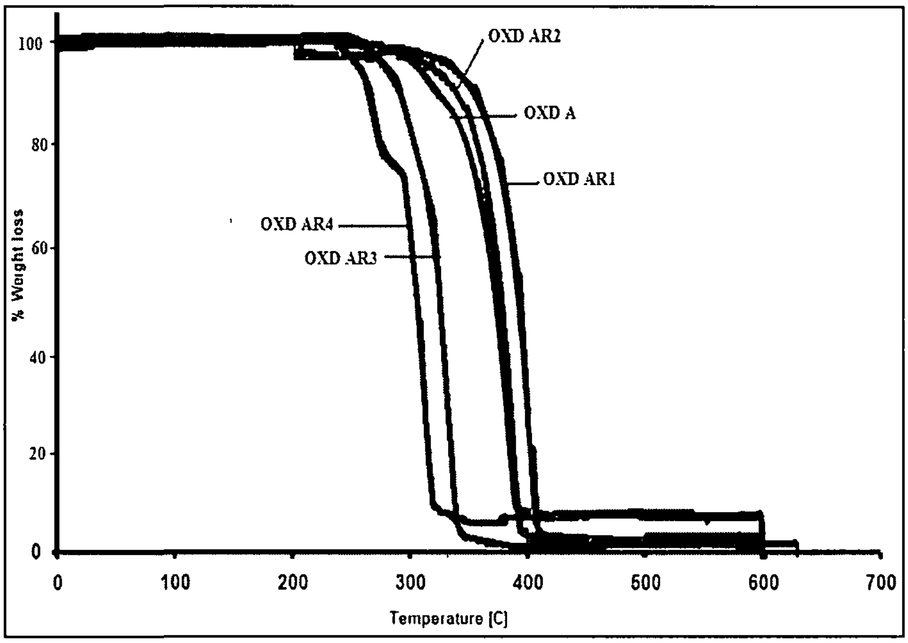


Figure 2.18: TGA thermogram of Poly 1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing polar end groups

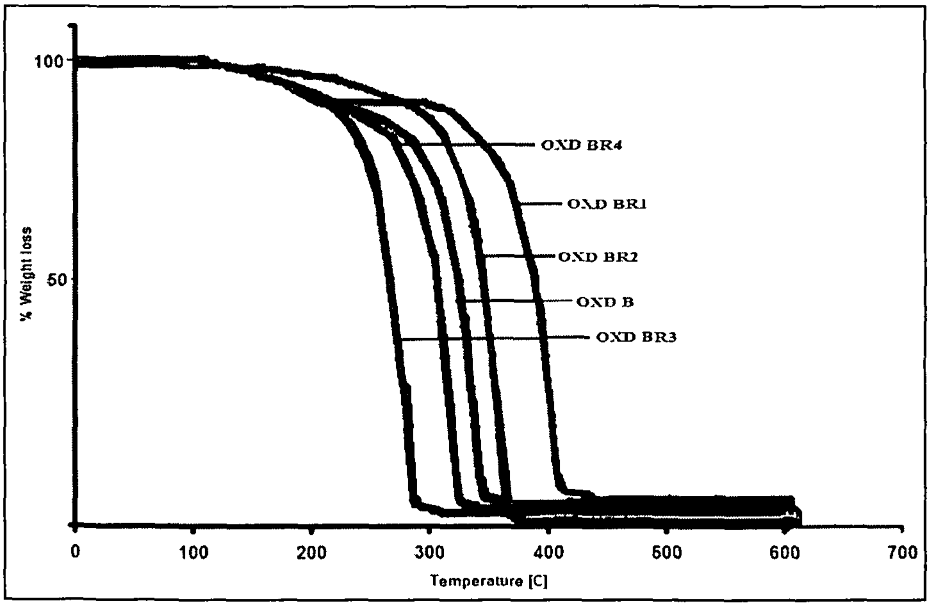


Figure2.19: TGA thermogram of Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing polar end groups

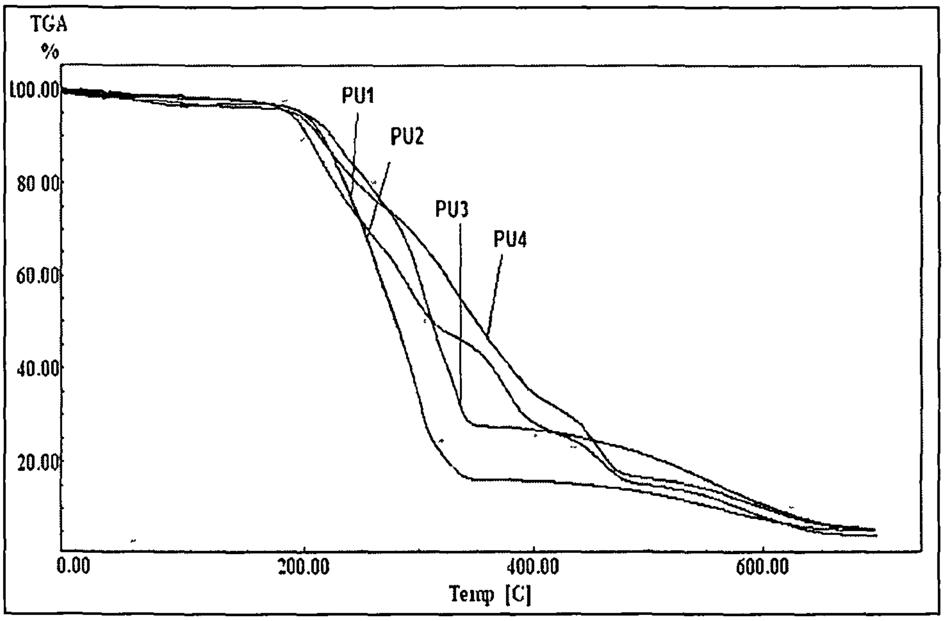


Figure 2.20: TGA thermogram of polyurethane containing oxadiazole moiety

Table 2.9: Weight loss of the polymers in different temperatures

Polymer	**% weight loss Temperatures in °C**			
	Onset degradation temperature T_d	**5-10**	**10-40**	**40-60**
OXD A	320	225	-	-
OXD AR1	362	-	-	-
OXD AR2	334	210	-	-
OXD AR3	300	211	-	-
OXD AR4	278	-	278	-
OXD B	269	153	-	-
OXD BR1	340	-	-	-
OXD BR2	314	-	-	300
OXD BR3	225	-	-	-
OXD BR4	253	125	-	-
PU1	210	-	-	350
PU2	198	-	-	256
PU3	245	-	250	-
PU4	225	-	250	-

From the above thermal behaviour the polymers OXDAR1, OXDAR2, OXDBR1, OXDBR2, PU1, PU2, PU3 and PU4 are the thermally stable suitable material for the OLED application. It is desirable that the polymer should not degrade during the fabrication of the device for optoelectronic application.

Differential scanning calorimetry analysis

Differential scanning calorimetry (DSC) of poly1,3,4-oxadiazoles containing polar end groups under nitrogen atmosphere is shown in **Figure 2.21 and Figure 2.22**. It is found that the polymers behave in a similar fashion and the glass transition temperatures are found to be almost similar at ~ 122-125°C. The melting temperature for these polymers is not clear from the graph. From both TGA and DSC patterns, it is observed that a decomposition temperature of polyurethanes containing TDI backbone is higher than their respective Tg values. The polyurethane–oxadiazole polymers are thermally stable upto 200 °C and their glass transition temperature ranges in the region 110-120°C. From the DSC traces shown in **Figure 2.23**, it is observed that polyurethanes containing oxadiazole moiety and fully aromatic backbone (PU1 and PU3) exhibit relatively high glass transition temperature, T_g of 110-132 °C and melting temperature T_m 240-250°C due to the rigidity in the backbone. On the other hand the PU2 and PU4 exhibit lower T_g values due to the long methyl flexible linkage in the polymer chain. High glass transition temperatures (T_g) and thermal stability are required to withstand inevitable Joule heating encountered during LED operation, especially at higher electric fields and current densities [26-27].

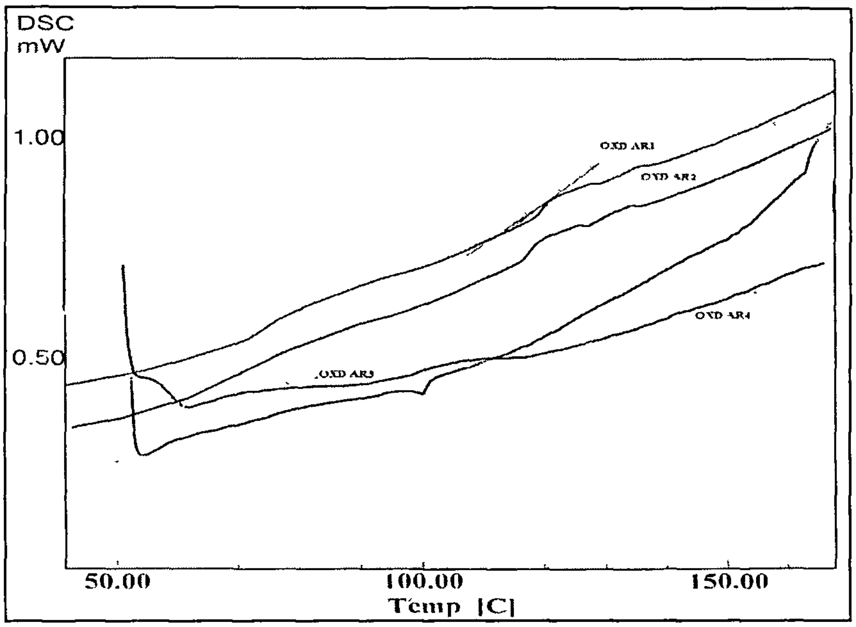


Figure 2.21: DSC thermogram of Poly 1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing polar end groups

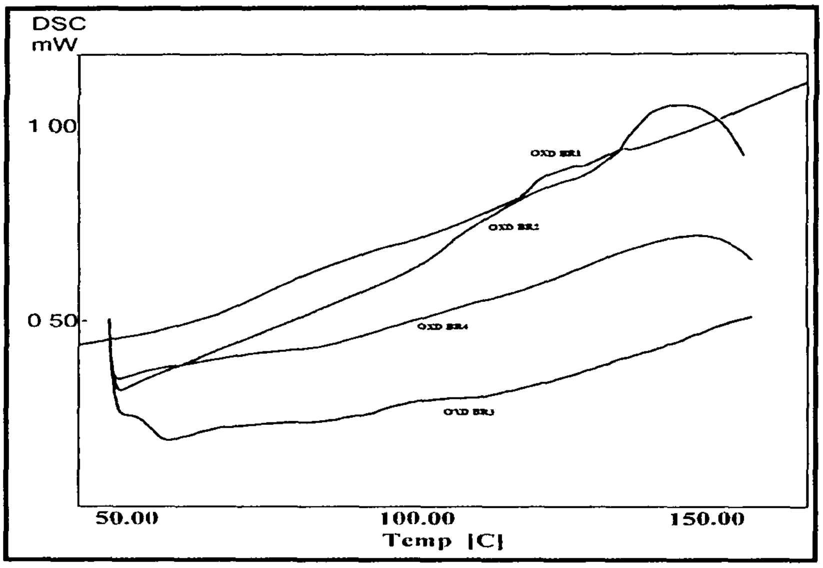


Figure 2.22: DSC thermogram of Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing polar end groups

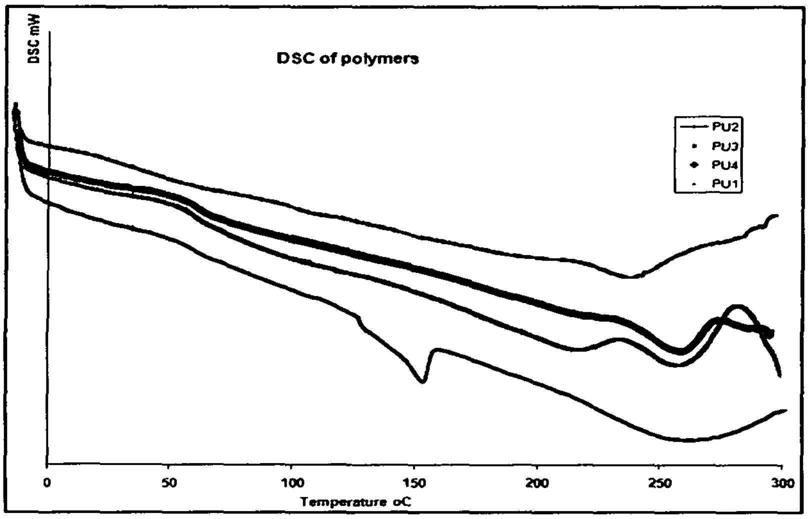


Figure 2.23: Comparative DSC thermogram of polyurethanes

Table 2.10: T_g and T_m of polymers

Polymer	Glass transition temperature, T_g in °C	Melting temperature, T_m in °C
OXD A	122	150
OXD AR1	125	153
OXD AR2	122	-
OXD AR3	126	-
OXD AR4	121	-
OXD B	123	155
OXD BR1	123	-
OXD BR2	122	-
OXD BR3	125	-
OXD BR4	122	-
PU1	110	240
PU2	132	156
PU3	125	220
PU4	125	261

2.5.6 UV- Visible spectroscopic analysis

The UV- Vis spectra of monomers and polymers are shown in **Figure 2.24**. The maximum absorption (λ_{max}) of monomers and polymer and their shifting are given in **Table 2.11**. The position of λ_{max} depends upon the end group composition of the polymers. The positive mesomeric effect causes a red shift in the spectra rather than the blue shift in negative mesomeric groups. In case of the polyurethane containing the oxadiazole moiety the extent of π conjugation causes the shift of the λ_{max} to the shorter wavelength region.

The incorporation of the different polar groups both electron donating/electron accepting groups in the main chain is causing enhancement of the luminescence property of the poly(1,3,4-oxadiazole) polymers. UV-visible spectra (**Figure 2.24**) of the polymers in NMP solution show the strong absorption peaks in the visible region 216-300 nm as well as two arms in the spectra due to the presence of the polar groups in the main chain assignable to the π-π^* transition resulting from the conjugation between the aromatic rings and nitrogen atoms that combines the characteristic π-π^* transition of the polar groups at the end of the chain. OXD AR1 shows maximum absorption at [255, 300] nm and OXD AR2 at [266,300] nm which are assigned maximum in that polymer series. Same as that with the OXD AR3 and OXD AR4 polymers with the methyl and hydroxyl end groups they absorb at [230,280] nm and [235,283]nm. The end group participation in the absorption of light affects the λ_{max} of these polymers. So the possibility of these polymers to show high emission property can be predicted.

The meta polymers with the polar end groups show maximum absorption for OXD BR1 and OXD BR at273nm and 265 nm respectively(**Figure 2.25**). Whereas OXDBR3 and OXD BR4 emits at [210, 230, 235] nm and [200, 220] nm. The absorption bands at longer wavelength (bathochromic shift) is due to the presence of strong electron donating groups methyl and the hydroxyl (n to π^* transition). It is worth noticing that the resolutions of a well defined structure in the spectras are minimum in all the polymers. This phenomenon implies that the polymers have a regular structure[28-30].

Similarly in the third set of polymer; the polyurethanes in DMAc exhibited absorption maxima in the range of 300-360 nm, because of π- π^* transition contributed from the conjugated segments (**Figure 2.26**). The absorption intensity in the polymers is seemed to decrease with the less conjugated structure in PU2 and PU4. PU1 and PU3 assigned to have highest absorption maxima due to their fully conjugated structure. The two absorption peaks in the figures is due to the oxadiazole at ~350 nm and the urethane linkage at ~300nm[31-32].

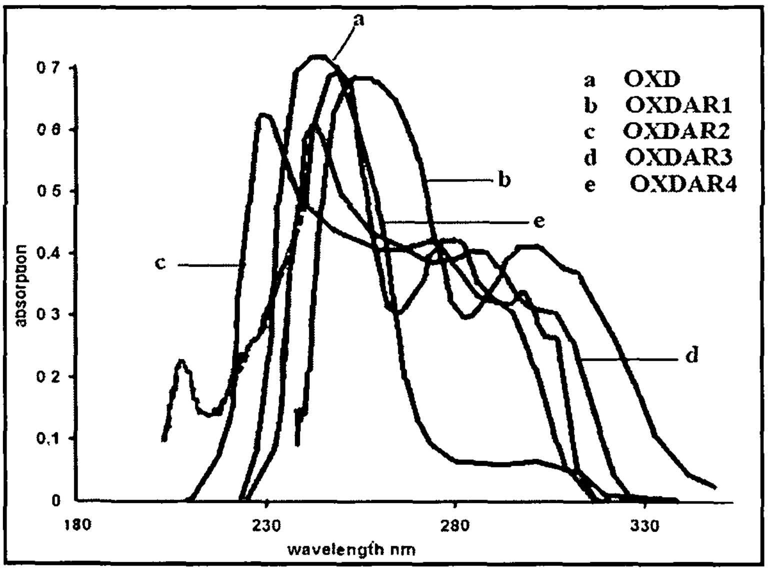


Figure 2.24: UV spectra of poly 1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing polar end groups

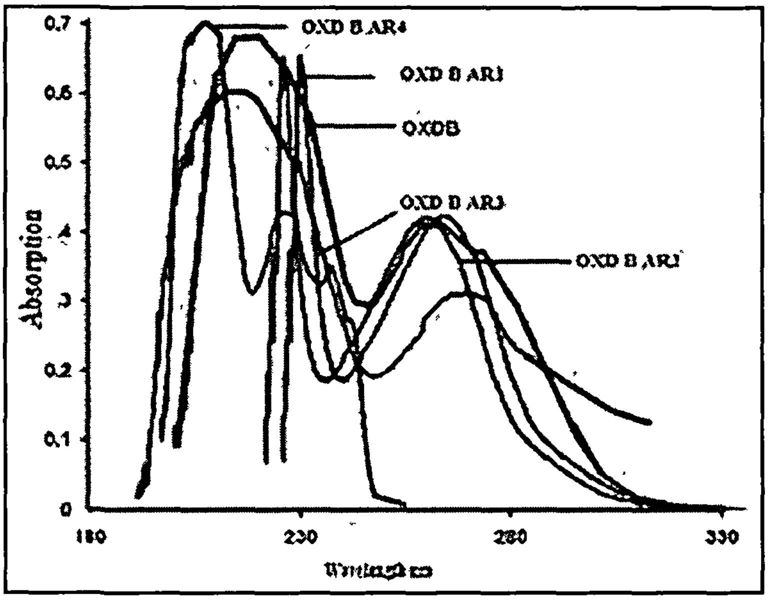


Figure 2.25: UV spectra of poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing polar end groups

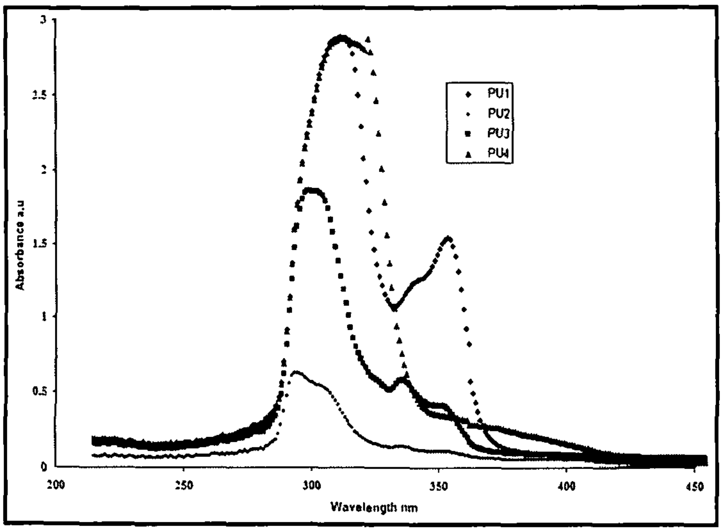


Figure 2.26: UV spectra of polyurethanes

Table 2.11: λ_{max} of the polymers from UV spectra

Polymer	UV(nm),λ_{max} Solution in NMP
OXD A	243,283
OXD AR1	255, 300
OXD AR2	266, 300
OXD AR3	230, 280
OXD AR4	235, 283
OXD B	217,270
OXD B R1	235, 273
OXD B R2	222,265
OXD B R3	210, 230, 235
OXD B R4	220, 200
PU1	312, 355
PU2	292, 305
PU3	300, 332
PU4	317

2.5.7 Optical band gap

Optical absorption in conjugated polymers which are mostly amorphous or semicrystalline may due to the transition of electron and hole carriers, through a forbidden energy gap, called optical band gap. Attempts have been made to determine the optical band gap using the equation[33] 1.

$$Eg^{opt}\ (eV) = 1240 / \lambda_{edge}\ (nm) \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where Eg^{opt} is the optical band gap of polymers and λedge is the absorption edge. The absorption edge (λ_{edge}) and optical band gap (Eg^{opt}) of polymers are listed in **Table 2.12**. The band gap of polymers is found to be 3.1-3.9eV. The aromatic moiety containing polymers show higher band gap.

Table 2.12: Optical band gap of the polymers

Polymer	**Absorption edge of polymer(nm)**	**Optical band gap**
OXD A	340	3.6
OXD AR1	371	3.34
OXD AR2	346	3.58
OXD AR3	330	3.75
OXD AR4	316	3.92
OXD B	330	3.75
OXD BR1	400	3.1
OXD BR2	378	3.28
OXD BR3	366	3.38
PU1	450	2.75
PU2	435	2.83
PU3	450	2.75
PU4	425	2.91

Calculation of the optical band gap for the polymers

The optical band gap of the polymers are calculated from the λ onset value using the relation band gap $E_g=hc/\lambda$. The calculated value is found to be large as that of electrochemical band gap. Absorption spectroscopy, measuring transitions between electronic states, provides essential information about the spectral coverage and the magnitude of the band gap. Although information about the location of molecular orbital energies cannot be obtained, optical absorption measurements have great resemblance with the charge-generation process in luminescent polymers and are of utmost importance when characterizing the polymer for OLED application. The difference in the band gap results can be explained by the dissimilar nature of the measurements where different energy processes contribute to band gap estimation. The UV spectra results from the absorption of the electromagnetic radiation by the molecule; whereas the redox process in the polymeric material involves the oxidation or the reduction of the oxidizable and reducable moiety only. However, results from optical absorption are in agreement with the conclusion from electrochemistry that an electron-deficient system gives a larger band gap. Incorporation of electron rich polar end groups to the polymeric chains show an absorption spectrum furthest extended to lower energies, corresponding to the decrease in the optical as well as the electrochemical band gap. The incorporation of the different polar groups both electron donating/electron accepting groups in the main chain added to the luminescence property of the 1,3-Bis(phenyl-1,3,4-oxadiazole)s polymers. UV-visible spectra (**Figure 2.24-2.26**) of the polymers in NMP solution (**Chapter 2**) show the strong absorption peaks in the UV region 217-280 nm as well as two arms in the spectra due to the presence of the polar groups in the main chain assignable to the π-π^* transition resulting from the conjugation between the aromatic rings and nitrogen atoms that combines the characteristic π-π^* transition of the polar groups at the end of the chain. The absorption bands at longer wavelength (bathochromic shift) is due to the presence of strong electron donating groups (n-π^* transition). It is worth noticing that the resolutions of a well defined structure in the spectras are small in all the polymers. This phenomenon implies that the polymers have a regular structure. In case of polyurethane polymers; the optical band gap of the polymer is calculated as 4.29.eV. For all of the polymers studied, the Stokes shift is <100 nm indicating a limited degree of coupling to vibrational states in these materials. This is an important point to emphasize since such coupling processes may give rise to excessive heating in LED devices[34-36].

2.6 Conclusion

Synthesis of the polymers

Two series of poly(1,3,4-oxadiazole) containing polar end groups viz Poly 1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene $-NO_2$, -Cl,$-CH_3$, -OH and Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene–NO_2, -Cl,$-CH_3$, -OH and a series of polyurethanes containing 1,3,4-oxadiazolein the main chain are synthesized by the simple polycondensation and chemical cyclization method. The multistep synthesis of the polymers involves the low temperature condensation of the aromatic dicarboxylic acid chloride with dihydrazide and the cyclization of the resulting polyhydrazide. The yield of the product was 48-53%. Polyhydrazides then undergo a chemical cyclization process resulting in the polyoxadiazoles with 54% yield. The polycondensation process is slow but with a good quality and yield of the products. The polyurethanes containing 1,3,4-oxadiazolein the main chain involved the synthesis of the 1,3,4 oxadiazole containing diol monomer and binaphthol followed by the condensation of the diol monomers with the diisocyanate. All the monomers and the polymers are characterized by FTIR and 1H-NMR spectroscopy. The monomer yield was high 49-89%, but the condensation products polyurethanes are comparatively low yield 46-48%.

Solubility, molecular weight and the inherent viscosity

The polymers are soluble in DMAc, DMF, NMP and partly soluble in THF. The inherent viscosities of the polymers are in the range of 0.41-0.46 dl/g and the polymers are oligomeric in nature. The number average molecular weights of polymers are measured from the THF soluble part of the polymers and it was found in the range of 2425 to 4617 g / mole. The polydispersity index of the polymers lying in the range 1.08-1.12 implies the homogeneity in the polymer chains.

Optical properties of the polymers

The absorption maximum in UV-Vis spectra of the polymers is in the range of 245-332 nm. All the polymers show shifting of absorption maximum with respect to the side groups attached with the polymer chain and the spacer group present in the polymer chain. . Optical band gap of the polymers is found to be 2.7-3.9eV.

Thermal property of the polymers

Polymers possess good thermal stability with the onset decomposition temperature around 225-362°C under nitrogen atmosphere. Thermal stability increases with the increase in molecular weight of polymers. The polymers exhibit a glass transition temperature (T_g) in the range of 110-125°C. It is observed that T_g of the polymers varies with the variation in the side groups and the spacer groups.

References

1. Zheng,M.; Ding,L.; Rel, E. E. G.; Lahti,P. M.; Karasz,F. E. Oxadiazole containing conjugated-nonconjugated blue and blue-green light emitting copolymers. *Macromolecules* **34,** 4124-4129 (2001).
2. Lee,K. Kim,H. Cho, J. C. and Kim, J. Chemically and photochemically stable conjugated poly(oxadiazole)derivatives: a comparison with polythiophenes and poly(p-phenyleneethynylenes), *Macromolecules* **40**, 6457-6463 (2007).
3. Ng, S.-C. *et al* Blue electroluminescence from a novel donor/acceptor polymer structure. *Adv. Mater.* **12,** 1122-1125 (2000).
4. Park, S. H. *et al* A blue-light-emitting polymer with a rigid backbone for enhanced color stability, *Adv. Funct. Mater.* **17**, 3063–3068 (2007).
5. Kalsi, P.S. *Spectroscopy of organic compounds* (New Age International Publication, sixth edition, 2006)
6. Banwell, C. N.; McCash, E.M. *Fundamentals of molecular spectroscopy* (Tata McGraw Hill Publishing Company Ltd. Fourth edition, 2001).
7. Campbell, D.; Pethrick, R. A.; White, J. R. *Polymer Characterization: Physical Techniques*(Staneley Thorns, UK, 2000).
8. Turi, E. A. *Thermal Characterization of Polymeric Materials*(Academic Press; 2 edition, 1997).
9. Billmeyer *Textbook of PolymerScience* (Wiley-India, 2007).
10. Gomes. D. Nunes, S. P. Pinto, J. C. and Borges, C. Synthesis and characterization of flexible polyoxadiazole films through cyclodehydration of polyhydrazides. *Polymer* **44,** 3633-3639 (2003).
11. Oikawa, E. and Nozawa, H. Synthesis and properties of polyhydrazides and polyoxadiazoles containing pyridine rings in the polymer backbone. *Polym. Bull.* **13,** 481-488 (1985).
12. Hsiao, S.-H.; Yu, C.-H. Novel aromatic polyhydrazides and poly (amide-hydrazide)s based on ''multiring'' flexible dicarboxylic acids. J. Polym. Sci.: Part A: Polym. Chem. **36**, 1847–1854 (1998).
13. Brian,S. F.; Antiony, J. H.; Peter, J. S.; Austin, R. T. *Vogel's Textbook of Organic Chemistry* (Fifth edition, 1996).
14. Pokhrel, B.; Dolui, S. K. Synthesis and characterization of 1,1-bis-2-naphthol chromophore containing polyurethanes and study of their electrochemical and photoluminescence properties. *J Polym. Mater.* **26** 417-426(2009).

15. Kim,D. Y.; Cho, H. N.; Kim, C. Y. Blue light emitting polymers. *Prog. Polym.Sci.* 25, 1089-1139(2000).
16. Bach, H. C.; Hinderer, H. E. Polymers and fibers of *para-* and *meta*-phenylene oxadiazole—*n*-methyl hydrazide copolymers: high strength—high modulus materials of increased molecular flexibility. *ACS Symposium Series.* **195,** 363-369 (1982).

17. Saegusa, Y.; Iwasaki,T.; Nakamura, S .Synthesis and characterization of 1,3,4-oxadiazolecontaining polyethers from 2,5-bis(4-fluoropheny l)-1,3,4-oxadiazole and various aromatic diols. *Macromol. Chem. Phys.* **198,** 1799-1808 (1997).
18. Zheng,M.; Ding,L.; Rel, E. E. G.; Lahti,P. M.; Karasz,F. E. Oxadiazole containing conjugated-nonconjugated blue and blue-green light emitting copolymers. *Macromolecules* **34,** 4124-4129 (2001).

19. Menon,A. *et al* Polydispersity effects on conjugated polymer light-emitting diodes. Chem. Mater. **14**, 3668-3675 (2002)

20. Concilio, S.; Bugatti, V.; Iannelli, P.; Piotto, S. P. Synthesis and Characterization of New Photoluminescent Oxadiazole/Carbazole-Containing Polymers. *Int. J. Polym. Sci.* **2010**, doi:10.1155/2010/581056 (2010).

21. Pankratova , L. A. *et al* Investigation of the molecular weight distribution of poly1,3,4-oxadiazole synthesized by a two-stage method. *Polym. Sci. U.S.S.R.* **16**, 3105-3110 (1974).
22. Blackhall, A.; Brydon, D. L.; Seddon, J. D. Oxadiazole polymers.US Patent 1978/4066601.

23. Cassidy, P.E. Fawcett, N.C. thermally stable polymers: polyoxadiazoles, polyoxadiazole-n-oxides, polythiazoles, and polythiadiazoles. *Polym. Rev.***17, 209 – 266 (1979).**

24. Liou,G.-S.; Huang,N.-K.; Yang,Y.-L. Thermally Stable, Light-Emitting, Triphenylamine-Containing Poly(amine hydrazide)s and Poly(amine-1,3,4-oxadiazole)s Bearing Pendent Carbazolyl Groups. J. Polym. Sci.: Part A: Polym. Chem. **45**, 48–58 (2007).

25. Simon, J.; Barla, F.; Kelemen-Haller, A.; Farkas, F.; Kraxner, M. Thermal stability of polyurethanes. *Chromatographia* **25,** 99-106 (1988).

26. Mansoori, Y.; Sarvari, R.; Zamanloo, M.R.; Imanzadeh, G.H. Thermally stable polymers based on 1,3,4-oxadiazole rings. *Chin. J. Polym. Sci.* **28**, 21-28 (2010).

27. Moriyama, H.; Tsukuda, A. Method for producing a film of an aromatic amide oxadiazole polymer containing an oxadiazole structure and the film so produced.US Patent Application 2010/0016521.

28. Li, X.-C. *et al* The synthesis, optical and charge transport properties of poly (aromatic oxadiazole) s, *Synth. Met.* **76,** 153-156 (1996).

29. Guan, M. *et al* The host materials containing carbazole and oxadiazole fragment for red triplet emitter in organic light-emitting diodes. *Organic Electronics* **7,** 330–336(2006).

30. Yin, S. *et al* Synthesis, Photo-, and Electroluminescent Properties of the Soluble Poly[*(2,5-diphenylene-1,3,4-oxadiazole)-4,4′-vinylene]. J. Appl. Polym. Sci.* **74**, 3535–3540 (1999).

31. Lima, H. *et al* Organic electroluminescent devices based on polyurethane derivatives:effects of substituents on electroluminescent and photoluminescent properties. *Thin Solid Films* **363,** 152-155 (2000).

32. Lin, K.-R. *et al* New hole-transport polyurethanes applied to polymer light-emitting diodes. *Europ. Polym. J.* **43**, 4279–4288(2007).

33. Rajendran,V.; Marikeni, A. *Materials Science* (Tata McGraw-Hill, fifth ed., 2006).

34. Manjunatha, M.G.; Adhikari, A. V., Hegde, P. K. Optical and electrochemical properties of a new donor-acceptor type conjugated polymer derived from thiophene, carbazole and 1,3,4-oxadiazole units. *Mater. Sci. Forum* **657**, 46-55(2010)

35. Peng, Q.; Xu,J.; Li, M.; Zheng, W. Blue emitting polyfluorenes containing dendronized carbazole and oxadiazole pendants: synthesis, optical properties, and electroluminescent properties. *Macromolecules* **42**, 5478–5485 (2009).

36. Sung, H.-H.; Lin, H.-C. Novel alternating fluorene-based conjugated polymers containing oxadiazole pendants with various terminal groups. *Macromolecules* **37**, 7945-7954(2004).

CHAPTER 3

Electrochemical, photoluminescence and electroluminescence properties of 1,3,4-oxadiazole containing polymers

Chapter 3: Electrochemical, photoluminescence and electroluminescence properties of 1,3,4-oxadiazole containing polymers

3. 1 Introduction

The electroluminescence in the polymeric systems is a long standing effort of the chemists in the recent years. There are reports on high photoluminescence quantum efficiency in organic semiconductors. But there has long been interest in the light emission from these systems through a charge carrier under a strong electrical field; more commonly termed as the 'electroluminescence'[1]. The stability in the light emitting systems were achieved by moving from molecules to macromolecular materials, conjugated macromolecules and the polymers with heteroaromatic systems are good choice. They can, in principle provide good charge transport and high quantum efficiency for luminescence in the visible region. Advantages in the processibility and flexibility for the large area flat panel displays with smaller and variable shapes and sizes made the electroluminescent polymers a fanatical field of study and development. Hole transportation within the polymer was achieved with a lots of interest but the development of efficient electron deficient system for the PLED device fabrication and application requires lots of research. Attempts were made to develop different systems out of which electron deficient 1,3,4-oxadiazole moiety containing systems are most promising materials for the electron transportation and emission particularly in the blue region. The immense application in the luminescence and the device operation of polyoxadiazoles were limited due to their rigid compact structure which leads to the insolubility. The solubility of the polyoxadiazoles can be improved by the incorporation of the alkoxy side groups, polar end groups and insertion of flexible chain in the main chain of the polymer or by incorporating metals with the polymer. The effect of substituents on the luminescence efficieny is also enormous. The tuning of the band gap and the change in the luminescence colour can be tailor made by the incorporation of different substituents into the polymer chain. The solid state fluorescence of the oxadiazole containing polymers is very good and the electrochemical band gap usually higher; emitting light in the blue-green region only. The red shifting of the emission spectra attributed to the lowering of the band gap respective to the participating groups or molecules present in the polymer chain. The presence of the electron withdrawing system in the polyoxadiazoles enhance the blue light emission as they make the system more electron deficient; that in turn lowers the LUMO energy level. The incorporation of the both hole and electron transporting moiety in the same chain enhances the luminescence in the longer wavelength, it is desirable to develop material with wide band gap to achieve the blue light. That is why in our work it has been attempted to develop low molecular weight polymeric materials with polar end groups to enhance solubility and luminescence efficiency. The polymers with the electron withdrawing moiety show luminescence in the blue region with a good intensity. Another system with conjugated and non conjugated system polyurethanes are also very efficient in PL intensity and emits blue light from the device fabricated. The semiconducting behaviors of the polymers are acceptable for the polymers to be used in the electroluminescent semiconductor devices[2-8].

The photoluminescence behavior of the polymers reveals the emissive nature of the polymers in the visible region; the intensity of the emission and the type of emission. The effect of substituents on the emission property is clearly detected from the emission spectra of the polymers. The +I effect of the polar groups attached to the polymer chain attributed to the blue shift whereas red shift was encouraged by the polymers with the +I-effect. More is the conjugation; the more is the emission in the higher wavelength than the systems with long chain non conjugated systems in polyurethanes[9-11].

In the polymeric OLEDs the matching of HOMO and LUMO energy levels of the emissive materials with the work function of electrodes as well as their optical, chemical and electrical stabilities are of paramount importance. The electronic energy levels of the polymers determine the device, selection of the material for the electrodes and charge transporting materials. Cyclic voltammetry(CV) is the technique used to determine the HOMO-LUMO band gap of the polymer. It provides the information regarding the reversibility and reusability of the polymer, redox property of the polymers, and stability of the polymer on the electrode during the oxidation and the reduction processes as the semiconducting luminescent polymers make their end use based on those properties only. CV gives direct measurement of the oxidation and the reduction potentials. The oxidation process involves the removal of electron from the HOMO energy level and the reduction is associated with the addition of electron in the LUMO energy level of the material. The current arises from the transfer of electrons between the energy level of working electrode and the molecular energy levels of the materials under study. The onset oxidation and reduction potential of the material can be correlated to the ionization potential I_p and the electron affinity E_p according to the empirical equation proposed by Bredas et al. The onset potentials are determined from the intersections of the two tangents drawn at the rising current and baseline charging current of the CV traces. The electrochemical band gap calculated from the HOMO and the LUMO energy levels as calculated from the onset oxidation and reduction potential respectively. The optical band gap can be calculated from the onset of the absorption spectra. The cyclic voltammetric study for the polymers is important in respect to the polymers for a better device application. The substituent effects on the polymers tuned the band gap as calculated from the cyclic voltammetry studies. There are several structural and morphological changes take place during the oxidation-reduction processes, different electrical conductivity of oxidized and reduced forms of polymers, and anion movement during redox switching of polymers. Therefore the I_p and E_p values and the band gap calculated from the CV as compare to the UVPS and optical band gap for a more generalized and relevance form of data[12-16].

The electroluminescence is the emission of light from a material when electrical energy passes through the material. The operation of light emitting diode follows the technique of electroluminescences; which involves a multistep process of charge formation, transfer, and recombination and finally decay by a radiative or non radiative way. EL process is related to the PL process; sometimes the same excited is responsible for the both el and pl. El process involves both the electrical and the optical phenomenon; charge transportation associated with the colour in LEDs. It is the utmost requirement for a polymer to be electroluminescent to be applied as an emissive material in OLEDs; the polymers must provide the properties like high quantum efficiency, stability and low operating voltage[17-23].

The fabrication of the electrochemical cell for the cyclic voltammetry study is somewhat similar to that of the LEDs. Therefore CV plays an important role in the fabrication and the choice of material for the OLED application. To achieve balanced and efficient injection of both electrons and holes, a low work function cathodes and high work function anodes are required to minimize injection barriers. The disparity 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 commonly used anode is indium-tin-oxide (ITO) because of its transparency and low resistivity. Yet, 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. 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 emitter polymer system. Similarly, incorporation of an interlayer 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. 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. Though the mechanism behind the role of LiF in electron enhancement yet not achieved properly; it makes its use wide in the OLED application[24-26].

In this chapter, the photoluminescence, electrochemical and electroluminescence properties of synthesized polymers have been discussed. The photoluminescence spectra of the polymers in solid and solution form were recorded in fluorescence spectrophotometer. The relative quantum yield of polymers with respect to anthracene was measured. The oxidation and reduction potential of different polar end group containing poly(1,3,4-oxadiazole)s and 1,3,4-oxadiazole containing polyurethanes were determined by cyclic voltammeter method. We have discussed the influence of substituents on the redox properties and the luminescence of the polymers. Redox stability of polymers was tested by cyclic voltammeter upto 10 cycles. Furthermore, band gap of polymers was measured by electrochemically and compared with optical method. The electroluminescence properties of polymers were studied by fabricating LED device with configuration ITO /PEDOT: PSS /Polymer/ LiF / Al. The device properties were evaluated using the Keithly sourcemeter to measure the I-V characteristics, turn on voltage and electroluminescence for the polymers used in the devices.

3.2 Experiment

3.2.1 Material

Dimethyl acetamide and N-methyl -2-pyrrolidone (NMP) were purified by distillation under reduced pressure over basic alumina and stored over 4 Å molecular sieves, $LiClO_4$ (Aldrich), acetone, 2-propanol and trichloroethane were of analytical grade and used as received. Poly(ethylene dioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) (Aldrich), LiF (Merck, Germany), ITO coated glass (Vin Karola, USA) were used as received. The polymers used are prepared earlier and the methods, properties and the formulation are given in Chapter 2.

3.2.2 Instrumentations

Cyclic voltammeter

Polymer films were spin cast from DMAc 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 calomel (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.

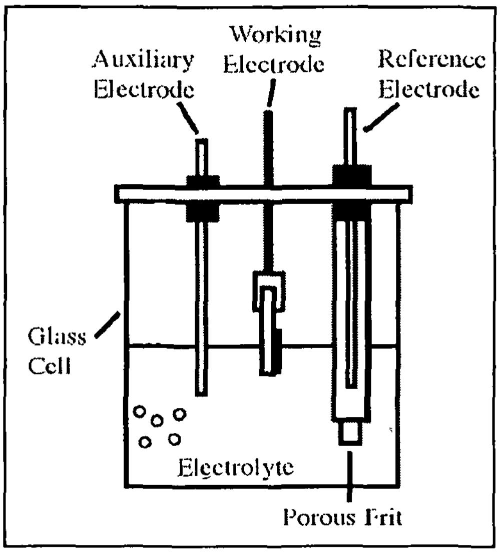


Figure 3.1: Typical 3-electrodeelectrochemical cell

All potentials are reported with respect to reference electrode. Acetonitrile containing $LiClO_4$ (0.1M) was used as the electrolytic medium. $LiClO_4$ was used in the system as electrolyte salt which furnishes ions for charge transport. Acetonitrile was used as electrolyte medium which dissolves our polymers and $LiClO_4$. Also its oxidation and reduction potential of acetonitrile are quite different from the polymer systems. The measurements were calibrated using ferrocene as the standard and the scan rate was 0.01-0.1 V/s. The experiments were conducted on a Sycopel AEW2-10 cyclic voltammeter.

Photoluminescence spectroscopy

Photoluminescence spectroscopy can be used to analyze fluorescent compound at very low concentration (in the parts per billion ranges). Both solids and liquid samples can be analyzed using fluorimetry. Fluorescence spectra are produced when ions or molecules absorb electromagnetic radiation at short wavelengths (higher energy) and are capable of radiating at longer wavelengths (lower energy). Besides uniquely identifying fluorescent compounds, these spectra provide information on the structure of fluorescent substances. Photoluminescence spectra were recorded using a Hitachi F-2500 Flourescence Spectrophotometer, by excitation of the polymer at maximum absorption wavelength. The fluorescence spectrum of polymer solution was recorded in DMAc solvent. Fluorescence of solid state polymers was measured by preparing the polymer film on the glass substrate.

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

Device fabrication and testing for electroluminescence and current-voltage relationship

The electroluminescence (EL) devices were fabricated on patterned 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 120°C. The ITO substrates were treated with plasma radiation 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 2000 rpm from the corresponding NMP solution (1 wt %) on top of the vacuum dried PEDOT: PSS layer and then vacuum dried for 2h for 140°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) and I – V characteristic of LED devices were measured by Keithley 2400 programmable current voltage digital source meter.

3.3 Results and discussion

3.3.1 Photoluminescence behaviour properties of the polymers

PL in solid state

PL spectra of the polymers were taken as because the luminescence in solid state will be practically responsible for the emission property of the polymers in PLEDs. The photoluminescence spectra in solid state was taken by coating a thin film on glass substrate and excited the samples in their λ_{max} calculated from their absorption spectra already discussed in the Chapter 2. The polymers show emission in the blue-violet region with a good intensity. The high intensity of emission is due to the 1,3,4-oxadiazole moiety and the chromophoric groups present in the polymer. Depending on the presence of different polar groups and the chromophoric groups, extent of π conjugation and stacking; the intensity and the position of the PL spectra varies. The aggregation of the unsaturated system results in the broadening of the spectra[27-33].

The solid state PL spectra of the 1,3,4-oxadiazole polymers containing the polar end groups as well as the polyurethanes containing 1,3,4-oxadiazole moiety in the main chain show intense emission peak in the visible region. The nature of the emission spectra's and the comparative study of the emission maxima of the polymers are discussed in the **Figure 3.2, 3.3 and 3.4** and **Table 3.1**.

Photoluminescence (PL) spectra (**Figure 3.2 and 3.3**) could provide a good deal of information on the electronic structure of the conjugated polymers. As 1,3,4-oxadiazole itself is an electron deficient system having three electron rich atoms delocalized over the ring that can act as π electron acceptor. The incorporation of the electron withdrawing groups (-NO_2, -Cl) in OXD AR1 and OXD AR2 allows the red shift of the wavelength (longer wavelength) to 375 and 300 nm. The electron donating groups (-CH_3, -OH) at the end of the main chain in OXD A31 and OXD AR4 shifts the wavelength to the shorter wavelength (blue shift) 300 and 373 nm respectively.

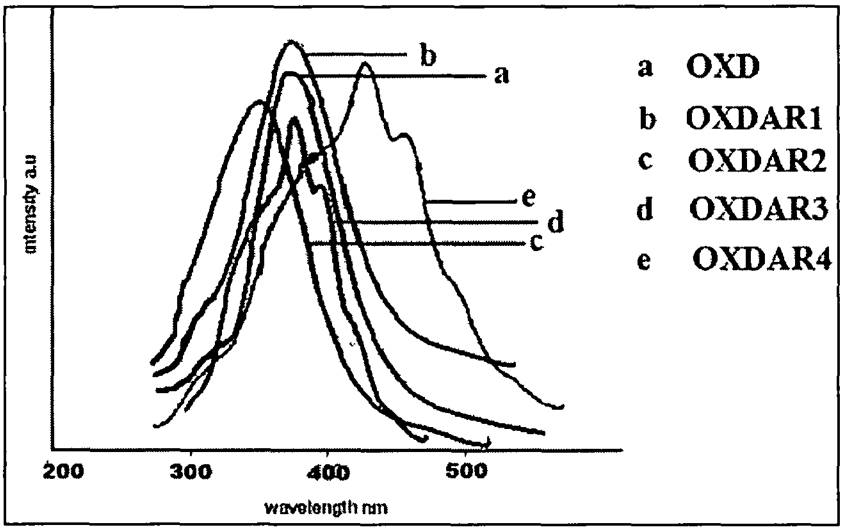


Figure 3.2: PL spectra of Poly 1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing polar end groups in solid state

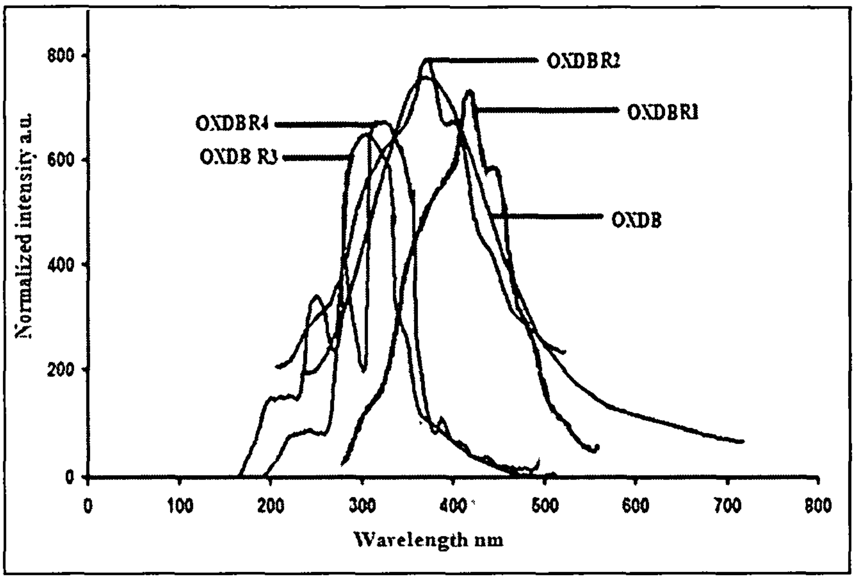


Figure 3.3: PL spectra of Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing polar end groups

This implies to the interaction of the side groups with the polymer backbone and there occurred an internal charge transfer along the polymer backbone in the excited state to enhance luminescence intensity and position as well. The overlapping of the emission and absorption spectra of these polymers is very little, which indicates the reabsorption of the emitted light by the polymer is negligible. The broadening of the spectra is due to the molecular aggregates present in the film as the spectra were taken in solid form only. The more electronegative nitro and chloro group create a polar effect in the polymer chain and thus make the polymer system more electrons deficient. The π electron delocalization and the effective conjugation length is somehow disturbed in the Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene polymers due to the disturb in the symmetry the luminescence emission intensity and the shifting of the wavelength is slightly more blue shifted as compared to the first set of polymers. Only the nitro group containing polymer shows the emission in the visible blue region. The second arm in the emission spectra in OXD B R2 is due to the structural asymmetry of the set of polymers unlike the Poly 1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene polymers. Because the π-conjugation, resonance in *meta* linkage does not exist between adjacent phenylene units compared to *para* linkage polymer.

The emission maxima observed in the range of 400-440nm for the polyurethanes containing the 1,3,4-oxadiazole moiety. The presence of a well-defined vibronic structure in the emission spectra indicates that the polymers have rigid and well-defined backbone structures. The presence of single emission spectra in polymer solution indicates the emission is only due to the conjugated oxadiazole moiety in the polymer chain. Among the four polymers PU3 shows maximum emission intensity even in very low slit width about 4 mm of light in PL spectrophotometer.

The optical band gap of the polymer was calculated as 2.75-2.91eV. For all of the polymers studied, the Stokes shift is <100 nm indicating a limited degree of coupling to vibrational states in these materials. Therefore the polyurethanes containing the 1,3,4oxadiazole moiety are promising candidates for the blue light emitting polymer for OLED application as evident from the above discussions. This is an important point to emphasize since such coupling processes may give rise to excessive heating in LED devices.

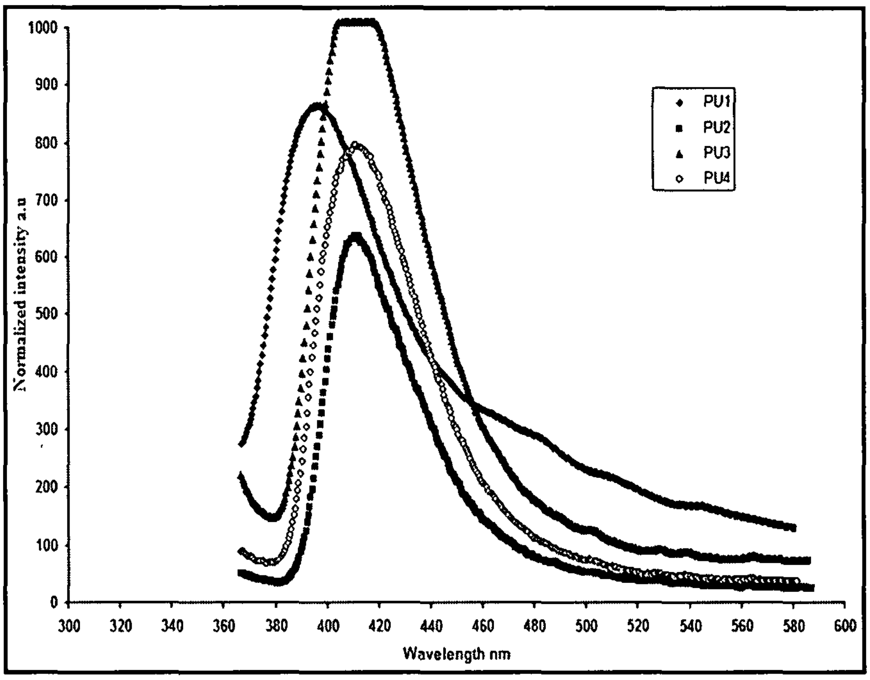


Figure 3.4: PL spectra of polyurethanes containing 1,3,4-oxadiazole in the main chain(PU1, PU2, PU3, PU4)

3.3.2 PL in solution state and quantum yield calculation

The polymers are soluble in polar amide solvents and hence solution PL spectra were recorded using DMAc as solvent. The calculated stokes shift is also given in the **Table 3.1**.

The luminescence quantum yield of the polymers is determined from the PL spectral data taking a standard fluorescence sample Anthracene as the reference as it emits in the region similar to that that of the polymers we have synthesized[34-35]. The maximum intensity of emission in different concentrations is considered for the quantum yield calculations. The fluorescence quantum yield of Anthracene is taken as 0.27 as per literature and it emits in the region 360-480 nm. 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[36]

$$\varphi_s = \varphi_r(Ar/As \times Is/Ir) \qquad [1]$$

Where As and Ar are the absorbance of the sample and reference solutions, respectively, at the excitation wavelength; Ir and Is are the corresponding relative integrated fluorescence intensities. The quantum yield was measured from the polymer solutions at 0.0125 wt% concentrations (**Table 3.1**).

The **Figure 3.5** and **Figure 3.6** show the change in the nature and intensity of emission the OXD A and OXD B polymers in solution. The intensity of the emission decreases with dilution. This is possibly due to the aggregation of the molecules in dilute medium which lead to the less absorption and less emission. The sharpness of the spectra with dilution is due to the emission of the sole chromophoric group present in the molecules i.e. oxadiazole moiety; the presence of the side groups does not impart so much in the PL emission in dilute solutions as the dilution resulted in the less availability of the polar groups to take part in the absorption and emission. The 1,3,4-oxadiazole polymers carrying the nitro end OXD AR1and OXD BR1 group show the maximum emission in both sets of polymers around 450nm and the peaks are very intense too. This is due to the lone pairs of electron present in the system interacts with the polymer chain through delocalization of electrons and absorbs more energy to emit in the blue region with a high intensity.

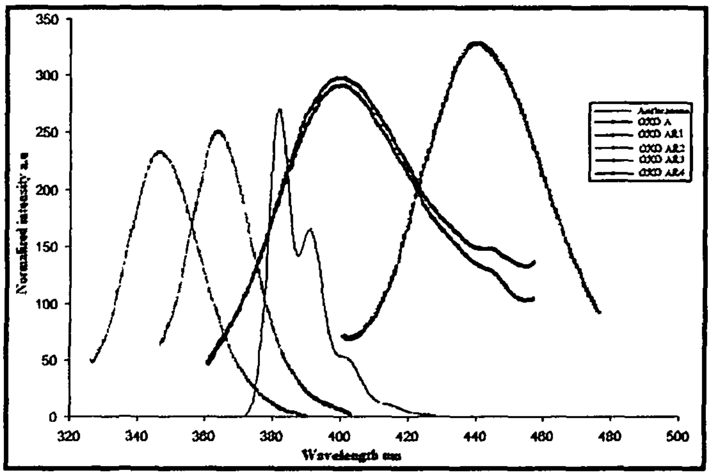


Figure 3.5: PL spectra of poly-1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing polar end groups in solution (0.0125%) with reference to anthracene

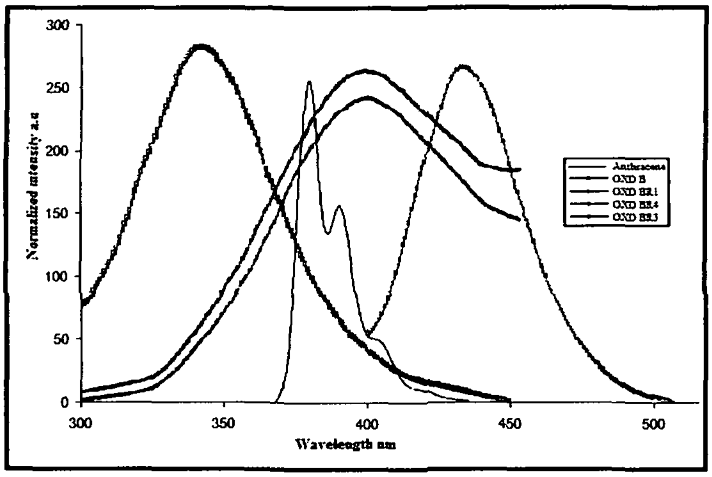


Figure 3.6: PL spectra of poly-1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing polar end groups in solution (0.0125%) with reference to anthracene

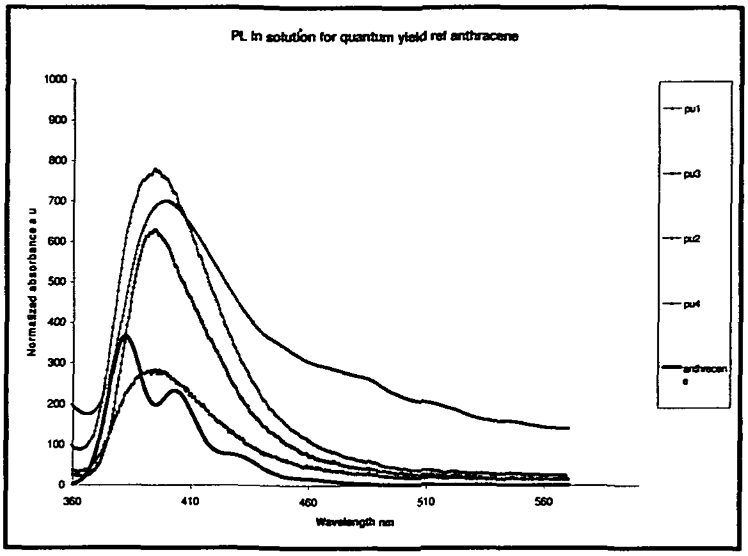


Figure 3.7: PL of polyurethane containing 1,3,4-oxadiazole moiety in solution (0.0125%) with reference to anthracene

On the other hand, the presence of electron withdrawing chloro group in the polymers OXD AR4 and OXD BR2 show PL emission around 400 nm due to the less concentration of the moiety in the system and no valence electron to take part in the delocalization process. The solution emission spectra are compared with anthracene to determine the relative quantum yield of the polymers. Again, with the dilution of the polymer solution the intensity of the emission of the polymers PU2 and PU4 decreases and hence there are decrease in the relative quantum yield for PU2 (0.57 to 0.31) and PU4 (0.61 to 0.58) also relative to the quantum yield of Anthracene 0.27. Usually the fluorescence efficiency increases with the dilution because the molecular aggregation is less in low concentration. But the reverse phenomenon in this case may be due to the presence of the flexible aliphatic chain in the polymer backbone that breaks the conjugation of the polymer system keeping the fluorophore far apart. The other two polymers PU1 and PU3 shows the increase in the fluorescence with the lowering in the concentration for PU1 (0.23 to 0.51) and PU3 (0.25 to 0.47). This is because of the more rigid conjugated backbone imparted by the carbon-carbon double bonds.

The increase in PL intensity as well as the increase in the relative quantum yield in respect to Anthracene with dilution agrees with the fact that due to fluorescence quenching at higher polymer solution concentration; as non emissive excimer complexes most easily formed in the more planar conjugated structure at higher concentrations. The luminescence quantum yield of the polymers found to be 2.3-4 times higher than the Anthracene taken as reference indicating the influence of the side groups in the polymer chain (**Table 3.1**).

The change and the variation in the absorption and emission properties of the polymers can be explained on the basis of the aggregation of the polymer chain as well as the formation of the interchain species. The longer segments will have a low energy gap whereas the exciton energy of the shortest segments will be much higher. The polyurethanes containing the 1,3,4-oxadiazole moiety show emission quantum yield PU1(85%), PU2(88%), PU3(67%) and PU4(78%); which is due to the smaller stokes shift for these polymers. Though on the contrary OXD AR1, OXD AR4, OXD BR1and OXD BR2 show higher stokes shift as well as high quantum yield due to the side group participation in the emission spectra and the intramolecular energy transfer after π- π^* excitation. The presence of electron withdrawing systems in the chain increases the possibility of the π- π^* interaction within the molecules. Due to the bulky rigid oxadiazole ring, the steric hindrance increases in the polymer chain as a result the molar extinction coefficient. This leads to the high stoke shift without disturbing the quantum yield of the poly1,3,4-oxadiazole containing nitro and the chloro groups in the main chain.

The featureless absorption spectrum consists of an inhomogeneous superposition of absorptions from segments with different conjugation lengths and thus, different energy gaps. The more structured emission spectrum, whose vibronic features reflect the excited-state displacement in the C=C stretch, is highly Stokes-shifted because excitons on high-energy segments will undergo rapid energy transfer to lower-energy segments, so that nearly all the emission comes from low energy, long conjugation length chromophores. The formation of the interchain species has significant implications for charge transport and light emission in conjugated polymer-based devices. The mobility of electrical charges along the backbone of a single polymer chain in solution is quite high, approaching that of many common metals. In the films which form the active layer of conjugated polymer-based devices, the individual polymer strands are not mobile, providing no way to "heal" the twists in the chain that break the conjugation. Moreover, spin-coating tends to leave the polymer chains lying in the plane of the film so that rarely there is a single polymer chain bridging the electrodes in a sandwich structure (electrode/thin polymer film/electrode) device. Thus, charge transport through conjugated polymer films requires intimate electrical contact between the polymer segments

Table 3.1: Absorption, emission, stokes shift and quantum yield of the polymers

Code	**UV(nm),λ_{max} Solution in NMP**	**PL(nm), λ_{max} Solid**	**PL(nm), λ_{max} Solution in NMP**	**Stokes shift(nm)**	**Fluorescence quantum yield of polymer at 0.0125 wt%(relative)***
OXD A	243,283	383	398	155	0.53
OXD AR1	255, 300	375	400	145	0.66
OXD AR2	266, 300	400	440	174	0.82
OXD AR3	230, 280	300	342	112	0.53
OXD AR4	235, 283	376	358	123	0.57
OXD B	217,270	400	400	183	0.69
OXD B R1	235, 273	400,403	400	165	0.89
OXD B R2	222,265	450, 452	450	185	0.55
OXD B R3	210, 230, 235	250,300	247,300	40	0.83
OXD B R4	220, 200	300,340	300,340	80	0.57
PU1	312, 355	395	405	50	0.85
PU2	292, 305	408	403	98	0.88
PU3	300, 332	412	402	70	0.67
PU4	317	410	402	85	0.78

3.3.3 Electrochemical properties of the polymers

Redox stability and redox properties of the polymers

Cyclic Voltammetry was employed to investigate the redox behaviour of the polymers, oxadiazole based polyurethanes to estimate their HOMO and LUMO energy levels. The polymer films were spin–coated onto ITO electrodes and scanned positively and negatively at a scan rate of 0.10 mV/S in a 0.1M solution of lithium perchlorate ($LiClO_4$) in anhydrous acetonitrile. From the onset oxidation potentials (φ_{ox}) and the onset reduction potentials (φ_{red}) of the polymers, HOMO and LUMO energy levels as well as the energy gap (E_g^{ec}) of the polymer were calculated according to the equation[37]

$$\mathrm{HOMO} = -(\varphi_{ox} + 4.3)\ (\mathrm{eV});\quad \mathrm{LUMO} = -(\varphi_{red} + 4.3)\ (\mathrm{eV});$$

$$E_g^{cc} = (\varphi_{ox} - \varphi_{red})\ (\mathrm{eV}) \qquad [2]$$

Where the units of φ_{ox} and φ_{red} are oxidation potential and redox potential. The calculation is based on ferrocene / ferrocenium (Fc/Fc^+) redox standard in CH_3CN. The HOMO and the LUMO values along with calculated ectrochemical band gap are listed in **Table 3.2** and cyclic voltammograms are shown in **Figure 3.8-3.21**.

The presence of two distinct redox peaks in the recorded cyclic voltametrogram clearly indicates the semiconducting behaviour of the polymers (**Figure 3.8-3.21**). The oxidation potential observed at 2.8-2.9 V and the oxidation onset potentials at 0.8-1.65 eV. Two oxidation peaks are observed in each polymer system. These anodic processes are associated with two cathodic waves occurring by reversing scans. Such a behavior might correspond to the formation of the radical cations of oxadiazole and the urethane units during the first oxidation step followed by their oxidation into dications through the second step as polyoxadiazole and polyurethane oxidation scan infers for the polaron dominated mid gap states for the removal of one electron and the second one for the electron generation bipolaron dominated states. The reason for which the two oxidation peaks are formed may be due to the oxidation of the terminal group and then the main chain groups but also to the difference between the charge transport resistances to the film with the two considered potential domains. Use of the ITO coated electrodes allows observing the colour changes with two oxidation processes. The polymer films show the colour transition from the colourless to mild blue and from mild blue to bright blue colour upon electrochemical oxidation in the range 0-2.8V.

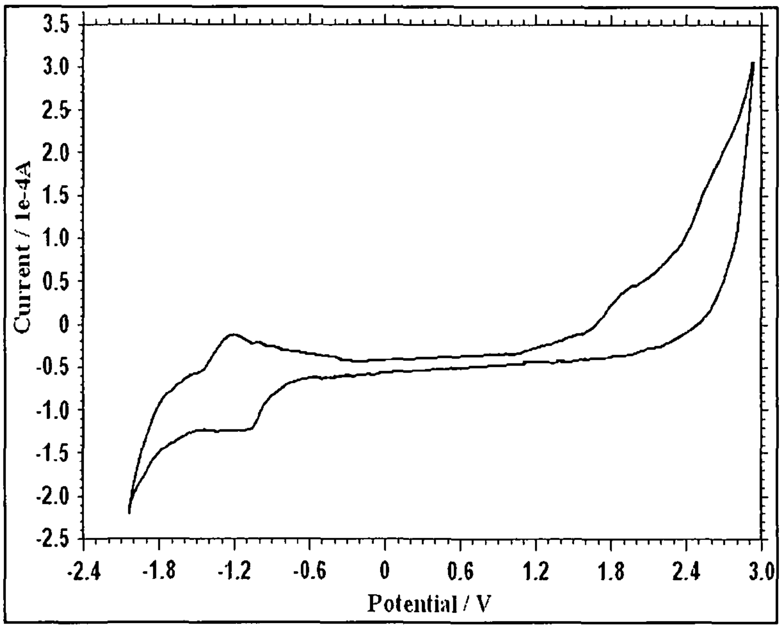


Figure 3.8: CV of OXD A

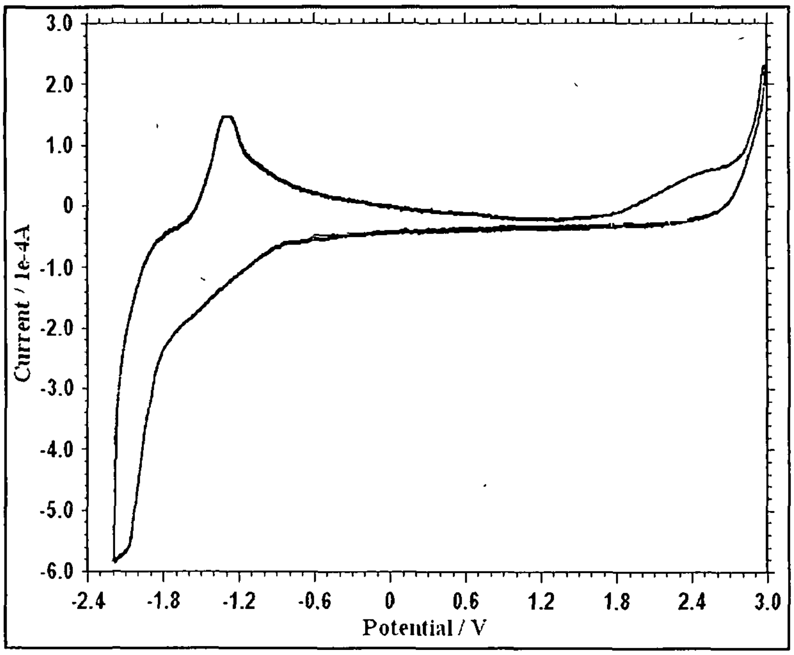


Figure3.9: CV of OXD AR1

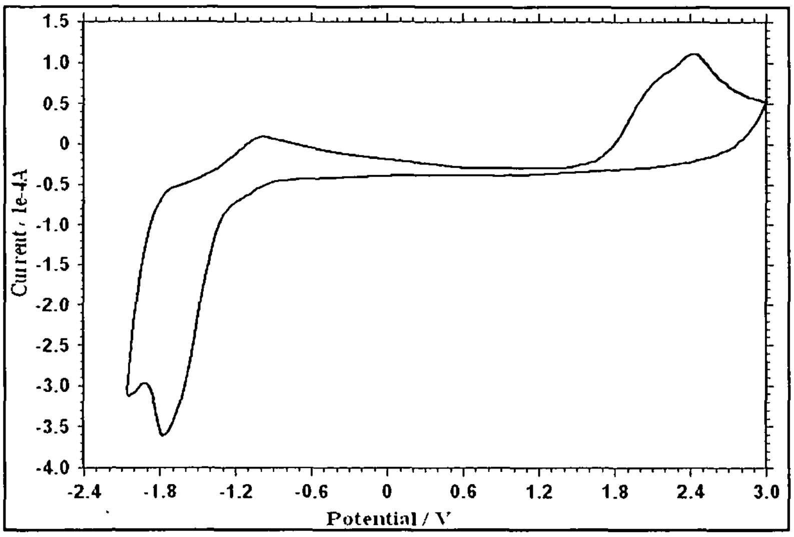


Figure 3.10: CV of OXD AR2

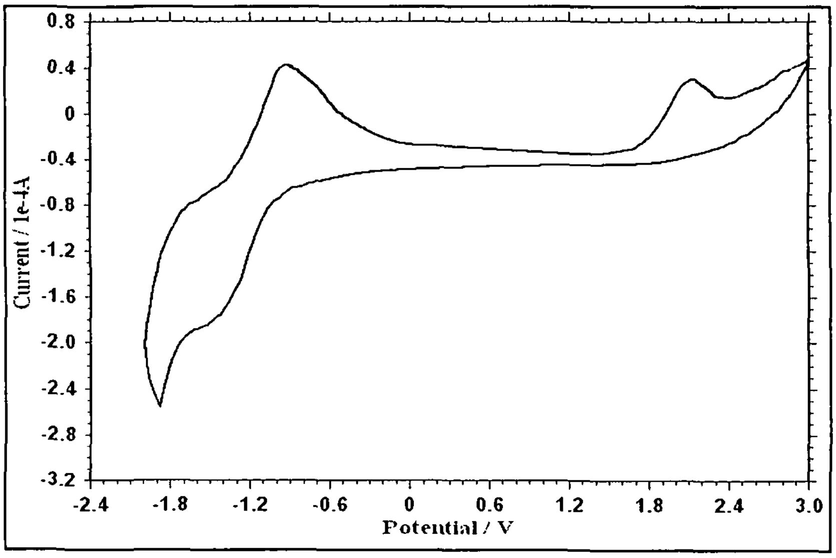


Figure 3.11: CV of OXD AR3

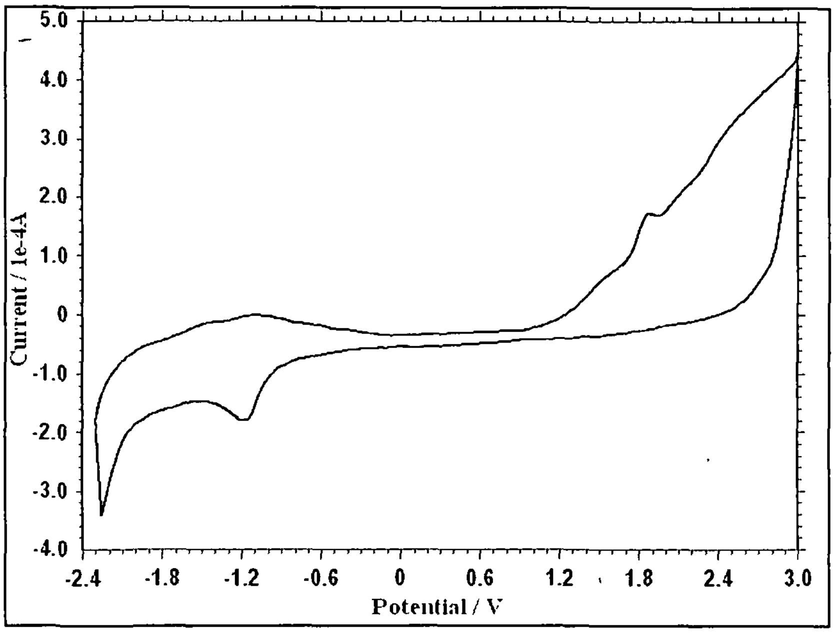


Figure 3.12: CV of OXD AR4

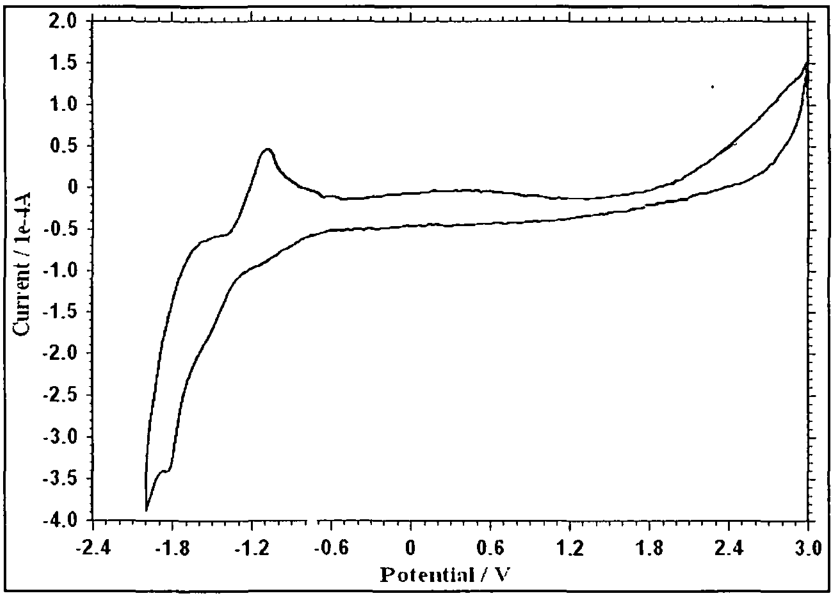


Figure 3.13: CV of OXD B

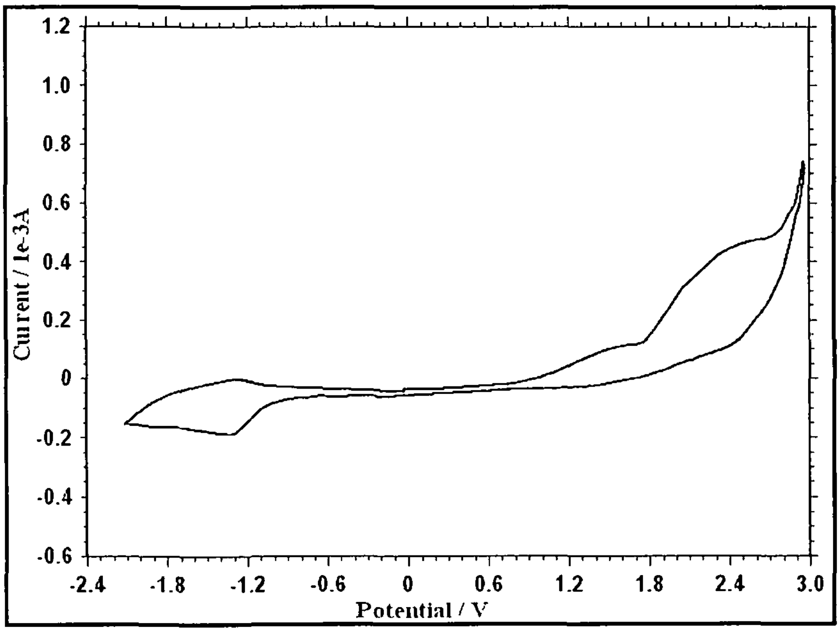


Figure 3.14: CV of OXD BR1

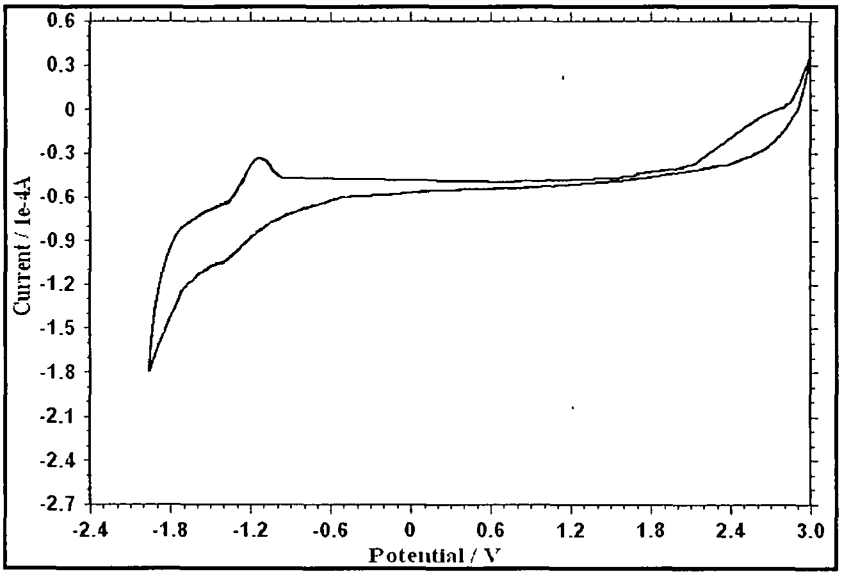


Figure 3.15: CV of OXD BR2

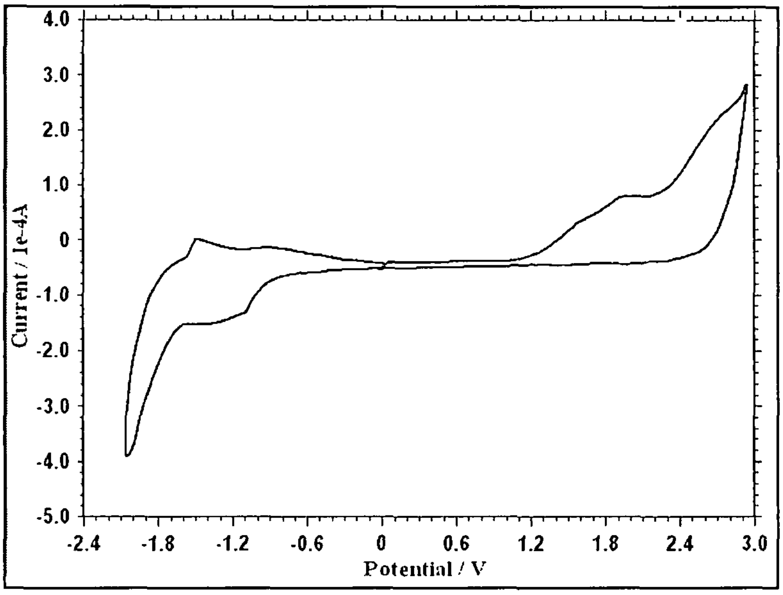


Figure 3.16: CV of OXD B R3

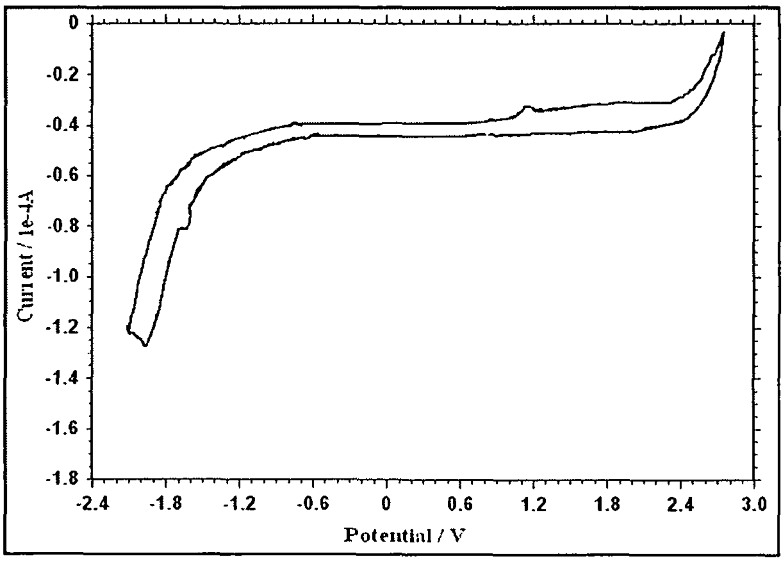


Figure 3.17: CV of OXD BR4

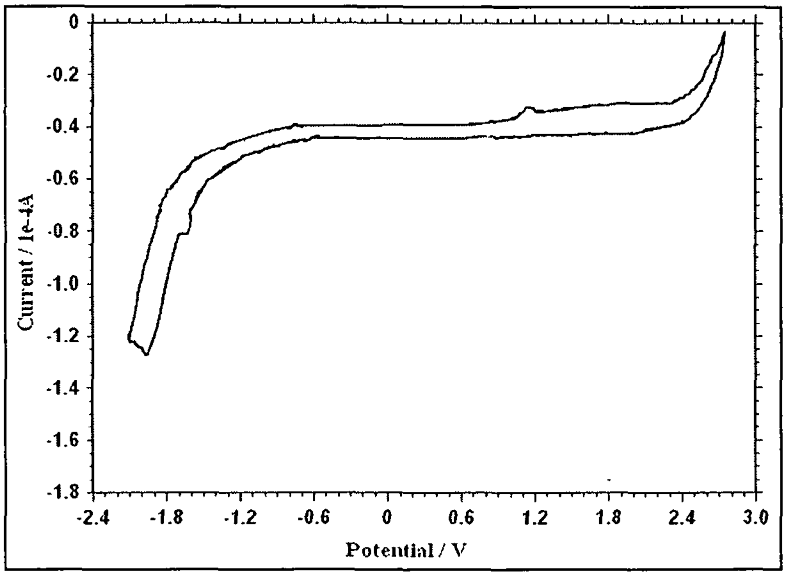


Figure 3.18: CV of PU1

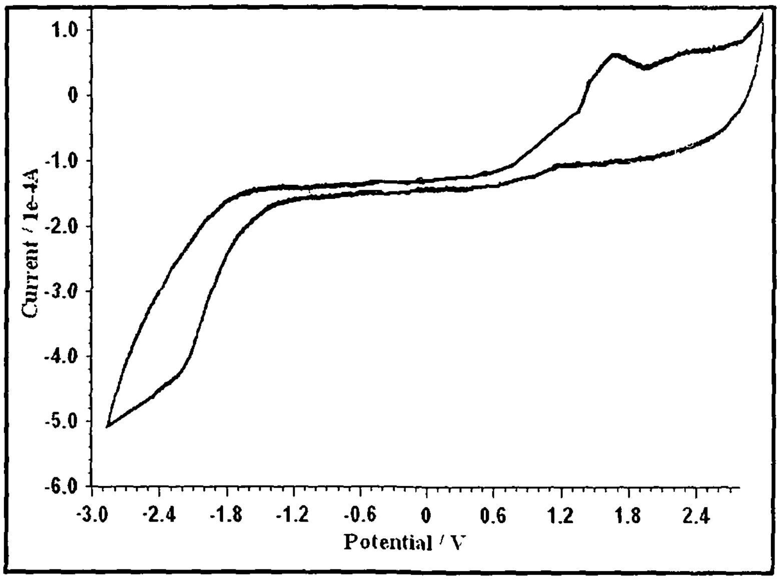


Figure 3.19: CV of PU2

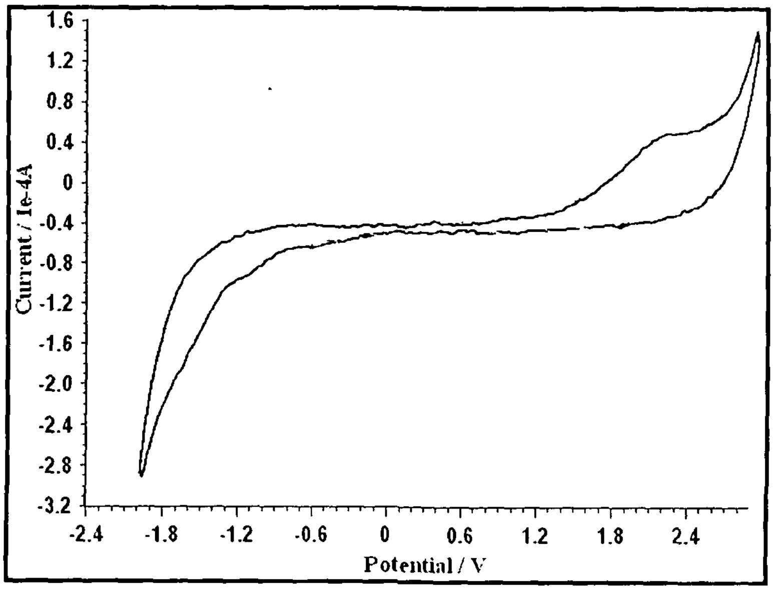


Figure 3.20: CV of PU3

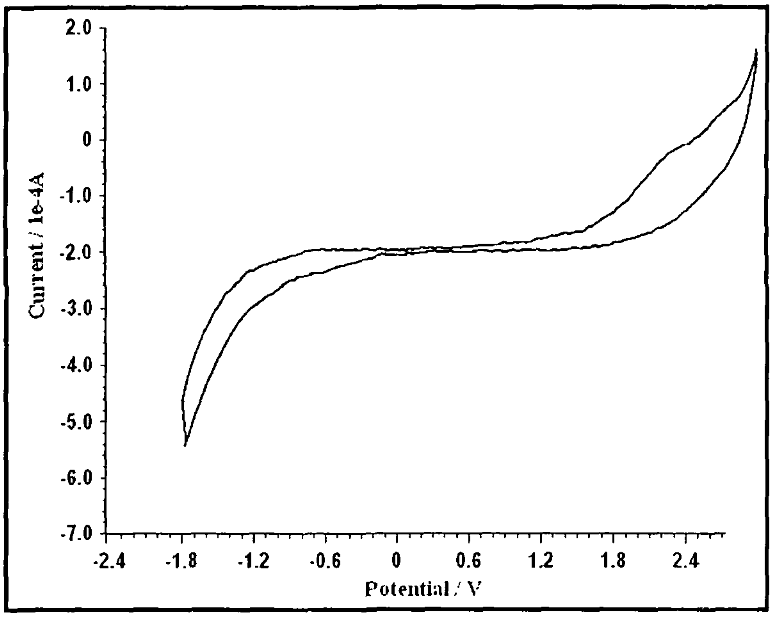


Figure 3.21: CV of PU4

Electrochemical band gap of the polymers

The electrochemical band gap of the polymers is calculated from the onset oxidation potentials and onset reduction potentials of the polymer. HOMO and LUMO energy levels and the band gap of the polymers were calculated according to the equation. The E_g^{ec} for the polymers is 1.8-2.6 eV, and that supports for the wide band gap polymer for emission of light from the colourless to blue region. There used to be some conformational reorganization and the modification in the energy level of the polymeric materials in the charging process during doping in the electrochemical analysis. Thus only the onset potential probes inject charges to neutral polymers in the ground state. Onset potential is also advantageous when two or more redox peaks are not fully resolved. The onset values have been worked out by drawing two tangents for each peak and are assumed to be where the two tangents cross (**Figure 3.22**). The plot describes the process of evaluating the onset values from the voltammogrammes.

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

Polymers	Onset of oxidation potential(V)	*HOMO eV	Onset of reduction potential(V)	*LUMO eV	Oxidation potential V	Reduction potential V	Electrochemical band gap E_g
OXD A	1.35	5.65	-0.87	3.43	2.9	-2.05	2.22
OXD AR1	1.5	5.8	-1.1	3.2	3.0	-2.20	2.60
OXD AR2	1.45	5.75	-1.0	3.3	3.0	-1.88	2.45
OXD AR3	1.5	5.8	-0.9	3.4	3.0	-1.9	2.4
OXD AR4	1.2	5.5	-0.9	3.4	3.0	-2.25	2.1
OXD B	1.8	6.1	-0.73	3.57	3.0	-2.0	2.53
OXD B R1	0.8	5.1	-1.05	3.25	2.9	-2.0	1.85
OXD B R2	2.0	6.3	-0.6	3.7	3.0	-1.95	2.6
OXD B R3	1.2	5.5	-0.9	3.4	2.85	-2.0	2.1
OXD B R4	0.8	5.1	-0.9	3.4	2.6	-1.95	1.7
PU1	0.8	5.1	-1.0	-5.3	2.8	-1.9	1.8
PU2	0.7	5.0	-1.4	-5.7	2.8	-2.9	2.1
PU3	1.5	5.8	-0.85	-5.15	2.9	-2.0	2.35
PU4	1.4	5.7	-1.2	-5.13	3.1	-1.8	2.6

*HOMO = 4.3 + (E_{ox} onset) and *LUMO = 4.3 + (E_{red} onset)

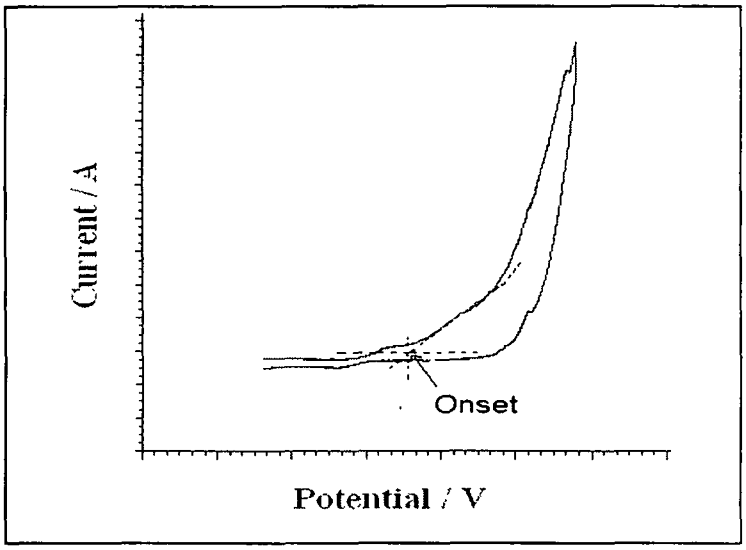


Figure 3.22: Measurement of onset potential in CV

Redox stability

The redox stability of a polymer is important for the OLED application, so that the material can withstand the repeated oxidation and the reduction during the device operation as a semiconducting material. A repeated 10 cycles of oxidation and reduction was performed with the polymers coated on ITO coated glasses in the cyclic voltammetry show no significant changes during the operation (**Figure 3.23-3.34**). The oxidation potential in the forward bias and reduction potential in the reverse bias for all the repeated cycles show no significant changes. As the degradation of the polymer films is proportional to the number of electrons passes through the polymer, the results are significant to conclude the stability and lifetime of the polymers. This implies the suitability of the material for OLED application. The stability of the material is due to the

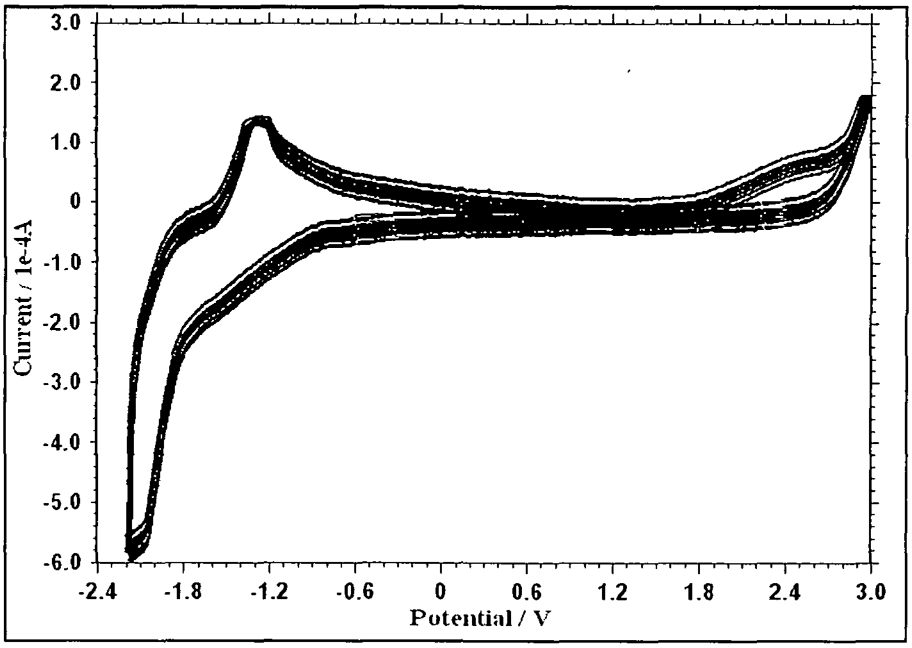


Figure 3.23: CV (10 cycles) of OXD AR1 in thin films on ITO coated glass

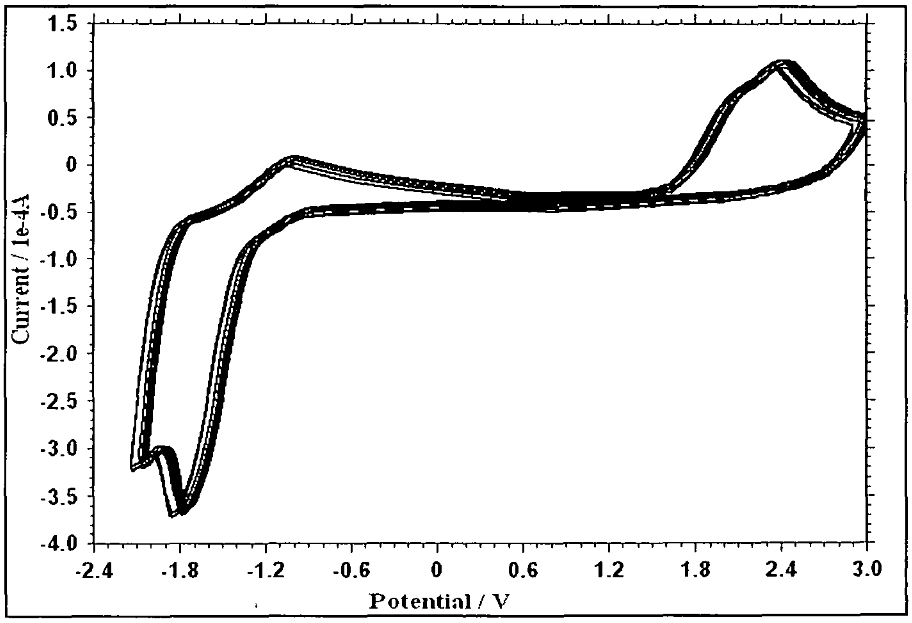


Figure3.24: CV (10 cycles) of OXD AR2 in thin films on ITO coated glass

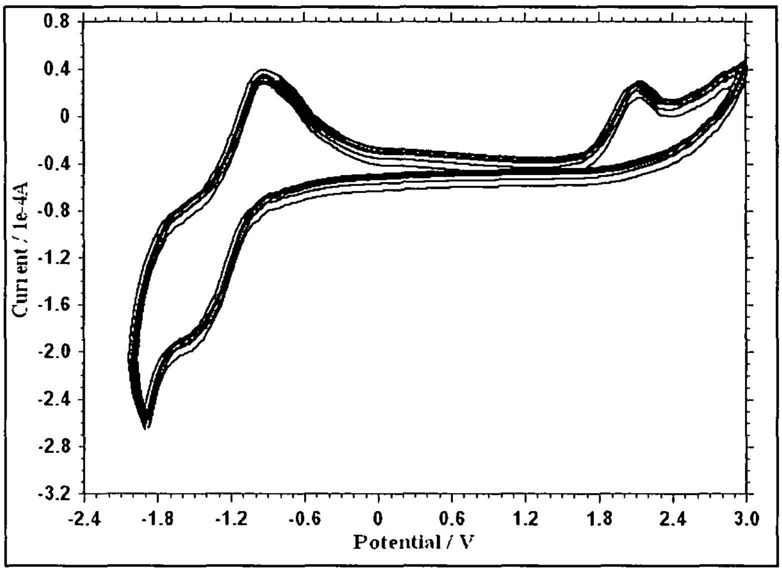


Figure 3.25: CV (10 cycles) of OXD AR3 in thin films on ITO coated glass

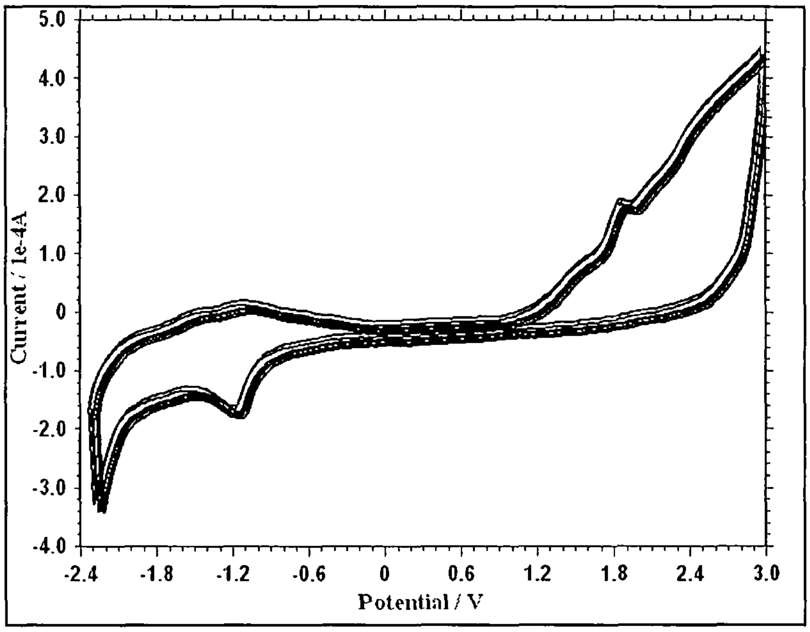


Figure 3.26: CV (10 cycles) of OXD AR4 in thin films on ITO coated glass

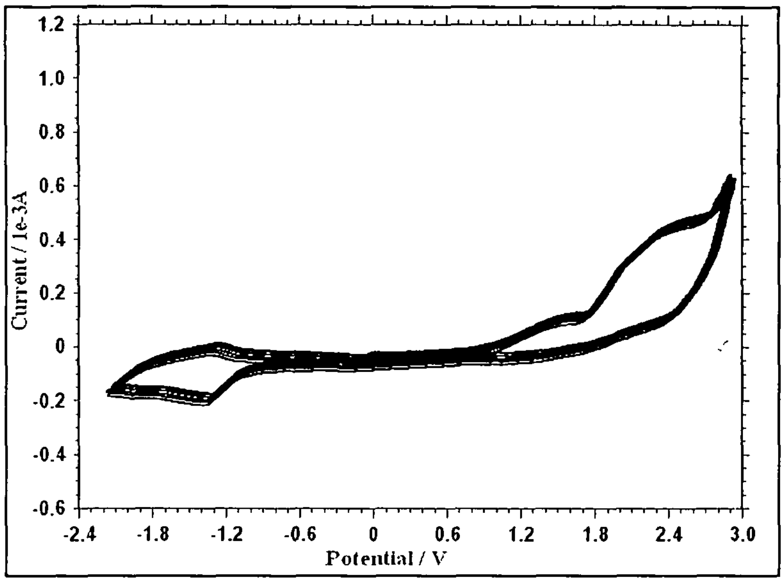


Figure 3.27: CV (10 cycles) of OXD BR1 in thin films on ITO coated glass

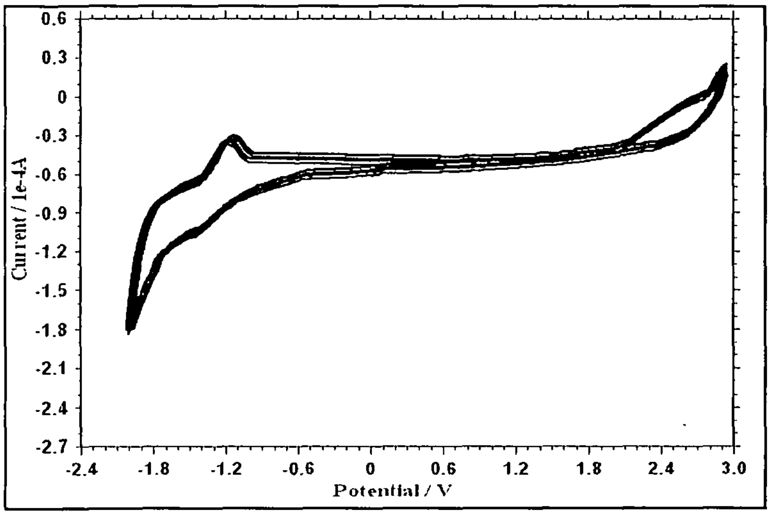


Figure 3.28: CV (10 cycles) of OXD BR2 in thin films on ITO coated glass

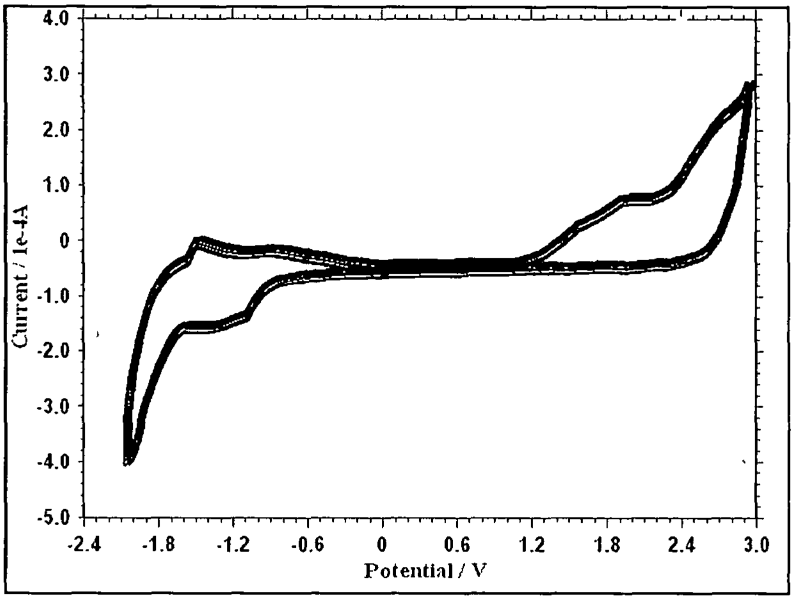


Figure 3.29: CV (10 cycles) of OXD BR3 in thin films on ITO coated glass

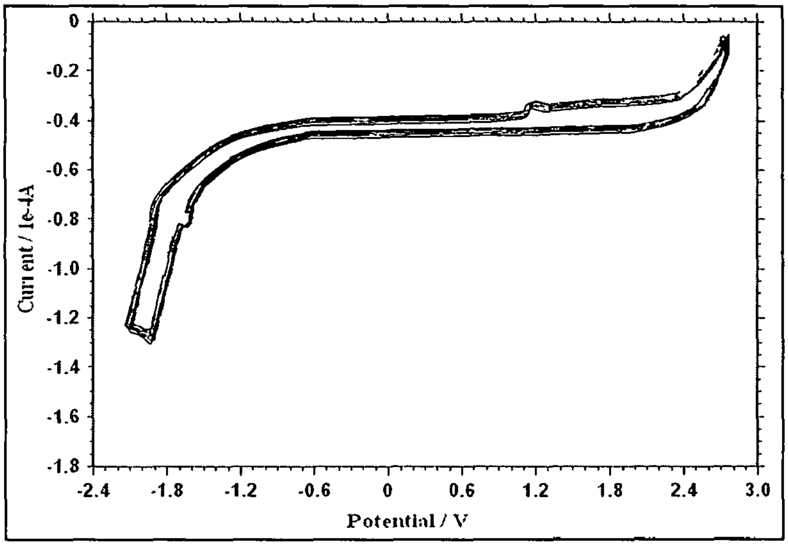


Figure 3.30: CV (10 cycles) of OXD BR4 in thin films on ITO coated glass

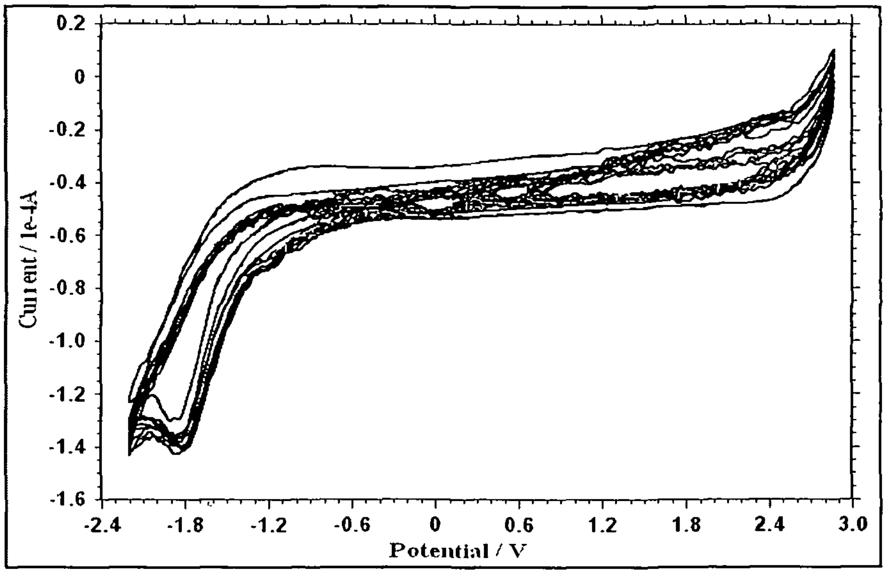


Figure 3.31: CV (10 cycles) of PU1 in thin films on ITO coated glass

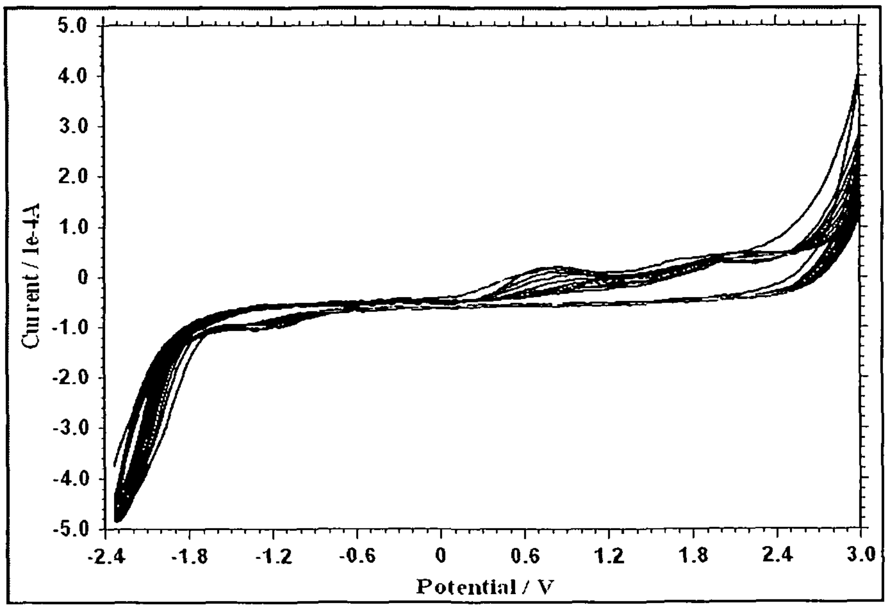


Figure 3.32: CV (10 cycles) of PU2 in thin films on ITO coated glass

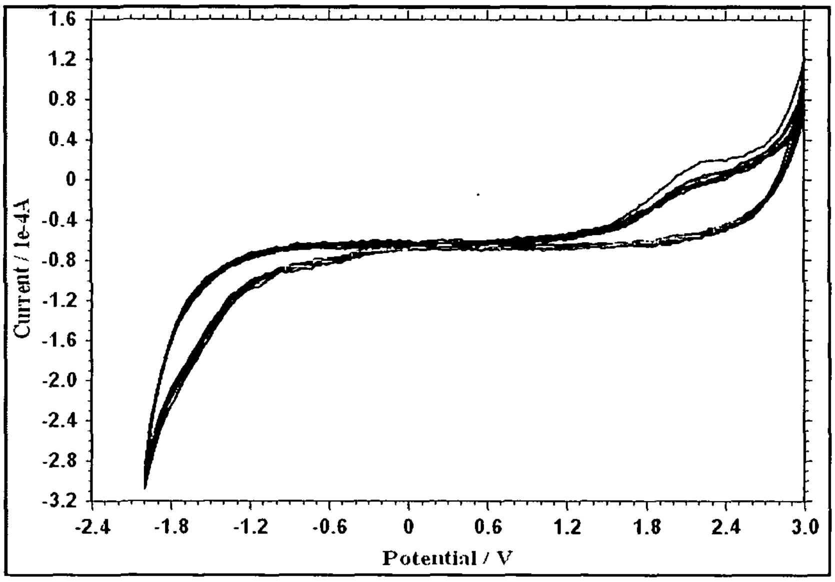


Figure 3.33: CV (10 cycles) of PU3 in thin films on ITO coated glass

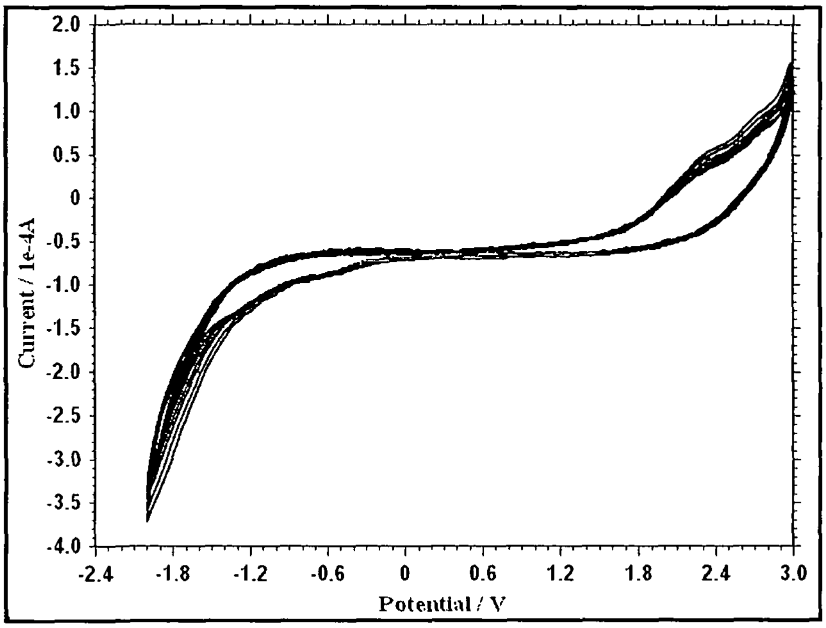


Figure 3.34: CV (10 cycles) of PU4 in thin films on ITO coated glass

3.3.4 Electroluminescence properties of polymers

The PLED 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, hole 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 termed as excitons, which subsequently emit radiation i.e. light. **Figure 3.36 and 3.37** shows the EL spectra of polymers. The EL maxima of OXD AR1 and the OXD BR1 are 402 and 405 nm respectively at 15 V. it emita light blue colour on illumination.

The mechanism of electroluminescence diagrammatically from a polymer is represented here (**Figure 3.35**).

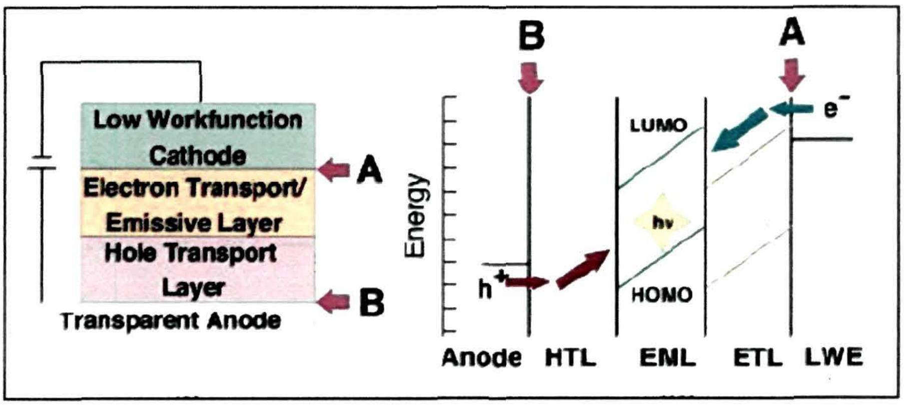


Figure 3.35: EL mechanism

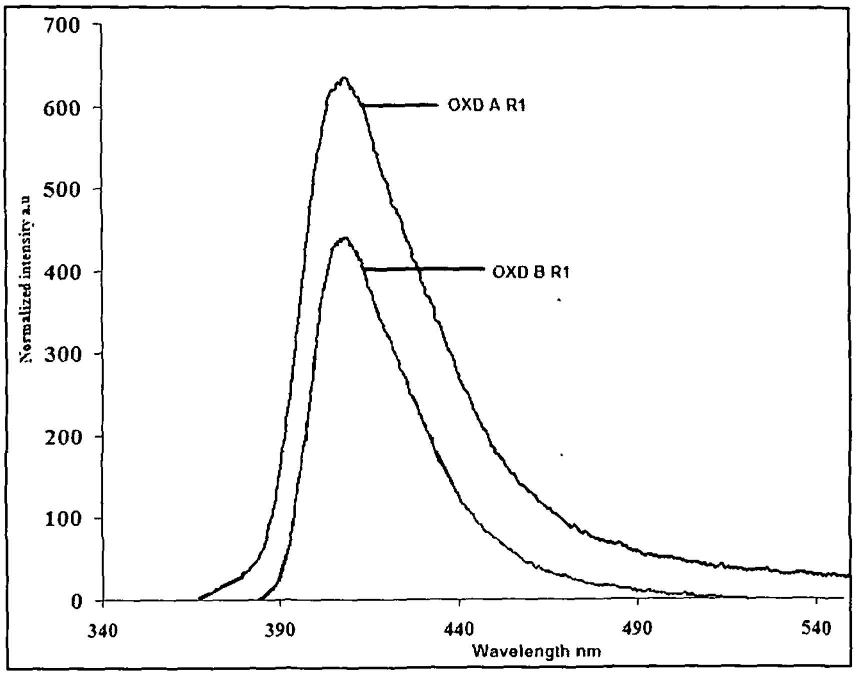


Figure 3.36: The electroluminescent spectra of OXD AR1 and OXD BR1 at 15V

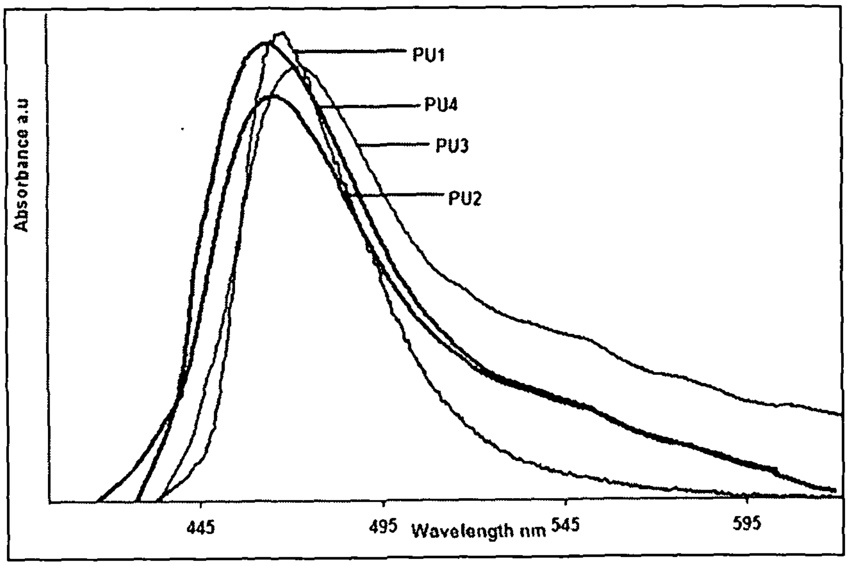


Figure 3.37: The electroluminescent spectra of PU1, PU2, PU3 and PU4 at 12V

The emission maxima for the polyurethanes containing the 1,3,4-oxadiazole moiety are at 471(PU1), 463(PU2), 475(PU3) and 461(PU4) (**Figure 3.37**)which are nearly similar to their corresponding photoluminescence maxima. The polymers emit bright blue colour under electric potential.

Figure 3.38 show the blue light emission from one pixel of the OLED device. Light emission of the EL device was too weak to be measured for other polymers and the device damaged due to the voids in the films after baking at high temperature; hence no emission was observed for those polymers. This may be due to the weak film forming capability and low intensity of PL in solid state of oligomeric materials. This results in poor interaction of interfaces for charge transport of carrier in LED device.

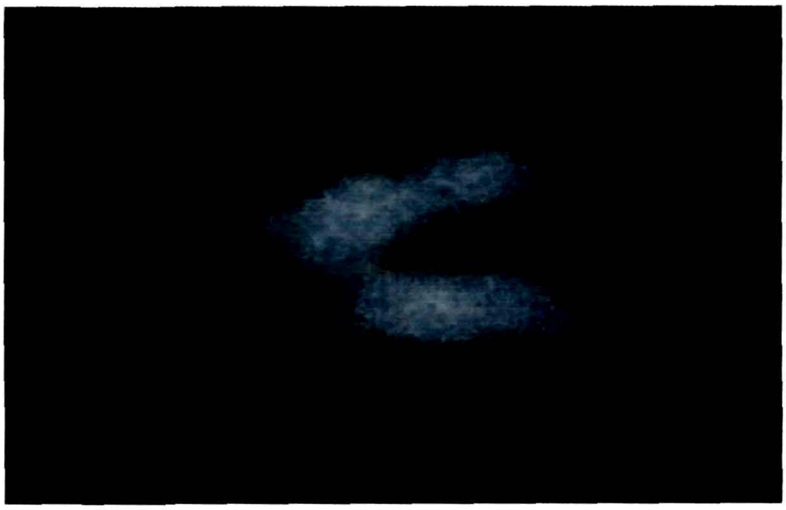


Figure 3.38: Blue light emission from OLED device

3.3.5 I-V measurement

Current - Voltage characteristic of device

Figure 3.39 and 3.40 show the current voltage(I-V) characteristic of the devices. The turn on voltage of the devices is in the range of 6V to 8V for current injection. The current densities i.e. charge carrier capacities of polyurethanes are higher than the polyoxadiazoles. Thus these polymers are effective for the light emission in LED device.

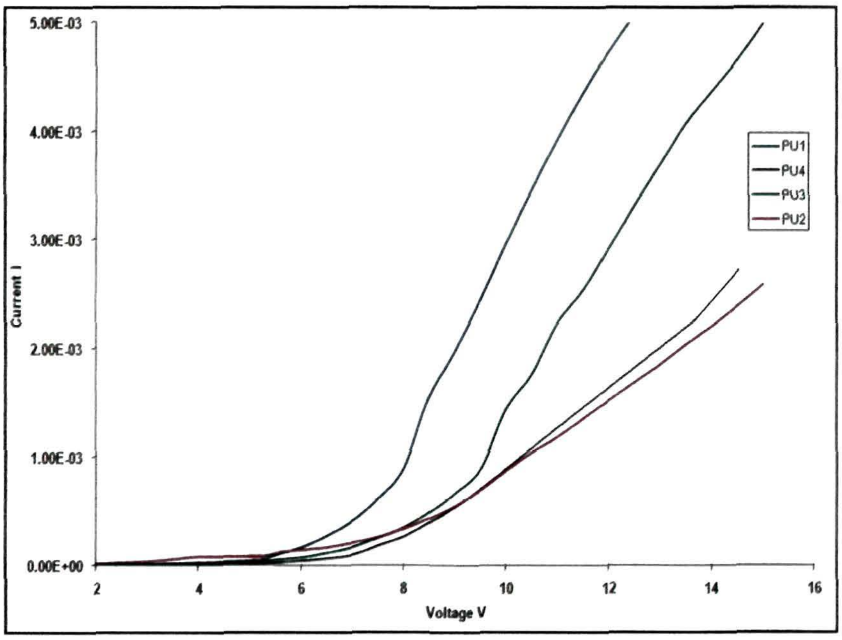


Figure 3.39: I-V characteristic curve of polyurethanes

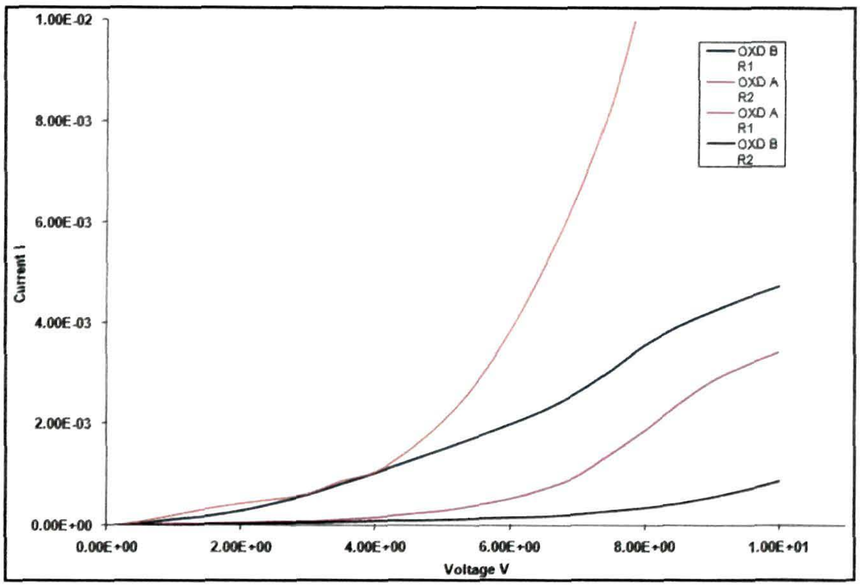


Figure 3.40: I-V characteristic curve of polyoxadiazoles

3.4 Conclusion

The fluorescence emission maximum of the polymers is found to be in the range of 350-440nm. The emission maxima were seen highest for the polymers OXDAR1, OXDAR4, OXDBR1, OXDBR4, PU3 and PU4. The light emission is in the violet-blue region region. Stokes shifts of the polymers are in the range of 40-185nm. Stokes shift is highest for OXDAR4, OXDBR1 and OXDBR4. The PL intensity of the oxadiazole containing polymer are high both in solid as well as solution state. The solution PL intensity is somehow lower as the flourophores are far apart in solution in the polyoxadiazoles whereas the solution PL of the polyurethanes increases in the solution state. The relative quantum yields of the polymers are found in the range of 0.53-0.88 with respect to anthracene. The PL intensity of the more electron deficient systems and the polyurethanes are highest among the polymers. The enhanced fluorescence efficiency of polymers is achieved at the cost of their solubility.

The electrochemical study of the polymers by cyclic voltammetry indicates that the oxidation potentials of polymers are in the range 2.85-3.0 V and the results vary with the substituent present. The more electron withdrawing group in the main chain causes the deficiency of electron in the main chain resulting in the slight increase in the oxidation potential. Similar observation was made in case of reduction potential of polymers. The reduction potential of the polymers is in the range of 0.7-1.05 V. It was observed that more electron deficient systems show decrease in the reduction potential. All the polymers seem to be stable under cyclic oxidation and reduction potential (upto 10 cycles). HOMO and LUMO energy levels and the band gap of the polymers were calculated. The E_g for the polymers are found to be 1.8-2.6 eV. This supports for the wide band gap polymer for emission of light from the colourless to blue region. OXD AR1, OXD AR4 OXD BR1, OXD BR2, PU1, PU2 PU3 and PU4 show high E_g value. The electrochemical band gap is lower than the optical band gap as the methods are not same.

The EL emission of the polymers show violet to blue colour in the visible range same as that of the PL emission spectra for the polymers OXDAR1, OXDBR1, PU1, PU2, PU3 and PU4. The turn on voltage of devices is in the range of 6-8 V for charge injection. The operating voltage for OXDAR1and OXDBR1 is 15V and for PU1, PU2, PU3 and PU4 is 12 V.

Chapter 3: Electrochemical, photoluminescence and electroluminescence properties of 1,3,4-oxadiazole containing polymers

References

1. Akcelrud, L. Electroluminescent polymers. *Prog. Polym. Sci.* 28, 875–962 (2003).
2. Malinsky, J. E. *et al* Self-assembly processes for organic led electrode passivation and charge injection balance. *Adv. Mater.* **11**, 227-231(1999).
3. Huang, B. *et al* Synthesis and properties of new poly(terfluorene) derivatives containing spirobifluorene and electron transport groups for stable blue electroluminescence. *J. Polym. Sci.: Part A: Polym. Chem.* **43**, 4517–4529 (2005).
4. Bruma, M. Aromatic polyoxadiazoles with silicon in the main chain. *Rev. Roumaine De Chim.* **53**, 343–355 (2008).
5. Wang, G.; Zhang, J. P.; Wang, L. X.; Jing, X. B.; Wang, F. S. A novel emitting polymer with bipolar carrier transporting abilities. *J App. Polym. Sci.* **88**, 50–53 (2003)
6. Zheng,M.; Ding,L.; Rel, E. E. G.; Lahti,P. M.; Karasz,F. E. Oxadiazole containing conjugated-nonconjugated blue and blue-green light emitting copolymers.
7. Murata, H. Ukishima, S. Hirano, H. and Yamanaka, T. A novel fabrication technique and new conjugated polymers for multilayer polymer light-emitting diodes. *Polym. Adv. Technol.* **8**, 459–464 (1997).
8. Saxena, K. Jain, V.K. Mehta, D. S. A review on the light extraction techniques in organic electroluminescent devices. *Opt. Mater.* **32,** 221–233(2009)
9. Sung, H.-H.; Hong-Chen, L. Novel alternating fluorene-based conjugated polymers containing oxadiazole pendants with various terminal groups. *Macromolecules* **37,** 7945-7954 (2004).
10. Korshak, V. V.; Berestneva, G. L.; Vinogradova, S. V.; Gergaya, M. S.; Tur, D. R. Investigation of the structure and properties of poly-1,3,4-oxadiazoles. *Chem. Heter. Comp.* **7**, 1357-1362 (1971).
11. Jiang, X.; Register, R. A. Effect of carbazole–oxadiazole excited-state complexes on the efficiency of dye-doped light-emitting diodes. *J. Appl. Phys.* **91**, 6717-6724(2002).
12. T. Johansson, W. Mammo, M. Seensson, M. A. Andersson, O. Inganas, Electrochemical bandgaps of substituted polythiophenes. *J. Mater. Chem.* **13**, 1316-1323 (2003).
13. Skompska, M.; Szkurlat, A. The influence of the structural defects and microscopic aggregation of poly(3-alkylthiophenes) on electrochemical and

optical properties of the polymer films: discussion of an origin of redox peaks in the cyclic voltammograms. *Electrochim. Acta,* **46,** 4007-4015(2001).

14. Hillman, A. R.; Efimov, I.; Skompska, M. Dynamics of regioregular conducting polymer electrodes in response to electrochemical stimuli. *Faraday Discuss.***121** 423-439 (2002).
15. Zhang, K. *et al* Synthesis and Properties of Carbazole Main Chain Copolymers with Oxadiazole Pendant toward Bipolar Polymer Host: Tuning the HOMO/LUMO Level and Triplet Energy. *Chem. Mater.* **20**, 7324–7331 (2008).
16. Liu, C.; Zhao, P.; Huang, W. New oxadiazole derivatives as promising electron transport materials: synthesis and characterization of thermal, optical and electrochemical properties. Central Europ. J. Chem. **5**, 1303-315(2007)
17. Kim, J. S.*et al* Indium–tin oxide treatments for single- and double-layer polymeric light-emitting diodes: The relation between the anode physical, chemical, and morphological properties and the device performance. *J. Appl. Phys.* **84,** 6859-6870 (1998).
18. Campbell, A. J. *et al* Transient and steady-state space-charge-limited currents in polyfluorene copolymer diode structures with ohmic hole injecting contacts. *Appl. Phys. Lett.* **76,** 1734-1736(2000).
19. Carter, S. A.; Angelopoulos, M.; Karg, S.; Brock, P. J.; Scott, J. C. Enhanced electron injection in organic electroluminescence devices using an Al/LiF electrode. *Appl. Phys. Leti.* **70,** 2067-2069 (1997).
20. Kim, J. S.; Friend, R. H.; Cacialli, F. Improved operational stability of polyfluorene-based organic light-emitting diodes with plasma-treated indium–tin–oxide anodes. *Appl. Phys. Lett.* **74,** 3084-3086 (1999).
21. B. Ballarin, A. F. Morgera, D. Frascaro, S. Marazzita, C. Piana, L. Setti, Thermal inkjet microdeposition of PEDOT:PSS on ITO-coated glass and characterization of the obtained film. *Synth. Met.* **146,** 201-205 (2004).
22. L. S. Hung, C. W. Tang, M. G. Mason, Enhanced electron injection in organic electroluminescence devices using an Al/LiF electrode. *Appl. Phys. Lett., 70,* 152-154 (1997).
23. Jin, Y. D. *et al* Role of LiF in polymer light-emitting diodes with LiF-modified cathodes. *Org. Electro.* **5**, 271- 281 (2004).

24. Kim, Y. E.; Park, H.; Kim, J. J. Enhanced quantum efficiency in polymer electroluminescence devices by inserting a tunneling barrier formed by Langmuir–Blodgett films. *Appl. Phys. Lett.* **69**, 599-601 (1996).
25. Choudhury, K. R.; Yoon, J. H.; So, F. LiF as an n-Dopant in Tris(8-hydroxyquinoline) Aluminum Thin Films. *Adv. Mater.* **20,** 1456-1461 (2008).
26. Hohertz, D.; Gao, J. How Electrode Work Function Affects Doping and Electroluminescence of Polymer Light-Emitting Electrochemical Cells. *Adv. Mater.,* **20**, 3298-3302 (2008).
27. Yin, S. *et al* Synthesis, Photo-, and Electroluminescent Properties of the Soluble Poly[(2,5-diphenylene-1,3,4-oxadiazole)-4,4′-vinylene]. J. Appl. Polym. Sci. **74**, 3535–3540 (1999).
28. Lima, H. *et al* Organic electroluminescent devices based on polyurethane derivatives:effects of substituents on electroluminescent and photoluminescent properties. *Thin Solid Films* **363,** 152-155 (2000).
29. Lin, K.-R. *et al* New hole-transport polyurethanes applied to polymer light-emitting diodes. *Europ. Polym. J.* **43**, 4279–4288(2007).
30. 33. Rajendran,V.; Marikeni, A. *Materials Science* (Tata McGraw-Hill, fifth ed., 2006).
31. 34. Manjunatha, M.G.; Adhikari, A. V., Hegde, P. K. Optical and electrochemical properties of a new donor-acceptor type conjugated polymer derived from thiophene, carbazole and 1,3,4-oxadiazole units. *Mater. Sci. Forum* **657**, 46-55(2010)
32. 35. Peng, Q.; Xu,J.; Li, M.; Zheng, W. Blue emitting polyfluorenes containing dendronized carbazole and oxadiazole pendants: synthesis, optical properties, and electroluminescent properties. *Macromolecules* **42**, 5478–5485 (2009).
33. Sung, H.-H.; Lin, H.-C. Novel alternating fluorene-based conjugated polymers containing oxadiazole pendants with various terminal groups. *Macromolecules* **37**, 7945-7954(2004).
34. Melhuish, W. H. Quantum efficiencies of fluorescence of organic substances: effect of solvent and concentration of the fluorescent solute. *J. Phys. Chem.* **65,** 229-235(1961).
35. Williams, A. T. R.; Winfield, S. A.; Miller, J. N. Relative fluorescence quantum yields using a computer controlled luminescence spectrometer. *Analyst* **108**, 1067-1071(1983).

36. Davey, A. P.; Elliott, S.; O'Connor, O.; Blau, W. New rigid backbone conjugated organic polymers with large fluorescence quantum yields. *J. Chem. Soc. Chem. Commun.* 1433-1434 (1995).
37. Agrawal, A. K.; Jeneka, S. A. Electrochemical Properties and Electronic Structures of Conjugated Polyquinolines and Polyanthrazolines. *Chem. Mater.* **8**, 579-589 (1996).

CHAPTER 4

The metal polymer hybrid material for organic light emitting diodes (OLEDs) application

Chapter 4: The metal polymer hybrid material for organic light emitting diodes (OLEDs) application

4.1 Introduction

Optoelectronic materials and technology in the 21st century requires the miniaturization of devices into nanometer sizes while their ultimate performance should be dramatically enhanced. This raises many issues regarding the development of new materials for achieving specific functionality and selectivity. Nanophase and the nanostructured materials, a growing field in the material science, gaining popularity in its own, attracting a great deal of attention because of their versatile applications in the areas such as electronics, optics, catalysis, ceramics, magnetic data storage and nanocomposites. The unique properties and improved performances of nanomaterials are determined by their surface structures and inter particle interactions[1-6].

Nanocomposites are a special class of materials originating from suitable combinations of two or more nanoparticles or nanosized objects and a matrix in some suitable technique, resulting in materials having unique physical properties and wide application potential in diverse areas. Novel properties of nanocomposites can be derived from the successful combination of the characteristics of parent constituents into a single material. Materials scientists very often handle such nanocomposites, which are an effective combination of two or more inorganic nanoparticles. To exploit the full potential of the technological applications of the nanomaterials, it is very important to endow them with good processability which has ultimately guided scientists toward using conventional polymers as one of the components of the nanocomposites, resulting in a special class of hybrid materials termed "polymeric nanocomposites". These materials are also intimate combinations (upto almost molecular level) of one or more inorganic nanoparticles with a polymer so that unique properties of the former can be taken together with the existing qualities of the latter. In these cases the polymers not only act as a stabilizer but also enhance the processability, solubility and control of the growth of nanocrystalline material in a polymer matrix. It is worth noting that the key issue behind the synthesis of well-dispersed and well-stabilized nanocrystals is their processing chemistry, which is mostly related to the nature and structure of the matrix, the interaction between the inorganic core and polymer and the structure of inorganic particles. Moreover, the mostly utilized polymers for stabilizing semiconductors nanoparticles are still not satisfactory mainly due to the photooxidation of nanoprticles/polymer complexes or detachment of the polymers from the nanocrystals, resulting phase separation and nanocrystal aggregation, along with the luminescence diminishing or quenching of nanocrystals. The lifetime of LEDs based on semiconductor nanocrystals is short, which is likely a result of dissociation of the polymers from the nanocrystals due to the thermal effects of the devices during operation. To improve the interaction between polymer and nanostructured material, the introduction of covalent bonds between the polymer surface and the later may be one of the most efficient methods[6-12].

The incorporation of the inorganic particles into the polymeric system involves many techniques. Like the method of growth of both particles and the polymer simultaneously in the same system or the synthesis of the particle within a polymeric matrix or the ex situ system is the simple mixing or blending of the two systems prepared earlier separately. Conductive nanocomposites may be formed by incorporation of nanoparticles within the polymer medium by dispersion into the monomers or oligomers prior to the cross-linking reactions (ex situ formation) or formed by ion beam irradiation of the preformed polymer films (in situ formation)[13]. In most of blending or mixing of the components, the polymer is taken in solution or in melt form. Resulting nanocomposites have found successful applications in versatile areas viz. battery cathodes, microelectronics, nonlinear optics, sensors etc. The perspective is somewhat different with the class of polymer that possesses a very high thermal stability above 300°C and is infusible in nature rather degrade above the melting temperature. These conjugated conducting polymers have high glass transition temperature and are generally insoluble in common organic solvents. Such inherent intractability has prevented the polymers from combining with the foreign materials in conventional blending techniques to form nanocomposite. Therefore, synthetic techniques have to be found and optimized to incorporate the inorganic component into the conducting polymer; this added a separate dimension to the nanocomposite research. The blending or the mixing process has two disadvantages: the templating agent or surfactant is used to control nanocrystal size and shape can end up in the final composite an impurity, interfering with charge transfer. Secondly, co-solvents used to blend the materials can interfere with nanocrystal solubility causing aggregation of the nanocrystals and also interferes with the polymer chain conformation upon spin casting. In the conventional nanocomposites, the polymer adds flexibility to the system and improves processability to a large extent. In conducting polymer nanocomposites, on the other hand, the nanoparticles generally provide the system with some kind of processability (colloidal stability or mechanical strength), although the specific properties of the latter are also utilized in some respects[14-24]. So far, studies on ordered nanostructures and nanocomposites with the desirable properties in the optoelectronic technology for OLED application have been predominantly focused on inorganic materials and the organic polymers. Organic functional materials are capable of bringing new opportunities because of their soft nature, and thus allowing high flexibility. As a type of promising functional materials, conducting polymers have been investigated extensively over the past few decades. Apart from conventional polypyrrole and polyaniline based nanocomposites for the semiconductor device applications; electroactive polymers like polyhydrazides and their cyclized counterpart polyoxadiazoles with electron deficient centres are still to get more importance in the field of luminescence science. The incorporation of the metal nanaoparticles in these systems requires a different technique as the polymers possess a very high degradation temperature above 300°C. The solubility of the polymers is also restricted to limited solvents only. The uncyclized form of polyoxadiazoles is the polyhydrazides. The class of polymers mostly falls in the polyamide class of polymers having a good T_g though crystalline in nature. The cyclization of the polyhydrazides to polyoxadiazoles involves the chemical and the thermal cyclization method. Chemical cyclization involves the use of the corrosive cyclization agents like phosphorous oxychloride, polyphosphoric acid etc. They usually emit in the near UV region of the spectrum (Chapter 3) yet very effective as a material due to their thermal stability upto 200°C. The polyoxadiazoles on the other hand already marked a very good place in the OLED research due to their efficient electron transporting capability in the multilayer devices as the electron mobility from the electron injector to the emissive layer is very difficult as compared to the hole mobility as discussed earlier in the ***Chapter 1***. Such a rigid framework has the potential to effectively suppress nanoparticle aggregation. But simple polyoxadiazoles are lacking behind in the practical application due to their rigid compact structure and the poor solubility. The oligomeric polyoxadiazoles are made soluble and processible but they fall off in their performance as compared to the high molecular weight polymers[25-29].

4.1.1 Nanomaterials and the light emitting polymers

The effects of nanoparticles on the performance of electro-optic polymer devices is far from complete, it has been generally thought that the enhanced properties are due to either the ability of a group of nanoparticles to act as charge carriers, as electrooptically active centers, or as optical microcavities. In this work, we demonstrate that nanoparticles can enhance the performance of polymer light emitting diodes (PLED) based primarily on structural effects. This effect can result in low driving voltage, high radiance, and high efficiency devices. Traditionally, metal-polymer nanocomposites are prepared via multistep techniques, including plasma deposition, electrodeposition, self-assembly of functionalized nanoparticles and other hybrid approaches[30-32]. These methods are limited by the difficulty in controlling monodisperse nanoparticle formation over large areas, in addition to other drawbacks. For instance, the self-assembly example requires preformed nanoparticles (already having a size dispersity) to be isolated and then functionalized to ensure chemical compatibility with an appropriate polymer host. To date, there is considerable progress to be made in developing a facile route for the formation of robust metal nanoparticle-polymer composites. Here we present the synthesis of the nanocomposites in a different way depending upon the nature of the polymer used as matrix in the system and the metal salt used for the synthesis.

The basic idea behind metal nanoparticle based organic light-emitting diodes (OLEDs) is to achieve full color tune ability in a single host material. Organic semiconductors such as conjugated polymers represent large polymer chains that are soft and flexible. On the other hand, metal nanoparticles are as inorganic species are robust. Inorganic semiconductors are well known to change their emission color over a very wide spectral range, while in organic semiconductors this effect is less pronounced and often goes in hand with changed electrical properties. Although organic molecules span the entire visible spectrum in terms of emission wavelength, a change of material required to tune the color of emission can result in a dramatic modification of the charge transport properties and thus of the device characteristics. The naoparticles are important in OLED application as polymer-inorganic hybrid material; because the quantum confinement leads to an enhancement of the absorption coefficients of the particles compared to the respective bulk materials, making them efficient absorbers even in relatively thin devices. The performance in such devices is strongly dependent on the local and long-range film morphologies. Such molecular and nanoscale structural features can in many cases be modified by incorporation into a suitable polymer host matrix to form a composite material[33-39].

The nanomaterials used in the electroluminescent devices mainly include the inorganic semiconducting materials such as cadmium sulphide, lead sulfide, zinc oxide, zinc sulphide etc. whereas metal nanocrystals in optoelectronics involve nickel, copper, silver, carbon nanotube etc[40-46]. There have been recent efforts to make metal-based solutions, which can be used to make conductive device layers in the fabrication of microelectronic devices. One of the shortcomings of fabricating thin conductive layers with liquids comprising metal-based materials is that the layers tend to exhibit poor adhesion and delaminate from the substrate and/or form irregularities during and/or after the curing process. Further, there is a tendency for hillock formation and/or pin hole formation during and/or after the curing process. Therefore, there is a need to develop suitable substrates and/or methods for depositing, printing and/or imaging liquid metal-based materials, which provide improved adhesion and reduced topographical irregularities in the resultant films during and/or after the curing process and which can be used to form active device layers in the fabrication of microelectronic devices[47].

The nanoparticles and the polymer/nanomaterial hybrids can well characterized by their optical and electrical properties to find their application in the optoelectronics. To evaluate these properties the distribution of the particles within the polymer matrix and the size of the particles are two important factors to put emphasis on. Because the large size to volume ratio of the nanomaterials which results in the electronic states within the band gap of the metal particles; play a crucial role in determining the properties of the hybrid materials. These states are called surface states and influence the luminescence properties of the materials. The excited electrons are captured by the surface states either before or after the occurrence of direct radiative recombination which ultimately influences the photoluminescence intensities[50].

Nanoparticles can be only incorporated into the polyoxadiazole polymer matrix by two methods, direct addition and blending with the polymer or the ion irradiation method. Due to the oxidizing chemicals used in the cyclization of the polyhydrazide (**Chapter 2**); this may get in the way in the formation of the desired nanosized materials with the required properties. That is why the incorporation of the nanoparticles with the polyoxadiazoles is the preferred technique by ex-situ method. Therefore these types of composite materials better termed as the polyoxadiazole-nanomaterial hybrid material.

The experimental methods, materials and the property evaluation of the polyoxadiazole metal nano hybrids are described below.

4.2 Experimental

4.2.1 Materials

The raw materials used in the synthesis of nanoparticle are $AgNO_3$ (Mark), trisodium citrate (Fluka), sodium borohydrate (Mark), sodium hydroxide (Rankem), $CuSO_4$ (Mark) and $NiCl_2.6H_2O$ (Mark), hydrazine monohydrate (Fluka). The polymers; polyhydrazide and poly(1,3,4-oxadiazole)s are already synthesized as described in the Chapter 2.

4.2.2 Experiments

Preparation of the polyoxadiazole/silver nanoparticle hybrid material

Silver nanoparticle was synthesized by the chemical reduction method using sodium citrate as reducing agent. In a typical synthesis procedure, 0.2, 0.3 and 0.5% (with respect to the polymer weight) of silver nitrate solution in DMAc was taken in a three naked round bottom flask and the temperature was set to 80°C under nitrogen. 50ml of 0.1M molar tri-sodium citrate solution in DMAc was added dropwise from a dropping funnel to the $AgNO_3$ solution with constant stirring at 200rpm. The mixture was heated at 80° for 30min. After about 12min, initial pale yellow colour solution turned yellow and finally attained a dirty yellow brown colour indicating the formation of Ag nanoparticles. Cooling down to 60°c, 10 ml solution of 1g polyoxadiazole in DMAc was added slowly, the solution turned brown. The mixture was stirred vigorously for another 30 min and cast on glass plates and dried in vacuum for the further study.

The 0.3% silver salt loaded compound was used for the further studies as optimized from the dried film casted on the glass plate indicating smooth film formation and no phase separation.

Preparation of the polyoxadiazole/copper nanoparticle hybrid material

Similarly polyoxadiazole/copper nanoparticle hybrid material can be prepared from the ammonical cupric chloride solution as the copper source. 0.3% ammonical cupric chloride solution was purged with nitrogen for 15 min with stirring and then subsequently reduced by adding 0.1 M hydrazine hydrate slowly under nitrogen. The solution changed colour from pale blue to brown after 30 min. Then 1g polyoxadiazole in 10ml DMAc was added slowly and with constant vigorous stirring for another 15 min. The mixture was cast on the glass slide and dried in vacuum for the further study.

Preparation of the polyoxadiazole/nickel nanoparticle hybrid material

The preparation of the polyoxadiazole/nickel nanoparticle hybrid material involves the same procedure as stated above. Nickel chloride reduced to nickel by the reducing agent hydrazine hydrate followed mixing with the polymer solution. The hybrid solution was cast on a glass film, dried in vacuum for the further characterization and application.

4.2.3 Characterization Methods

Size determination

The different methods used for the size determination of the nanomaterial are X-Ray diffraction (XRD), Optical absorption and the Transmission electron microscopy (TEM).

X-Ray diffraction (XRD)

It is the first hand technique to identify and to investigate the crystal size of the nanomaterials. We can get the average size of the particles in the matrix from this method. 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. In a bulk system, one observes a set of narrowed peaks corresponding to a definite crystal structure. However diffraction lines at subsequent peaks are found to be broadened with size reduction. The particle size can be determined by using the Debye-

Scherrer equation which can give reasonably accurate particle diameter. The equation can be written as[48]

$$D= k\lambda/(\beta\cos\theta).........(1)$$

Where D is the main crystallite size, λ is the wavelength of the X-ray radiation($1.54A^{o}$), k is a constant to be taken as 0.9, β is the full width at half maximum height of the peak(FWHM) and θ is the diffraction angle.

Transmission electron microscopy (TEM)

It is one of the most accurate and promising method to determine the size of the nanomaterials and ascertain the distribution of the particles within the matrix. It allows the imaging of the individual crystallites and the development of a statistical distribution of the determination of individual crystallite morphology[49].

For the TEM analysis a Philips EM 400 was used with an acceleration voltage of 100 KV. All images were taken at a magnification of 60,000 or 120,000. For the TEM measurement, materials were first sonicated, and the samples were prepared by dropping highly diluted latexes on the carbon- coated copper grid and dried in a vacuum oven at room temperature[51].

Optical properties

The optical properties of the hybrid materials are determined by the UV-visible spectroscopy and photoluminescence spectroscopy. The device properties of these materials are determined by electroluminescence and I-V characteristic curve.

These characterization methods are already described in Chapter 2 and Chapter 3.

4.3 Results and Discussions

4.3.1 XRD analysis

XRD analysis is used for the particle size determination and the crystalline nature in the hybrid material. The XRD peaks and the spectra describe the different crystal phases corresponding to the formation of the metal particles. In order to determine the particle size and the crystalline nature of the polymer/nanoparticle hybrids, the thin film on the glass substrate was used for the examination. **Figure 4.1** shows the typical X-ray diffraction (XRD) pattern of the as-prepared polyoxadiazole and polyoxadiazole/silver, copper and nickel hybrids. The comparative study with the virgin polymer and the hybrids show the incorporation of the inorganic particles in the polymer indicating the crystal planes arise from the process.

The XRD study indicates the formation of silver (Ag), copper (Cu) and nickel (Ni) nano particles. **Table4.1** shows the experimentally obtained X-ray diffraction angle and the standard diffraction angle of polyoxadiazole/Ag, Cu and Ni hybrid specimens.

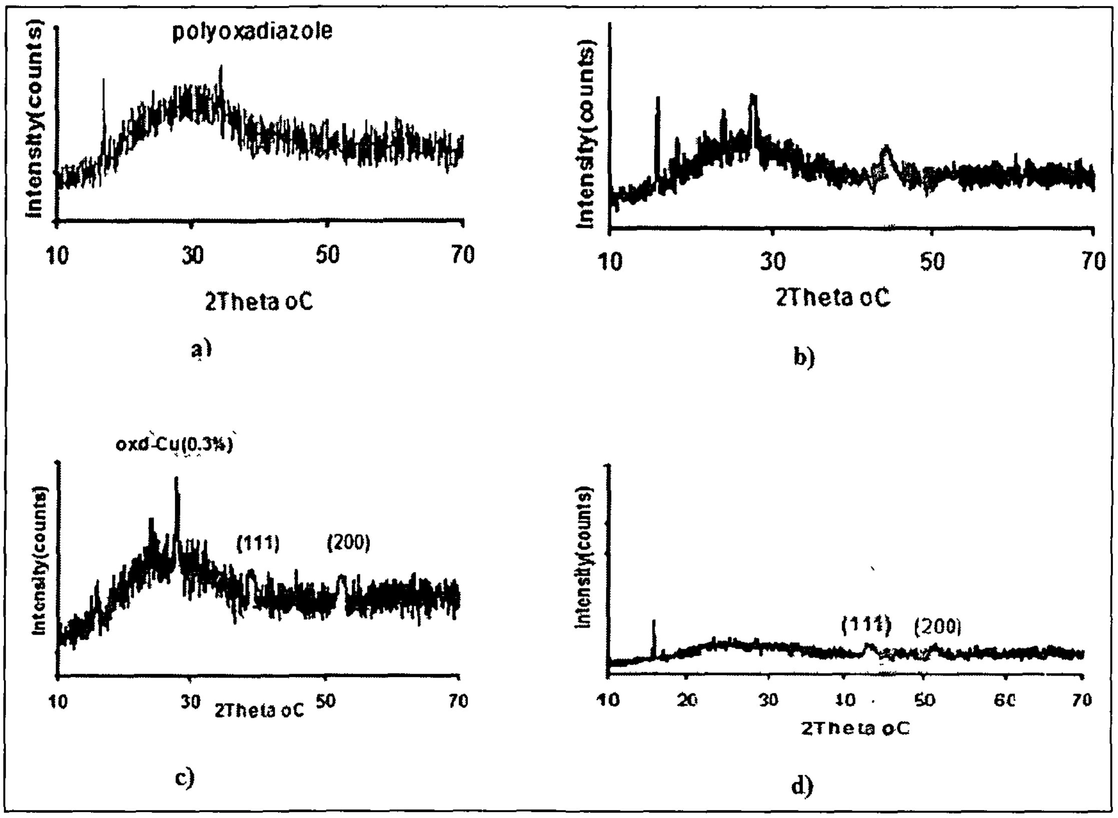


Figure 4.1: XRD for a)polyoxadiazole, b)polyoxadiazole/silver, c) polyoxadiazole/copper and the d)polyoxadiazole/nickel hybrid materials

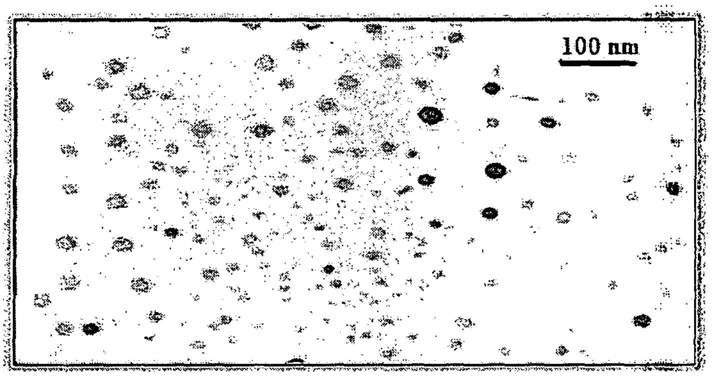
From this study, the diffraction peak at 2θ=44 for the plane (111) and 2θ at 53 for the plane (200) of nickel are observed. 2θ=43 for the crystal plane (111) and 2θ at 50.7 for the plane (200) of the copper confirms the formation of the particles. Silver nanoparticle/polyoxadiazole hybrids show XRD peaks at 2θ= 44 for (200) and 2θ at 65 for (220). The broadening of the peaks and the position of the crystal planes as per literature proves the formation of the nanoparticles within the polymer. The average particle sizes of the particles have been estimated by using **Debye–Scherrer** formulas. The average sizes of the particles lie nearly in the range of ~40 nm in the polyoxadiazle/ nanoparticle hybrids[50-52]

4.3.2 TEM analysis

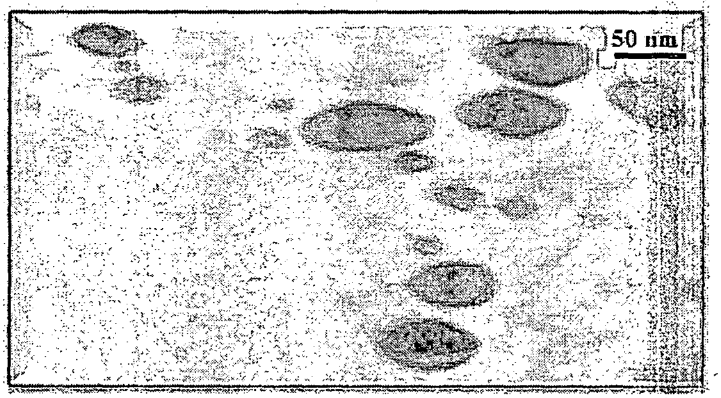
TEM images of the hybrids show the well distribution of the nanoparticles within the polymer matrix. The particles are spherical in shape although a few are irregular in shapes. The careful size measurements were done by taking 20 to 40 individual crystals in a single range. The size of the particles can also be predicted from the TEM micrograph and the particle size Cu nanoparticles are found to be ~40nm, Ni particles have the average size is around 35-40 nm and the silver nanoparticles nearly resides in the range of 50 nm[43-45, 50-53]. TEM micrograph shows the presence of nanoparticles within polymer matrix. However TEM micrograph does not reveal the distribution of nanoparticles in the polymer matrix. While taking TEM, sample was dispersed in a solvent. Therefore the original composite structure was not retained. **Table 4.1** describes the particle size of the metal particles within the polymer matrix as calculated from the XRD and the TEM images.

Table 4.1: Comparison of particle size of the metal nanoparticles from the XRD and TEM micrograph

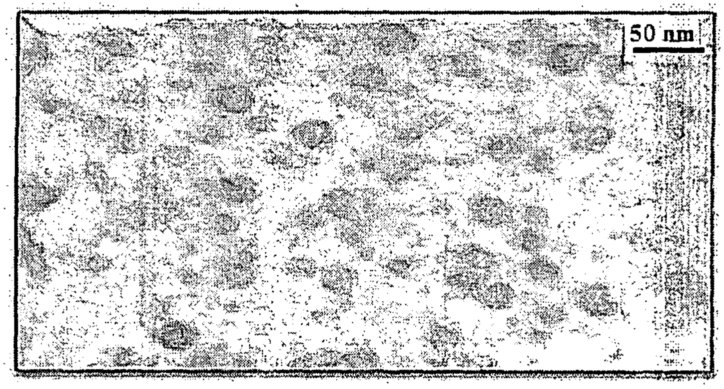
Sample	Diffraction peak 2θ (experimental)	Diffraction peak 2θ (standard)	Size from XRD	Size from TEM
Polyoxadiazole/ copper	43(111), 50.7(200)	51(200)	40 nm	37 nm
Polyoxadiazole/ nickel	44(111), 53(200)	44.5(111)	35-40nm	40nm
Polyoxadiazole/ silver	44(200), 65(220)	45(200)	50 nm	44nm



a) Polyoxadiazole/Cu nano; scale 1cm=100nm, magnification 100x



b) Polyoxadiazole/Ni nano; scale 1cm=50nm, magnification 200x



c) Polyoxadiazole/Ag nano; scale 1cm=50nm, magnification 200x

Figure 4.2: TEM images of a)polyoxadiazole/copper, b) polyoxadiazole/ nickel and the c)polyoxadiazole/ silver hybrid materials

4.3.3 Optical properties of the polymer/metal nanoparticle hybrids

The absorption and emission spectra of the polymer/metal nanoparticle hybrids were recorded with UV-vis spectrophotometer and the Fluorescence spectrophotometer. The samples are used as coated on a glass plate.

The UV absorbance spectra show the shifting of the absorption maxima of the polyoxadiazole when incorporated with the metal nanoparticles in **Figure 4.3**. The polymer absorbs in the region 285nm and 295 nm. The absorption intensity of the polymer decreased on incorporation of Ni and the Ag nanoparticles to the polymer. Ni nanoparticles do not absorb in the UV region and that is why it decreases the absorption intensity of the polymer/metal nanoparticle hybrid. Silver nanoparticle imparts the same effect like that of nickel. The phenomenon observed can be explained from the change in the band gap of the hybrid materials. As the polymers were doped with the metal particles, the band gap of the polymer is reduced. On the other hand the broad spectra of the polymer/copper nanoparticle are clearly due to the typical absorption nature of the copper nanoparticles that used to show the broad spectra[54-57].

The photoluminescence spectra of the hybrid materials were recorded by preparing thin films over glass plates. The PL spectra of the materials show a dramatic change in the emission nature to that of the virgin polymer irrespective of the absorption spectra. The emission maxima are in the green visible region around 480-490 nm and a large increment in the emission intensity accounts for the interaction of the metal nanoparticles with the polymer. The λ_{max} of emission could not be recorded as the peak show saturation in the plot. The polymer itself is a UV light emitting material, but the polyoxadiazole/ copper, nickel and silver metal nanoparticle hybrids emit in the visible region.

The enhanced luminescence state is due to the change in the surface states of the metal nanoparticles. The density of the surface states would increase with the decrease in the particle size due to the large surface to volume ratio[36].

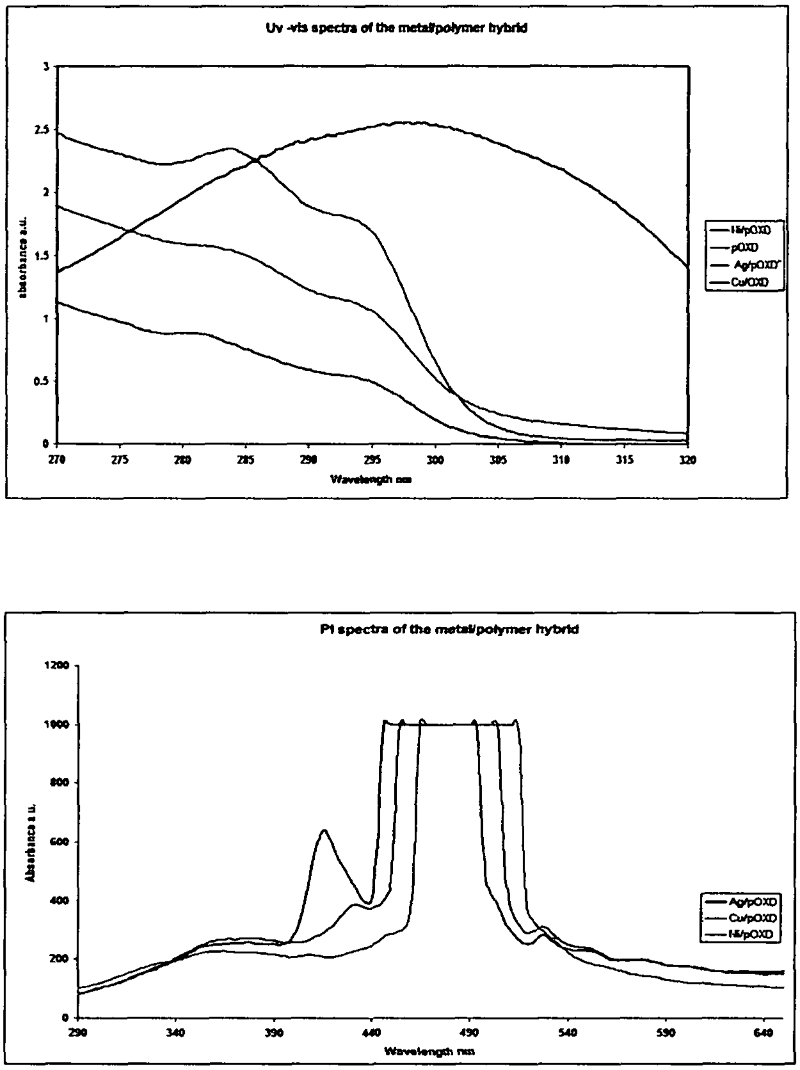


Figure 4.3: UV-vis and the photoluminescence spectra of the polyoxadiazole/metal nanoparticle hybrids

The presence of these surface states reduces the chance of excitonic emission via nonradiative surface recombination. The band edge or the excitonic emission thus overlaps with the absorption of the surface states which results photoluminescence at energies less than band gap. The peaks shift towards higherr energy for the hybrid materials as compared to the virgin polyoxadiazole. The sasturation in the PL spectra for the polymers is due to the same surface plasmon energy increases with the incorporation with the metal inorganic component[58-59].

4.3.4 Device fabrication and characterization

To determine the efficiency of the polymer/metal nanoparticle hybrid materials, devices were fabricated using the structure as ITO/PEDOT: PSS/material/LiF/Al. the electroluminescence spectra for the hybrid materials were recorded in a high resolution spectrometer (Ocean Optics, HR-2000CG UV-NIR). The device properties were determined by using the Keithly source meter to measure the I-V characteristic of the materials.

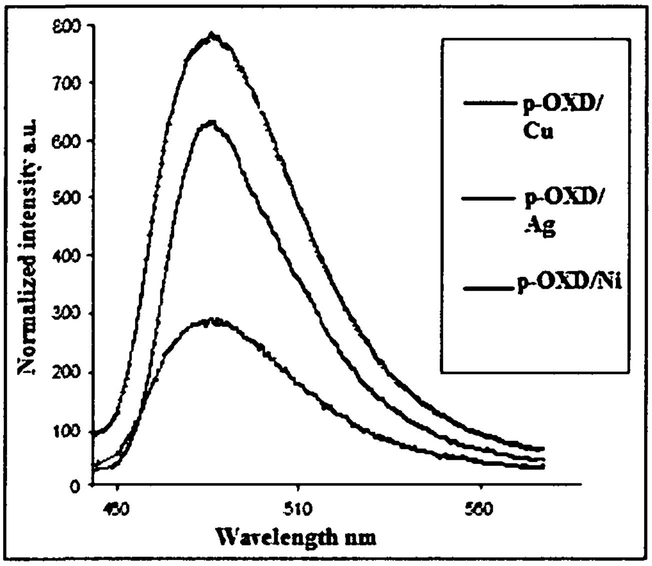


Figure 4.4: EL spectra of polyoxadiazole/nanoparticle hybrid materials

The electroluminescence spectra in **Figure 4.4** show the emission of light in the blue-green region around 500nm at a very low operating voltage of 10V. The emission maxima are comparable with the PL data. The emission intensity of the polyoxadiazole/copper nanoparticle material is more than those with silver and the nickel nanoparticles. This behaviour is found consistent with the PL spectra for these materials.

The materials are semiconducting in nature and tend to be metallic in their conductivity behaviour. The turn on voltage are around 2-4V for all the devices (**Figure 4.5**). This concludes that these hybrid materials can be used in the development of electroluminescent devices emitting blue to green light. The low turn on voltage and a low operating voltage make these materials commercially viable and beneficial materials.

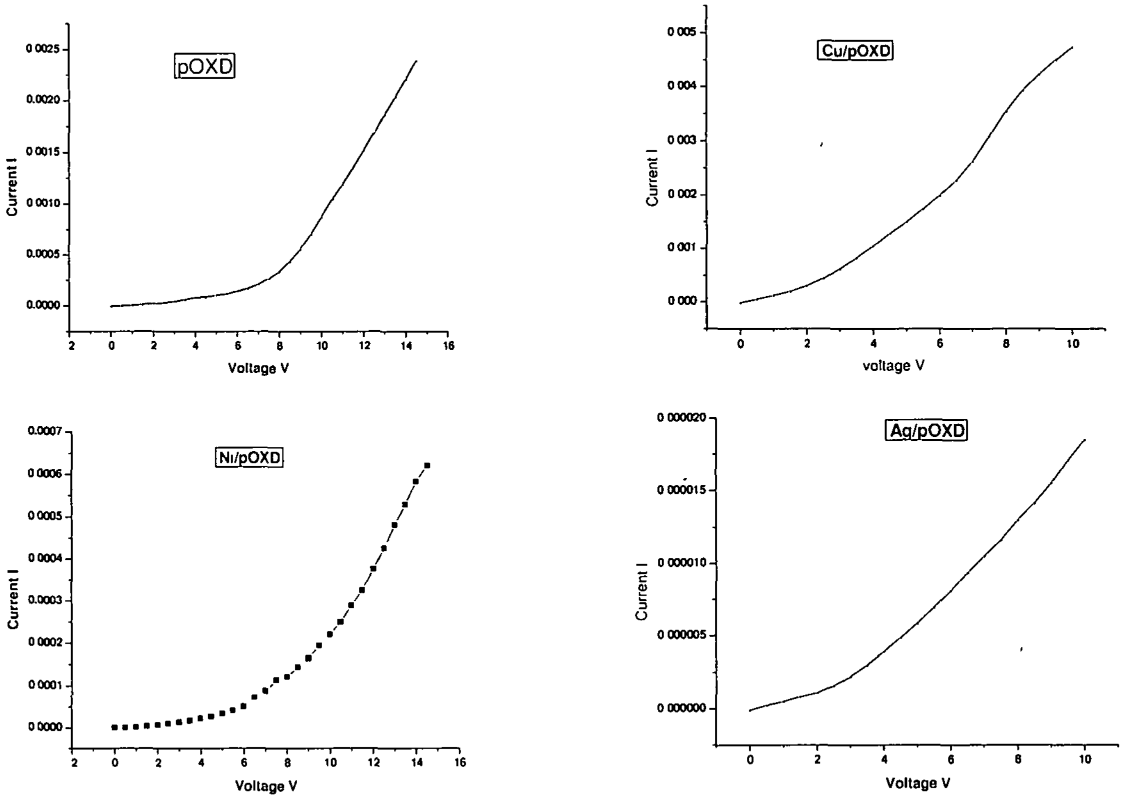


Figure 4.5: The I-V characteristic spectra of the devices made of the hybrid materials

4.4 Conclusion

The size of the metal nanoparticles within the polymer matrix was calculated from XRD data. The sizes reside in the range 35-50 nm. The results are consistent with the TEM data nearly similar. The broadening of the UV absorption spectra is due to the small variable sizes of the particles. The PL emission concludes the interaction of the particles with the polymer; the PL emission shows a prominent red shift from the UV region to the blue-green region. The I-V characteristics curve for the systems show semiconducting behaviour with a low turn on voltage around 2 V. The polyoxadiazole/metal nanoparticle hybrid materials are the promising candidate as a light emitting material with evenly distributed surface. They can be cast into thin films. The particle size of the metals can be controlled by the increasing the stirring time and the speed of stirring and mixing of the two components. The handling of the materials during the synthesis is very important to get the quality materials. The formation of the oxide particles can be avoided by carrying the reaction under inert atmosphere. The absorption spectra of the materials show the decrease in the intensity of the absorption due to the low concentration in the matrix. The broadening of the polyoxadiazole/copper nanoparticle is due to the surface plasmon energy that plays a role in controlling the nature of absorption and the emission spectra. The emission spectra show the luminescence in the visible region with a good intensity. By incorporating the metal nanopaticles, the intensity of the emission peak is greatly increased and the emission maxima shifted to a lower frequency.

Chapter 4: The metal polymer hybrid material for organic light emitting diodes (OLEDs) application

References

1. Sambandan, S.; Whiting, G.; Arias, A.; Street, R.A. Fast polymer semiconductor transistor by nano particle self assembly. *Org. Electron.* **11**, 1935-1941 (2010).
2. Xu, L.; Yang, M. In situ compatibilization between polystyrene-grafted nano-sized TiO_2 and polypropylene with Friedel-Crafts catalyst. *J. Appl. Polym. Sci.* **114**, 2755–2763 (2009).
3. Liu, H.; Webster, T. J. Ceramic/polymer nanocomposites with tunable drug delivery capability at specific disease sites. *J. Biomed. Mater. Res. Part A* **93A**, 1180–1192 (2010).
4. Ahn, S. H.; Guo, L. J. Dynamic nanoinscribing for continuous and seamless metal and polymer nanogratings. *Nano Lett. 9,* 4392–4397(2009)
5. Wang, X. *et al* Nano-photonic electro-optic polymer odulator based on photonic band gap engineering. *Conference Paper*, Integrated Photonics and Nanophotonics Research and Applications (IPNRA) Honolulu, Hawaii July 17, 2009.
6. Karttunen, M.; Ruuskanen, P.; Pitkanen, V.; Albers, W. M. Electrically conductive metal polymer nanocomposites for electronics applications. *J. Electron. Mater.* **37**, 951-954 (2008).
7. Blom, P. W. M.; Schoo, H. F. M.; Matters, M. Electrical characterization of electroluminescent polymer/nanoparticle composite devices. *Appl. Phys. Lett.* **73**, 3914-3916 (1998).
8. Sellinger, A. Self assembly of organic- inorganic nanocomposite thin film for use in hybrid organic light emitting devices (HLED). US Patent 2005/6861091.
9. Holder, E. Tessler, N and Rogach, A. L. Hybrid nanocomposite materials with organic and inorganic components for opto-electronic devices. *J. Mater. Chem.* **18**, 1064–1078(2008).
10. Chang, C.; Tsao, F.; Pan, C.; Chi, G. Electroluminescence from ZnO nanowire/polymer composite p-n junction. *Appl. Phys. Lett.* **88**, 173503-1-173503-3 (2006).
11. Fogg, D. E. *et al* Fabrication of quantum dot-polymer composites: semiconductor nanoclusters in dual-function polymer matrices with electron-transporting and cluster-passivating properties. *Macromolecules* **30**, 8433-8439 (1997).
12. Utracki, L. A.; Sepehr, M.; Boccaleri, E. Synthetic, layered nanoparticles for polymeric nanocomposites (PNCs). *Polym. Adv. Technol.* **18**, 1–37 (2007).

13. Segala, K.; Dutra, R.; Franco, C. V.; Pereira, A.; Trindadeb, T. In situ and ex situ preparations of ZnO/poly-{trans-[$RuCl_2(vpy)_4$]/styrene} nanocomposites. *J. Brazil. Chem. Soc.* **21** (2010) DOI: 10.1590/S0103-50532010001000026.
14. Web address: http://www.nanocompositech.com/review-metal-nanocomposite.htm.
15. Patole, A. S.; Patole, P.; Yoo, J.-B.; Ahn, J.-H.; Kim, T.-H. Effective in situ synthesis and characteristics of polystyrene nanoparticle-covered multiwall carbon nanotube composite. *J. Polym. Sci.: Part B: Polym. Phys.* 47, 1523–1529 (2009).
16. Faupel, F.; Zaporojtchenko, V.,; Strunskus, T.; Elbahri, M. Metal-Polymer Nanocomposites for Functional Applications. *Adv. Engineer. Mater.* **12**, 1177–1190 (2010).
17. Kim, H.; Abdala, A. A.; Macosko, C. W. Graphene/Polymer Nanocomposites. *Macromolecules* **43**, 6515–6530 (2010).
19. Schlabach, S.; Ochs, R.; Hanemann, T.; Szabó, D. V. Nanoparticles in polymer-matrix composites. *Microsyst. Technol.* DOI 10.1007/s00542-010-1176-8.
20. Carotenuto, G.; Nicolais, L. Nanocomposites, Metal-Filled. Encyclopedia of Polym. Sci. Technol. DOI: 10.1002/0471440264 (2003).
21. Reddy, K. R. *et al* Conducting polymer functionalized multi-walled carbon nanotubes with noble metal nanoparticles: Synthesis, morphological characteristics and electrical properties. Synth. Met. **159,** 595–603 (2009).
22. Kishore, P. S.; Viswanathan, B.; Varadarajan, T. K. Synthesis and Characterization of Metal Nanoparticle Embedded Conducting Polymer–Polyoxometalate Composites. Nanoscale Res. Lett. **3**, 14-20 (2008).
23. Benseba, F.; Lecuver, P.; Ding, J.; Firth, A. Hybrid nanocomposite semiconductor material and method of producing inorganic semiconductor therefor. US Patent 2009/0203195.
24. Gomes, D. *et al* Sulfonated polyoxadiazole composites containing carbon nanotubes prepared via in situ polymerization. *Compos. Sci. Technol.* **69**, 220-227(2009).
25. Bruma, M. Aromatic polyoxadiazoles with silicon in the main chain. *Rev.Roumaine De Chim.* **53**, 343–355 (2008).

26. Gomes, D.; Nunes, S. P.; Pinto, J. C.; Borges, C. Synthesis and characterization of flexible polyoxadiazole films through cyclodehydration of polyhydrazides. *Polymer* **44**, 3633-3639 (2003).

27. Lee, K.; Kim, H.; Cho, J. C.; Kim, J. Chemically and photochemically stable conjugated poly(oxadiazole)derivatives: a comparison with polythiophenes and poly(p-phenyleneethynylenes). *Macromolecules* **40**, 6457-6463 (2007).
28. Oikawa, E.; Nozawa, H. Synthesis and properties of polyhydrazides and polyoxadiazoles containing pyridine rings in the polymer backbone. *Polym. Bull.* **13**, 481-488 (1985).
29. Carter, S. A.; Scott, J. C.; Brock, P. J. Enhanced luminance in polymer composite light emitting devices. *Appl. Phys. Lett.* **71**, 1145-1147 (1997)
30. Zhou, Q. *et al* Single crystal tin nano-rod arrays electrodeposited by a soft template. *Chem. Commun.* 4941–4942(2005).
31. Marcinek, M.; Song, X.; Robert Kostecki Microwave plasma chemical vapor deposition of nano-composite C/Pt thin-films. *Electrochemistry Commun.* **9**, 1739–1743(2007).
32. Yaklin, M. A.; Duxbury, P. M.; Mackay, M. E. Control of nanoparticle dispersion in thin polymer films. *Soft Matter.* **4**, 2441–2447(2008).
33. Yang, S. Y.; Li, Q.; Chen, L.; Chen, S. Controllable synthesis of quantum dot–polymer networks with enhanced luminescence via the catalytic chain transfer polymerization (CCTP) technique. *J. Mater. Chem.* **18**, 5599–5603(2008).
34. Gangopadhyay, R.; De, A. Conducting polymer nanocomposites: a brief overview. *Chem. Mater.* **12**, 608-622 (2000).
35. Wood, V. *et al* Inkjet-printed quantum dot–polymer composites for full-color AC-driven displays. *Adv. Mater.* **21**, 2151–2155(2009)
36. Choulis, S. A.; Mathai, M. K.; Choong, V.-E. Influence of metallic nanoparticles on the performance of organic electrophosphorescence devices. *Appl. Phys. Lett.* **88**, 213503(1-3) (2006).
37. Sellinger, A.; Kaisher, C.K. Self assembly of hybrid organic-inorganic nanocomposite thin films for use in hybrid organic light emitting devices. US patent 2005/6861091.
38. Mohanraj, V.J.; Chen, Y. Nanoparticles – a review. *Tropical J. Pharmaceut. Res.* **5**, 561-573(2006)
39. Yua, B.-Z.; Maa, J.-F.; Lib, H.-L.; Zhang, Y.-F.; Lia, W.-X. Optical and electrical properties of multi-walled carbon nanotubes functionalized with oxadiazole chromophores. *Nature Precedings: hdl:10101/npre.2009.2749.1* 1-19 (2009).

40. Anlovar, A. et al Nanocomposites with nano-to-sub-micrometer size zinc oxide as an effective UV absorber. *Kategoriziraniradovi* **292**, 84-87(2008)
41. Khiew, P. S.; Huang, N. M.; Radiman, S.; Ahmad, S. Synthesis and characterization of conducting polyaniline-coated cadmium sulphide nanocomposites in reverse microemulsion. *Mater. Lett.* **58**, 516-521 (2004).
42. Magerramov, A. M.; Ramazanov, M. A.; Mustafaeva, A. K. Structure and properties of nanocomposites based on zinc sulfide and poly(vinylidene fluoride). *Russ. J. Appl. Chem.* **83**, 1324-1327 (2010).
43. Lee, J.; Kim, D.-K.; Kang, W. Preparation of Cu nanoparticles from Cu powder dispersed in 2-propanol by laser ablation. *Bull. Korean Chem. Soc.* **27**, 1869-1872 (2006).
44. Whitcomb, D. R.; Stwertka, B. J.; Chen, S.; Cowdery-Corvan, P. J. SERS characterization of metallic silver nanoparticle self-assembly within thin films. *J. Raman Spectrosc.* **39,** 421–426(2008).
45. Gopalan, E. V. *et al* Template-assisted synthesis and characterization of passivated nickel nanoparticles. *Nanoscale Res. Lett.* **5**, 889–897(2010).
46. Akamatsu, K. *et al* Nanocomposite polymeric microspheres containing Ni nanoparticles with controlled microstructures. *Chem. Mater.* **20**, 3042–3047(2008).
47. Haubrich, S. *et al* Interface layer for the fabrication of electronic devices. US Patent 2008/7315068.
48. Web address: http://www.cci.ethz.ch/vorlesung/de/pdf_ac1/pp/beugung-1.pdf.
49. Web address: http://ocw.mit.edu/courses/biology/7-343-protein-folding-misfolding-and-human-disease-fall-2004/readings/tem.pdf
50. Haque, K. M. A.; Hussain, M. S.; Alam, S. S.; Islam, S. M. S. Synthesis of nano-nickel by a wet chemical reduction method in the presence of surfactant (SDS) and a polymer (PVP). *African J. Pure Appl. Chem.* **4**, 58-63 (2010)
51. Das, R.; Nath, S. S.; Chakdar, D.; Gope, G.; Bhattacharjee, R.; Preparation of silver nanoparticles and their characterization. *J. Nanotech.* (online) (2009)DOI:10.2240/azojono0129.
52. Rifai, S.; Breen, C. A.; Solis,D. J.; Swager, T. M. Facile in situ silver nanoparticle formation in insulating porous polymer matrices. *Chem. Mater.* **18**, 21-25 (2006).

53. Li, C-M.; Lei, H.; Tang, Y-J.; Luo, J-S.; Liu,W.; Chen, Z-M. Production of copper nanoparticles by the flow-levitation method. *Nanotechnology* **15,** 1866–1869 (2004).

54. Choong, V.-E. *et al* Effects of Al, Ag, and Ca on luminescence of organic materials. *J. Vac. Sci. Technol. A* **15**, 1745-1749 (1997).

55. Gouanve, F.; Schuster, T.; Allard, E.; Méallet-Renault, R.; Larpent, C. Fluorescence quenching upon binding of copper ions in dye-doped and ligand-capped polymer nanoparticles: a simple way to probe the dye accessibility in nano-sized templates. *Adv. Funct. Mater.* **17**, 2746–2756(2007).

56. Ma, Y. *et al* High luminescence Gold(I) and Copper(I) complexes with a triplet excited state for use in light-emitting diodes. *Adv. Mater.* **11**, 852-857(1999)

57. Bekiari, V. *et al* Studies on hybrid organic/inorganic nanocomposite gels using photoluminescence techniques. *Monatshefte fuer Chemie* **132**, 97-102 (2001)

58. Beecroft, L. L.; Ober, C. K. Nanocomposite Materials for Optical Applications. *Chem. Mater. 9,* 1302-1317(1997)

59. Khang, Y.; Lee, E.; Lee, K.;Lee, J.; Im, S. Nanoparticle electroluminescence and method of manufacturing the same. US Patent 2006/0188707.

CHAPTER 5

Conclusion and future scope of the present investigation

Chapter 5: Conclusion and future scope of the present investigation

5.1 Conclusion

Electroactive polymers in display thechnology mainly in the production of OLEDs took over the market from the inorganic LEDs in terms of their unique physical properties and low cost. The flexible and procesible conjugated polymers are used as electroactive material for the display application rather than inorganic materials. Polymers are highly versatile materials whose properties can be changed by subtle change in their chemical structures. OLEDs which are promised to replace traditional LCDs, are capable of emitting light in all directions, even at low power creating brilliant images with wide viewing angles. The synthesis of different colour emitting luminescent polymers becomes a challenge now a day for the full colour RGB display. However, defects and other variations in chemical compositions are common on polymer chains. Oligomers can be more accurately synthesized and characterized. Therefore a number of conjugated electroactive polymers were developed during the last few decades like poly(N-vinylcarbazole)s, poly(fluorene)s (PFs), poly(p-phenylene vinylenes) (PPVs), poly(thiophenes) (PTs) and polyoxadiazoles(P-OXDs). Amongst various heterocyclic polymers, aromatic poly(1,3,4-oxadiazole)s are of special interest due to their high thermal stability in oxidative atmosphere and specific properties determined by the structure of 1,3,4-oxadiazole ring. The superior thermal stability of 1,3,4-oxadiazole ring is due to structural symmetry, chain rigidity and the thermoresistent property. More recently, the specific properties determined by the electronic structure of oxadiazole ring, particularly its electron-withdrawing character, promoted an intensive research on these polymers with the aim to use them as advanced materials. But, like other rigid aromatic polymers, fully aromatic polyoxadiazoles are not soluble in any organic solvent. They do not melt and do not show a glass transition temperature, or they degrade before melting, which makes their processing quite difficult. Among various ways to improving solubility and lowering glass transition temperature, while maintaining high thermal stability, the introduction of soluble polar end groups or flexible groups into the polyoxadiazole chain proved to be very efficient.

Chapter 5: Conclusion and future scope of the present investigation

This thesis is focused on the synthesis, characterization and electrochemical, photoluminescence and electroluminescent properties of poly(1,3,4-oxadiazole) containing polar end groups, 1,3,4-oxadiazole containing polyurethanes in the main chain and poly(1,3,4-oxadiazole)/metal nanoparticle hybrid material for the polymer-based light emitting diode devices.

The findings of the thesis are summarized and discussed below

1. Synthesis and characterization of 1,3,4 Oxadiazole containing polymers

Two series of poly(1,3,4-oxadiazole) containing polar end groups viz Poly 1,4-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing $-NO_2$, -Cl, $-CH_3$, -OH and Poly 1,3-bis(phenyl-1,3,4-oxadiazolyl)phenylene containing $-NO_2$, -Cl,$-CH_3$, -OH and a series of polyurethanes containing 1,3,4-oxadiazole in the main chain are synthesized by the simple polycondensation and chemical cyclization method. The multistep synthesis of the polymers involves the low temperature condensation of the aromatic dicarboxylic acid chloride with dihydrazide and the cyclization of the resulting polyhydrazide. The yield of the product was 48-53%. Polyhydrazides then undergo a chemical cyclization process resulting in the polyoxadiazoles with 54% yield. 1,3,4-oxadiazole containing polymer in the main chain was synthesized by the condensation of the diol monomers with the diisocyanate. All the monomers and the polymers are characterized by FTIR and 1H-NMR spectroscopy. The monomer yield was high 49-89%, but the yields for polyurethanes are low 46-48%.

The polymers are soluble in DMAc, DMF, NMP and partly soluble in THF. The inherent viscosity of the polymers is in the range of 0.41-0.46 dl/g and the polymers are oligomeric in nature. The number average molecular weights of polymers are measured from the THF soluble part of the polymers and it is found in the range of 2425 to 4617 g / mole. The polydispersity index of the polymers lying in the range 1.08-1.12 implies the homogeneity in the polymer chains. 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 245-332 nm. All the polymers show shifting of absorption maximum with respect to the side groups attached with the polymer chain and the spacer group present in the polymer chain. . Optical band gap of the polymers is found to be 3.34-3.9eV. Polymers possess good thermal stability with the onset decomposition temperature upto 379°C under nitrogen atmosphere. Thermal stability increases with the increase in molecular weight of polymers. The polymers exhibit a glass transition temperature (T_g) in the range of 110-132°C. It is observed that T_g of the polymers varies with the variation in the side groups and the spacer groups.

2. Electrochemical, photoluminescence and electroluminescence properties of 1,3,4 Oxadiazole containing polymers

The fluorescence emission maximum of the polymers is found to be in the range of 350-440nm. The emission maxima were seen highest for the polymers OXDAR1, OXDAR4, OXDBR1, OXDBR4, PU3 and PU4. The light emission is in the violet-blue region region. Stokes shifts of the polymers are in the range of 40-185nm. Stokes shift is highest for OXDAR4, OXDBR1 and OXDBR4. The PL intensity of the oxadiazole containing polymer are high both in solid as well as solution state. The solution PL intensity is somehow lower as the flourophores are far apart in solution in the polyoxadiazoles whereas the solution PL of the polyurethanes increases in the solution state. The relative quantum yields of the polymers are found in the range of 0.53-0.88 with respect to anthracene. The PL intensity of the more electron deficient systems and the polyurethanes are highest among the polymers. The enhanced fluorescence efficiency of polymers is achieved at the cost of their solubility.

The electrochemical study of the polymers by cyclic voltammetry indicates that the oxidation potentials of polymers are in the range 2.85-3.0 V and the results vary with the substituent present. The more electron withdrawing group in the main chain causes the deficiency of electron in the main chain resulting in the slight increase in the oxidation potential. Similar observation was made in case of reduction potential of polymers. The reduction potential of the polymers is in the range of 0.7-1.05 V. It was observed that more electron deficient systems show decrease in the reduction potential. All the polymers seem to be stable under cyclic oxidation and reduction potential (upto 10 cycles). HOMO and LUMO energy levels and the band gap of the polymers were calculated. The E_g for the polymers are found to be 1.8-2.6 eV. This supports for the wide band gap polymer for emission of light from the colourless to blue region. OXD AR1, OXD AR4 OXD BR1, OXD BR2, PU1, PU2 PU3 and PU4 show high E_g value. The electrochemical band gap is lower than the optical band gap as the methods are not same.

The EL emission of the polymers show violet to blue colour in the visible range same as that of the PL emission spectra for the polymers OXDAR1, OXDBR1, PU1, PU2, PU3 and PU4. The turn on voltage of devices is in the range of 6-8 V for charge injection. The operating voltage for OXDAR1and OXDBR1 is 15V and for PU1, PU2, PU3 and PU4 is 12 V.

3. The metal/polymer hybrid material for OLED application

The poly(1,3,4-oxadiazole) polymers incorporating with the metal nanaoparticles copper, silver and nickel show the improvement in the optoelectronic properties. The polymer/metal hybrid materials prepared by the ex-situ addition of the inorganic metal nanoparticles to the matrix polymer matrix results in a homogeneous mixture and defect free thin films over glass substrate. Some polyoxadiazoles are incapable to emit light in the visible region. But the incorporation of metal nanoparticles somewhat change the luminescence properties of the polymers. By incorporating the metal nanopaticles, the intensity of the emission peak is greatly increased and the emission maxima shifted to a lower frequency.

On the other hand metal nanoparticles are unique in their properties due to their small size and high surface to volume ratio. The XRD and the TEM analysis of the hybrid materials for the average size calculation of the metal nanoparticles are consistent with each other and are found to be around 40nm. The UV visible spectrum does not show any significant change in the position of the λ_{max} with the incorporation with the nickel and the silver nanoparticles to the polyoxadiazole. Because nickel and silver show a very weak UV absorption. But the polymer/copper hybrid shows a wide absorption in the UV-vis spectra characteristic to the copper nanoparticles. The PL spectra for the polymer/nanoparticle hybrids show a significant change in the position and the intensity of λ_{max} as compared to that of the virgin polymer. The surface plasmon energy of the inorganic particles interacts with the emission wavelength of the polymer are responsible for the intense emission in the blue-green region. The turn on voltage for the hybrid materials lie in the range of 2V which is a very important factor for a material used for the OLED application.

5.2 Future scope of the present investigation

- Study of the time of flight measurement for the polymers to ascertain the charge mobility behavior of the materials
- study of the time correlation fluorescence of the polyoxadiazoles
- Fabrication of the devices with different hole transporting and electron carrier systems
- Theoretical study of band gap and EL emission of the polymers
- Application and study of the polymers for the electrochromic device application
- Application of the polymers for the white light emitting device

Chapter 5: Conclusion and future scope of the present investigation

Papers in Journals

1. Huda, M. K.; Dolui, S. K. Synthesis of oligomeric poly(1,3,4- oxadiazole)s containing polar end groups: their photoluminescence and thermal behaviour. *J. Polym. Mater.* **26** (2009) 251-266
2. Huda, M. K.; Dolui, S. K. Luminescence property of poly 1,3-bis(phenyl-1,3,4-oxadiazole)s containing polar groups in the main chain. *J. Lumin.* **130** (2010), 2242-2246
3. Huda, M. K.; Dolui, S. K. Blue light emitting 1,3,4-oxadiazole containing polyurethane for electroluminescent devices. *J. Appl. Polym. Sci.(comm.)*
4. Huda, M. K.; Dolui, S. K. Thermal characteristics and luminescent property of optically active 1,3,4 oxadiazole containing polyurethane. *Iran. Polym. J. (comm.)*
5. Huda, M. K.; Dolui, S. K. Electroluminescence and cyclic voltammetric study of blue light emitting 1,3,4 polyoxadiazole containing polar end groups. *Polym. Bull.(comm.)*
6. Pokhrel, B.; Konwer, S.; Dutta, A.; Huda, M. K.; Ghosh, B.; Dolui, S. K. Study of photovoltaic performance of host-guest system comprising optically active polyurethane and rhodamine B dye. *J. Appl. Polym. Sci.(accepted)*
7. Huda, M. K.; Pokhrel, B.; Konwer, S.; Dolui, S. K. Electrochemical determination of the ionization potential and electron affinity of polyurethanes containing oxadiazole moiety *(comm.)*
8. Huda, M. K.; Dutta, A.; Dolui, S. K. Photoluminescent behaviour of metal nanoparticle/polyoxadiazole hybrid material for oled application *(comm.)*

Presentation in conference

1. M K Huda and S K Dolui, "Synthesis and characterization of soluble poly 1,3,4 Polyoxadiazole" **Condensed Matter Days(CMDAYS 2008)** Vishvabharati University, Shantiniketan, West Bengal, August 29-31,2008

2. M K Huda and S K Dolui, “The luminescence study of Lead sulfide nanocrystal-Polyhydrazide/1,3,4 polyoxadiazole composite” **MACRO 2009: Recent advances in polymer materials** IIT, Madras, Chennai, March 9-11, 2009
3. M K Huda, S K Dolui, “Luminescence properties of polyurethanes containing 1,3,4-oxadaizole chromophore for electroluminescent diode application” **International conference on recent frontiers in applied spectroscopy (ICORFAS 2010)** Annamalai University, Chidambaram, Tamil Nadu September 22-24, 2010.

   (Best paper awarded in the conference)

Patent:

M K Huda and S K Dolui, “Blue light emitting 1,3,4-oxadiazole containing polymer”(patent to be filed)