Design of Conjugated Polymers for Organic Light Emitting Diode

A major project submitted in the partial fulfillment of the requirement for the award of the degree of

Master of Engineering
in
Polymer Technology

In the Faculty of Technology,
University of Delhi, Delhi

Under the Joint Supervision of

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CERTIFICATE

This is to certified that Mr. **Raman Kumar Saini** has satisfactorily completed the project work entitled **"Design of Conjugated Polymers for Organic Light Emitting Diode"** in partial fulfillment of the requirement for the award of the degree of Master of Engineering in Polymer Technology of Delhi College of Engineering, Delhi University, Delhi during the academic session 2005-2006.This work has not been submitted in part or full in any other university or institution for the award of any other degree or diploma.
under our supervision at **National Physical Laboratory** in the Polymeric & Soft Materials Section.

The project work has been carried out from 27-Sept-2005 to 30-June-2006.

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Raman Kumar Saini

Dedicated to
My Grand Parents

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ABSTRACT

One of the most promising ideas of the Light-emitting diodes (LEDs) technology is the use of the π-conjugated polymers. Light-emitting diodes (LEDs) promises superior performance in brightness and color resolution, wider viewing angle, lower power consumption, a thin aspect ratio and better physical characteristics. The advantages make OLED display attraction for the next generation mobile flat penal display (FPD). Polymer Light Emitting Diodes have a good chance to become the main display system in the near future since diodes have many advantage concerning preparation and operation over other display system. The emissive color of a π-conjugated polymer is fine-tunable by controlling the effective π-conjugation. Electroluminescent efficiency can be improved by balancing the hole/electron mobility through chemical modifications like incorporating electron-donating or electron-withdrawing groups with in the polymer backbone or the side-chain. Regarding with device fabrication, a polymer system provides facile coating process such as spin coating and flexibility of the devices. In order to develop an emissive polymer showing desired LED performance, it is important to design the segments of a polymer. The Report on

"Design of Conjugated polymers for Organic Light emitting Diode"

contains the synthesis of four materials, PPP, copolymer of benzene and perylene, copolymer of toluene and perylene and copolymer of benzene and pentacene and the fabrication of device using these polymers as light emitting layer. The main purpose of device fabrication was to analyse the application of these materials as electroluminescent material. The Electroluminescence spectra (EL) and Current Voltage (I-V) characteristics of the devices were recorded and analysed to understand the characteristics of materials and applications as Electroluminescent layer in organic light emitting diodes. The materials were characterised by UV-VIS absorption spectra, Photoluminescence spectra (PL), FTIR, Thermogravimetric Analysis (TGA). The results of device characteristics, particularly ITO/Polymer/PEDOT/Al double-layered diode, are found highly promising.

CHAPTER -I

OLEDs: An Introduction

OLEDs: An Introduction

1.1 ORGANIC LIGHT-EMITTING DIODE (OLED) TECHNOLOGY

OLED short for organic light-emitting diode is a display device that sandwiches carbon-based film between two charged electrodes, one a metallic cathode and one a transparent anode. When electrical current is applied, a bright light is emitted. This process is called Electroluminescence. Unlike LCDs, which require backlighting, OLED displays are emissive devices - they emit light rather than modulate transmitted or reflected light. OLED technology was invented by Eastman Kodak in the early 1980s. It is beginning to replace LCD technology in handheld devices such as PDAs and cellular phones because the technology is brighter, thinner, faster and lighter than LCDs, uses less power, offer higher contrast and are cheaper to manufacture. OLEDs can provide desirable advantages over today’s liquid crystal displays (LCDs), as well as benefits to product designers and end users. OLEDs feature:

- Vibrant colors
- High contrast
- Excellent grayscale
- Full-motion video
- Wide viewing angles from all directions
- A wide range of pixel sizes
- Low power consumption
- Low operating voltages
- Wide operating temperature range
- Long operating lifetime
- A thin and lightweight
- Cost-effective manufacturability

Envision thin, lightweight displays that are bright and easy to read, that consume less power, that are flexible and, when turned off, even transparent. Or, think about a bright-white light panel that can replace today’s bulky and fragile incandescent bulbs and fluorescent tubes. These are a few of the possibilities that OLED technologies may bring to light.

1.2 Historical Evolution of OLED's

Human is using the materials available in nature since prehistoric time for betterment of human life and evolution of intelligent society. As human intelligence evolved his needs increased day by day. A pursuit for better and still better materials drove his passion and we see the sea change in the field of scientific invention. Fire was one of the simplest ways for prehistoric human to light his home. Since then a great change has been seen the way we are illuminating our home. Safe illumination, which always was a great challenge for human being, seems to came its end in near future. Electroluminescence is one of the scientific discoveries in the last century that changed the life of mankind immensely. Now the Electroluminescence from polymeric materials will certainly change not only the way we illuminate our home but also our life style.

In contrast to photoluminescence (PL), the light emission from an active material as a consequence of optical absorption and relaxation by radiative decay of an excited state, Electroluminescence (EL) is a non-thermal generation of light resulting from the application of an electric field to a substrate[1]. In the latter case, excitation is accomplished by recombination of charge carriers of opposite sign (electron and hole) injected into an inorganic or organic semiconductor in the presence of an external electric field.[2]

This phenomenon was first discovered for inorganic materials in 1936, when Destriau et al. observed high field Electroluminescence from a ZnS phosphor powder dispersed in an isolator and sandwiched between two electrodes.[2,4] General Electric introduced first LED based on inorganic emitter GaAsP in market in early 1960s. Later it was found that the materials that were generally used for inorganic LEDs are compounds of elements from group 13, 14 and 15 of the periodic table such as GaAs, GaP, AlGaAs, InGaP, GaAsP, GaAsInP and more recently AlInGaP. Semiconductors with large band gaps are difficult to obtain blue LEDs. Nevertheless, blue inorganic LEDs based on SiC, ZnSe, or GaN were developed, but exhibited distinctly lower efficiencies in comparison to others[2-5]. Since last few decades a lot of development is seen in the field of inorganic LEDs. Light emitting diodes (LEDs) of various colours with good quantum efficiencies have been fabricated and its economic benefit was exploited worldwide.

Destriau's discovery of electroluminescence (EL) in inorganic compounds (ZnS, phosphors) in 1936 and the discovery in 1947 that a transparent anode could be constructed by depositing a layer of Indium Tin Oxide (ITO) onto a glass surface opened the possibility of obtaining light emitting planar surfaces[6].

The fact that many aromatic organic molecules are photoluminescent suggested their use as electroluminescent materials. In1963, Pope et al. reported electroluminescence (EL) from an organic semiconductor. They observed emission from single crystals of anthracene, a few tens of micrometers in thickness, using silver paste electrodes and required large voltages to get emission typically 400 V. [7] Helfrich and Schneider made similar studies in 1965 using liquid electrodes. Considerable effort has been taken to understand the basic mechanism as well as to provide stable electroluminescent devices. Development of organic thin film electroluminescence (EL) advanced with the study of thin film devices. In1982, Vincett et al. reported blue electroluminescence (EL) from anthracene sublimed onto oxidised aluminium as one electrode, and were able to reduce voltage considerably, for at 12 V [6-7].

In 1983, the discovery of electroluminescence (EL) in poly (vinylcarbazole) led to a search for other electroluminescent materials covering other ranges of the visual spectrum. However, the developments of electroluminescent organic devices were not successful at that point due to the relatively poor lifetime and relatively low efficiency. Organic electroluminescent devices proved not to be competitive with incandescent light sources, and essentially all research was focused on traditional inorganic electroluminescent materials, since light-emitting devices (LEDs) based on these materials have been commercially available since 1960s [6-8].

In 1987, the group of Tang and Van Slyke et al. Eastman-Kodak demonstrated efficient electroluminescence (EL) in two layer sublimed molecular film devices comprised of a hole transporting layer of an aromatic diamine and emissive layer of 8-hydroxyquinoline aluminium (Alq3) [8-9]. This result provided a basic design for light emitting diode architecture, which was applicable to systems employing low molecular weight electroluminescent materials. The technique they used to emit light was to vacuum deposit small molecules to form a layered structure. The layered device structure was produced on an ITO (anode acts as hole injection layer) coated glass substrate over that electroluminescent material and a magnesium-silver alloy (cathode acts as electron injection layer) were vacuum evaporated one by one. The thin film layered structure permits a high electrical field at low voltage. Thus, light from thin film organic materials is usually produced at low voltage. High quality thin molecular layers were an important condition for the development of OLEDs [6-7].

In 1990, Burroughes et al. at the Cavendish Laboratories at Cambridge University presented the first LED using polymers as active material [10]. The active material used was a conjugated polymer [9, 11]. In comparison to the traditional solid state LED, the new organic approaches were believed to be much more efficient. In nature organic materials are in some cases able to perform in a chemical way a 100% relationship of energy consumption versus emission of light, e.g. the fireflies. Unfortunately such high efficiency is unrealistic in fabricated electroluminescent devices.

Conjugated polymers, and small molecules (oligomers and metal complexes) are considered as the two classes for OLEDs [6]. Despite of the fact that the two approaches only emitted a small amount of light that lasted only a few minutes, it caused a major interest among other researchers and companies. Much because of the predicted features of the organic displays would overcome the advantages for other display techniques, e.g. low voltage, low weight and wide viewing angle.

The above classifications of light emitting organic layers in the organic light emitting devices both possess luminescent and conductive properties. To achieve accurate functions of the material, a modification of the specific characteristics of the material were often done. Oligomers and small molecules have molecular structures of relatively short characteristics and consequently low molecular weights. The most commonly used material with the most explored properties among the small molecules were hydroxyquinoline aluminium (Alq3) and oligomer p-hexaphenyl.

Conjugated polymers are composed of a long repeating chain of similar smaller molecules, called monomers. They possess consequently, compared to small molecules, a molecular weight twenty to fifty times higher. A frequently used conjugated polymer is the poly (p-phenylene vinylene) (PPV).

1.3 POTENTIALS OF OLEDs

- Suitable for thin, lightweight, printable displays.
- Broad color range
- Good contrast.
- High resolution(<5μm pixel size)
- Fast switching (1-10 μs)
- Wide viewing angle
- Low cost of material

1.4 CLASSIFICATION OF OLEDs

OLEDs are broadly classified into two categories:

1.4.1 Small-molecular OLEDs

- Made by vacuum evaporating small molecules to the substrate similar to that used in semiconductor manufacturing.
- Well proven on fabrication of up to about 15 inches in diameter (shadow mask).
- Crystallization due to low glass transition temperature shortens lifetime and reliability.

1.4.2 Polymer OLEDs

- Made by depositing the polymer materials on substrates through vacuum deposition technique, spin coating process, an inkjet printing process or other solution processing methods under ambient conditions.
- Fabrication of large screen sizes

1.5 SMALL MOLECULE OLEDs vs. POLYMER OLEDs

The types of molecules used by Kodak scientists in 1987 in the first OLEDs were small organic molecules. Although small molecules emitted bright light, scientists had to deposit them onto the substrates in a vacuum (an expensive manufacturing process called vacuum deposition). Since 1990, researchers have been using large polymer molecules to emit light. Polymers can be made less expensively and in large sheets, so they are more suitable for large-screen displays.

1.6 INTRODUCTION TO POLYMER LIGHT EMITTING DIODES (PLEDs)

Plastic materials have long been known to provide useful insulating characteristics in electrical applications. Over the last 30 years there has been increasing interest in exploiting more exciting characteristics of some conjugated polymer materials, which emit light when stimulated electrically. These are polymers, which possess a delocalized π-electron system along the polymer backbone. The delocalized π-electron system confers semi-conducting properties to the polymer and gives it the ability to support positive and negative charge carriers with high mobility along the polymer chain.

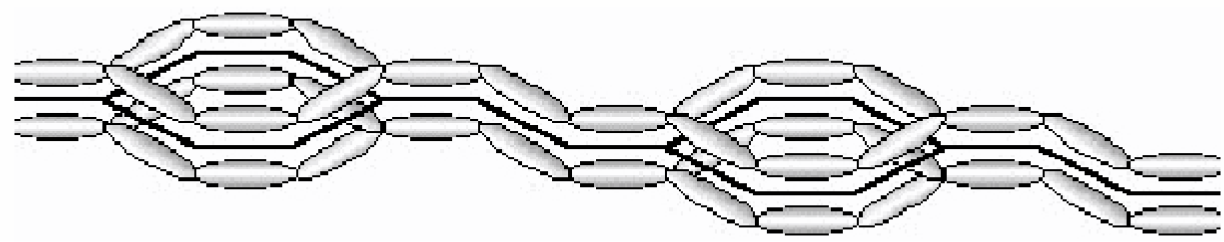


Figure 1.1 The above figure shows that Overlap of p_z orbitals leads to the formation of a delocalized π -electron cloud above and below the plane of the sigma bonds, which form the structural framework

The semiconductor properties of these materials arise from the overlap of p_z-orbitals that originate from the double or triple bonds. If the overlap is over several sites, the formation of well delocalized π valence and π* conduction bands occurs, with an energy gap between and this recipe for this semi-conductive behaviour. The mechanism for charge transport in these materials is not the same as in more traditional inorganic semiconductors: The amorphous chain morphology results in an inhomogeneous broadening of the energies of the chain segments and leads to hopping type transport. A secondary effect is the distortion of the chain around a charge carrier, with the result that the charged excitations are usually best described as ‘polarons’ in these materials.

Nevertheless, device engineering of the materials can take advantage of many of the lessons previously learnt for classical semiconductors. Thus device designs and material structures can be translated into the new technology [12]. Of course there are enormous advantages over the classical semiconductors both in terms of the ease of fabrication (compare spin-coating to epitaxial growth), as well as the design of new materials with different band gaps and electron affinities.

In the polymer case the structure is effectively amorphous, but the defects tend to have energy states outside the band gap (i.e. they are confining), and since the sigma bonds provide a strong structural framework, there are no dangling bonds (therefore the interfaces are not as sensitive to the environment and UHV processing is not required). The principal disadvantages are lifetime and mobility. Mobility is low due to the largely amorphous nature of conjugated polymer films. Carrier transport across thin films is limited by the mobility values. The hole mobility in PPV is of order 10^{-4} cm^2 V^{-1} s^{-1} allowing transport across a 1000 Å layer with typical fields of $5X10^5$ V/cm in 0.5 μs [13]. (Nevertheless, these switching times are quite adequate for use in many diode devices, such as light emitters, detectors and solar cells.)

Lifetime is also a big concern when considering commercial applications of the technology. Much work has taken place over the last 50 years to improve the resistance of everyday polymers to photo oxidation principally through the use of additives to prevent discoloration. It should come as no surprise that similar problems exist with conjugated polymers, particularly since in most electronic applications excited π* states are necessary intermediates - oxidation of these states can lead to degradation of the performance of the materials. Storage lifetimes of at least five years are typically required by most consumer and business products, and operating lifetimes of >20,000 hours are relevant for most applications[14-15]. Conducting polymer materials based on doped polyaniline (a conjugated polymer material that has been known for over 100 years) and polypyrrole already demonstrating the stability required for commercial applications. In the area of light emitting polymers, significant activity is taking place to improve material lifetime both through use of materials which have that are resistant to oxidation and through improved encapsulation.

1.7 BASIC MATERIALS AND GENERAL STRUCTURE OF OLEDs

Thin polymer layers can be produced by spin coating from solution. In addition big areas can be coated by techniques called “dip coating” or “doctor blading”. Commonly used polymers are poly (p-phenylene vinylene) (PPV) **[15]**, substituted PPV’s, PPP-derivatives**[16]** and appropriate copolymers, which exhibit a sufficient brightness and efficiency. Basic molecular structures of two basic electroluminescent polymers are shown in Figure 1.2:

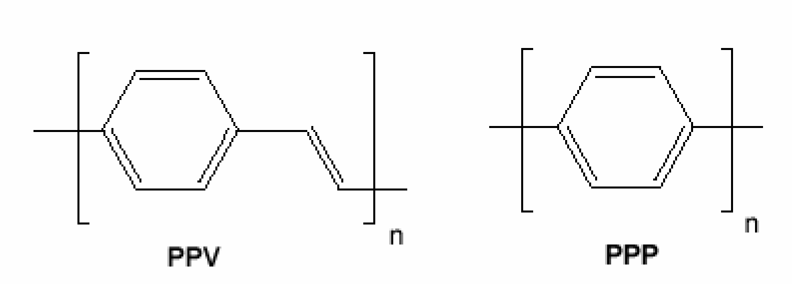


Figure1.2: Chemical structure of electroluminescent polymers: poly (p-phenylene vinylene) (PPV), poly (p-phenylene) (PPP).

Although monochromic operation, which is enabled by these polymers, is sufficient for some applications, the extension to multi-color devices does greatly enhance their technological impact. Multi-color OLED’s have been successfully fabricated by vacuum deposition of small Electroluminescent molecules, but solution processing of larger molecules (Electroluminescent polymers) results in a cheaper and simpler manufacturing process. However, it has proven difficult to combine the solution processing approach with the high-resolution patterning techniques required to produce a display. Recent attempts have focused on the modification of standard printing techniques, but those still have technical drawbacks. A new class of electroluminescent polymers with oxetane side groups that can be cross-linked photochemically can be patterned in a way similar to standard photoresist materials. These are soluble polymers utilized to produce insoluble polymer networks in desired areas. The resolution of the process is sufficient to fabricate matrix displays.

Electroluminescence from conjugated polymers was first reported in 1990, using Poly (p-phenylene vinylene) (PPV) as the single semiconductor layer between metallic or polymeric electrodes. Figure below illustrates a device structure with a PEDOT layer serving as the anodic contact. In this structure, the ITO layer functions as a transparent electrode, and allows the light generated within the diode to leave the device. The top electrode is conveniently formed by thermal evaporation of a metal. LED operation is achieved when the diode is biased sufficiently to achieve injection of positive and negative charge.

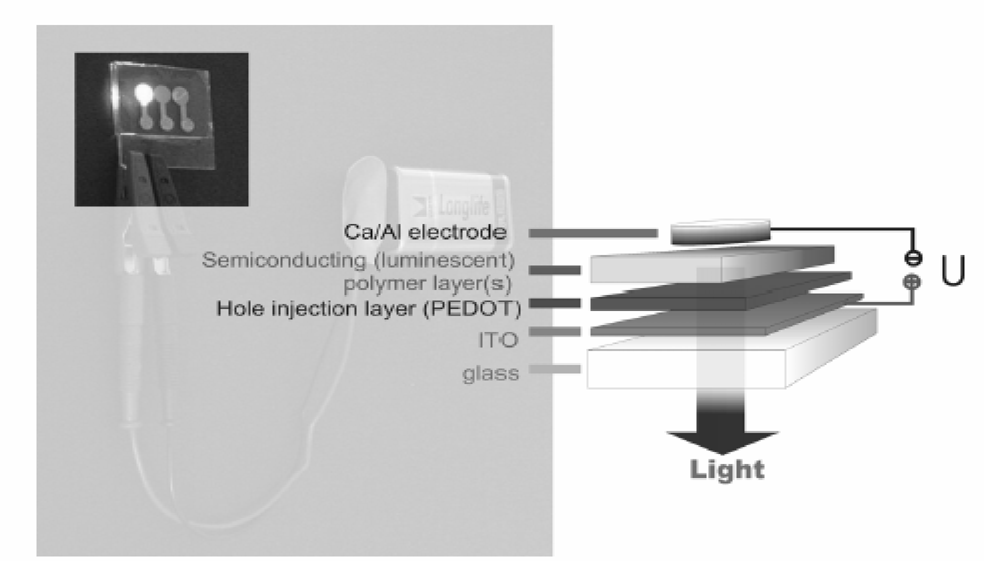


Figure1.3: Sketch of an organic light-emitting device (OLED). The transparent anodic contact (ITO/PEDOT) is followed by the electroluminescent polymer and at last the cathodic metal contact.

1.8 ELECTRODES AND INJECTION BARRIERS

The electrodes play an important role for the device performance. They are in direct contact with the adjoining semi-conducting polymer layer. Accordingly, electrons and holes have to overcome certain energy barriers before they are injected into the electroluminescent polymer layer. Lowered energy barriers are of high technological interest, since high barriers cause a limitation in current and a corresponding high operation voltage, which is in contradiction to battery powered portable devices. For a vanishing injection barrier, the highest possible current throughput, called space charge limited current (SCLC) [17] is achieved. SCL currents are typically different for different charge carriers, e.g. due to different charge carrier mobilities and/or space charge fields. But in order to reach the highest efficiency charge carrier densities have to be balanced. Therefore, it is often better to have a certain barrier for the major sort of charge carrier, which causes an injection-limited current (ILC) appropriate to the initial minor sort of charge carriers. Intuitively, balanced currents should cause recombination efficiency close to an optimum.

1.9 RECOMBINATION AND EFFICIENCY

After the charge carriers have been injected into the electroluminescent polymer charge transport plays an important role. For an efficient electroluminescence it is essential to have balanced hole and electron current densities. Different injection barriers and different mobilities of charge carriers lead to preconditions, which can be optimized. Since the mobilities are given by the electroluminescent material and cannot be optimized easily, the adjustment of the injection barriers is the key approach for an enhanced efficiency. Experimentally the efficiency η can be determined by measuring the IV-curves and the respective light output of a device. Thereafter η can be calculated and expressed in the common properties Candela per ampere (Cd/A) or lumen per Watt (lm/W).

1.10 COMPONENTS OF AN OLED

Like an LED, an OLED is a solid-state semiconductor device that is 100 to 500 nanometers thick or about 200 times smaller than a human hair. OLEDs can have either two layers or three layers of organic material; in the latter design, the third layer helps transport electrons from the cathode to the emissive layer. In this project, we'll be focusing on the one-layer design.

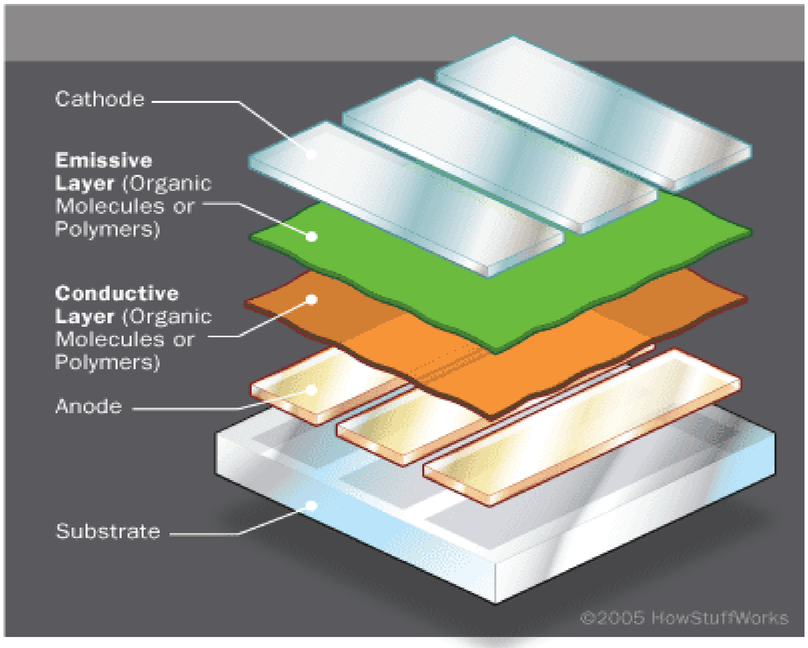


Figure1.4 Basic Structure of an OLED

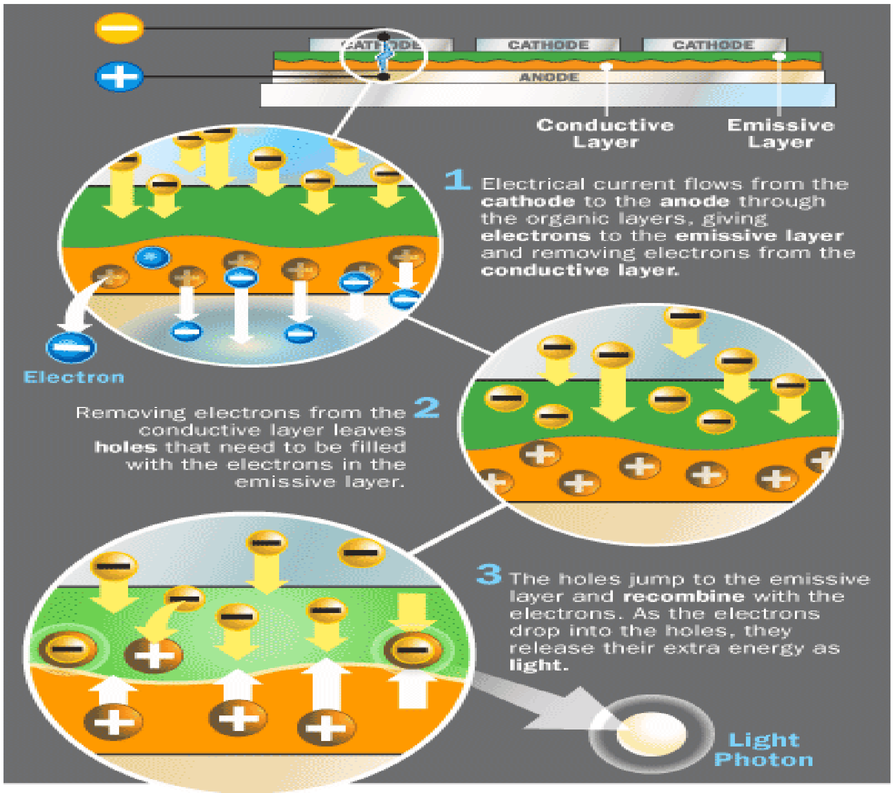
An OLED consists of the following parts:

- Substrate (clear plastic, glass, foil) - The substrate supports the OLED.
    - Anode (transparent) - The anode removes electrons (adds electron "holes") when a current flows through the device.
    - Conducting layer - This layer was made of organic plastic molecules that transport "holes" from the anode. One conducting polymer used in OLEDs is polyaniline and PEDOT.

- Emissive layer - This layer was made of organic plastic molecules (different ones from the conducting layer) that transport electrons from the cathode; this is where light is made. The polymers used in the emissive layer is polyfluorene, PPV, PPP etc
- Cathode (may or may not be transparent depending on the type of OLED) - The cathode injects electrons when a current flows through the device.

1.11 HOW DO OLEDs EMIT LIGHT?

OLEDs emit light in a similar manner to LEDs, through a process called electrophosphorescence.



1 Electrical current flows from the **cathode** to the **anode** through the organic layers, giving **electrons** to the **emissive layer** and removing electrons from the **conductive layer.**

2 Removing electrons from the conductive layer leaves **holes** that need to be filled with the electrons in the emissive layer.

3 The holes jump to the emissive layer and **recombine** with the electrons. As the electrons drop into the holes, they release their extra energy as **light.**

Figure1.5 OLEDs Creating Light

The process is as follows:

1. The battery or power supply of the device containing the OLED applies a voltage across the OLED.
2. An electrical current flows from the cathode to the anode through the organic layers (an electrical current is a flow of electrons).
    - The cathode gives electrons to the emissive layer of organic molecules.
    - The anode removes electrons from the conductive layer of organic molecules. (This is the equivalent to giving electron holes to the conductive layer.)
3. At the boundary between the emissive and the conductive layers, electrons find electron holes.
    - When an electron finds an electron hole, the electron fills the hole (it falls into an energy level of the atom that's missing an electron).
    - When this happens, the electron gives up energy in the form of a photon of light
4. The OLED emits light.
5. The color of the light depends on the type of organic molecule in the emissive layer. Manufacturers place several types of organic films on the same OLED to make color displays.
6. The intensity or brightness of the light depends on the amount of electrical current applied. The more current, the brighter the light.

1.11 SINGLE LAYER OLEDs

The device structure of a single layer polymer light-emissive device is intriguingly simple: A polymer film is sandwiched between two electrodes[17-18]. Applying a electric field across the polymer will eventually lead to injection of charges into the film as shown in Figure1.6:

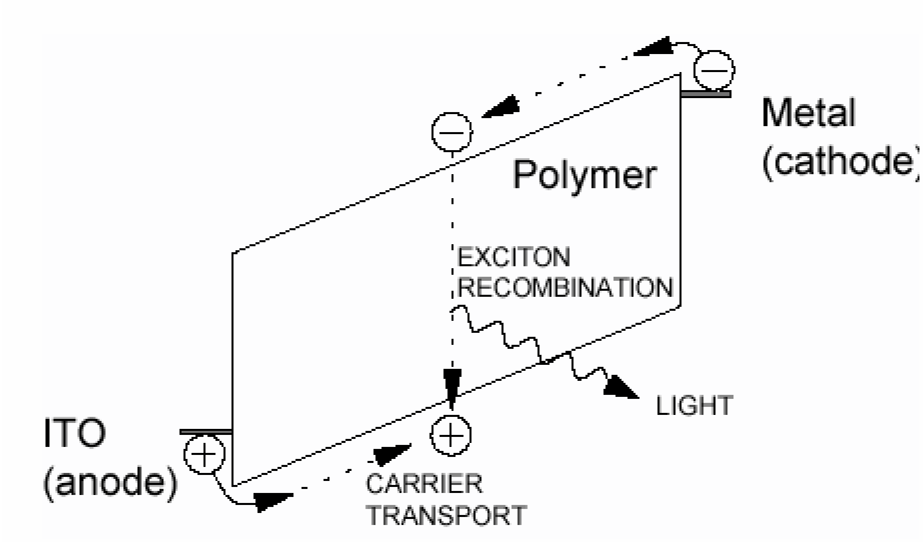


Figure1.6: Band diagram of an OLED.

The choice of material is of great importance for balanced charge injection and thus for the device efficiency. The work function of materials used as contacts should closely match the HOMO or LUMO level of the electroactive material to provide a good contact. In addition, at least one of the electrodes has to be transparent to allow emitted photons to escape.

1.12 ENERGY LEVEL DIAGRAM OF AN OLED

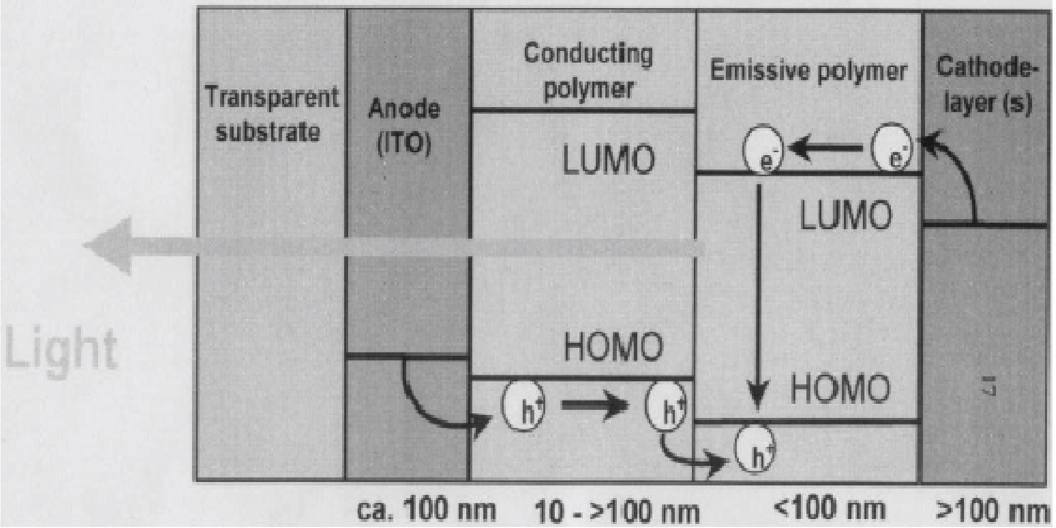


Figure1.7 Energy Level Diagram of an OLED

- Electrons injected from the cathode (Ca, Al, Ba, etc.)
- Holes injected from the anode (Indium tin oxide, PANI, PEDOT)
- Transport and radiative recombination of electron hole pairs at the emissive polymer

1.13 TYPES OF OLEDS

- Passive-matrix OLED
- Active-matrix OLED
- Transparent OLED
- Top-emitting OLED
- Foldable OLED
- White OLED

1.13.1 Passive-matrix OLED (PMOLED)

PMOLEDs have strips of cathode, organic layers and strips of anode. The anode strips are arranged perpendicular to the cathode strips[19-20]. The intersections of the cathode and anode make up the pixels where light is emitted. External circuitry applies current to selected strips of anode and cathode, determining which pixels get turned on and which pixels remain off. Again, the brightness of each pixel is proportional to the amount of applied current.

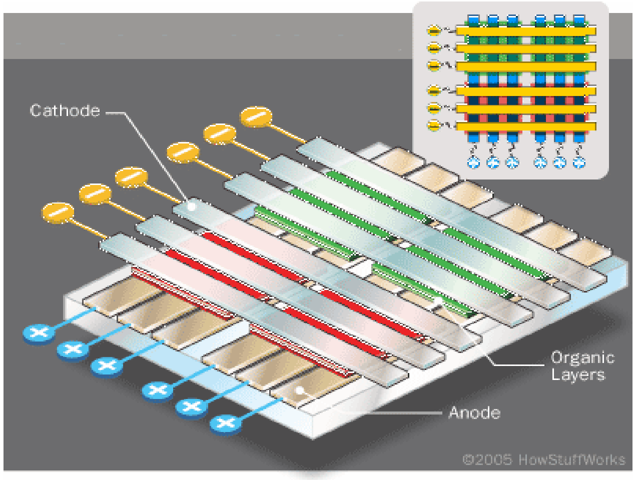


Figure 1.8 Passive matrix OLED

PMOLEDs are easy to make, but they consume more power than other types of OLED, mainly due to the power needed for the external circuitry. PMOLEDs have most efficient for text and icons and best suited for small screens (2- to 3-inch diagonal) such as those you find in cell phones, PDAs and MP3 players. Even with the external circuitry, passive-matrix OLEDs consume less battery power than the LCDs that are currently used in these devices.

1.13.2 Active-matrix OLED (AMOLED)

AMOLEDs have full layers of cathode, organic molecules and anode, but the anode layer overlays a thin film transistor (TFT) array that forms a matrix[19]. The TFT array itself is the circuitry that determines which pixels get turned on to form an image.

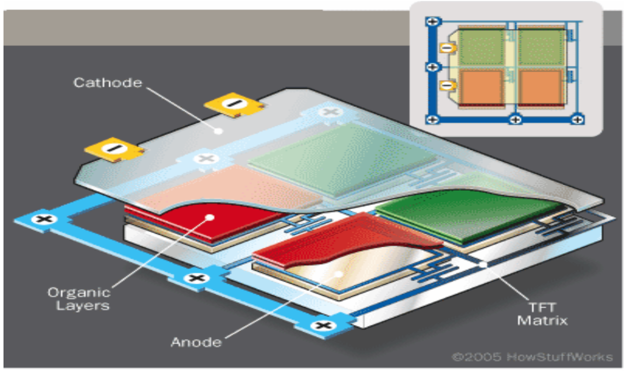


Figure 1.9 Active Matrix OLED

AMOLEDs consume less power than PMOLEDs because the TFT array requires less power than external circuitry, so they have efficient for large displays. AMOLEDs also have faster refresh rates suitable for video. The best uses for AMOLEDs in computer monitors, large screen TVs and electronic signs or billboards.

1.13.3 Transparent OLED

Transparent OLEDs have only transparent components (substrate, cathode and anode) and, when turned off, are up to 85 percent as transparent as their substrate. When a transparent OLED display is turned on, it allows light to pass in both directions[19]. A transparent OLED display can be either active- or passive-matrix. This technology can be used for heads-up displays.

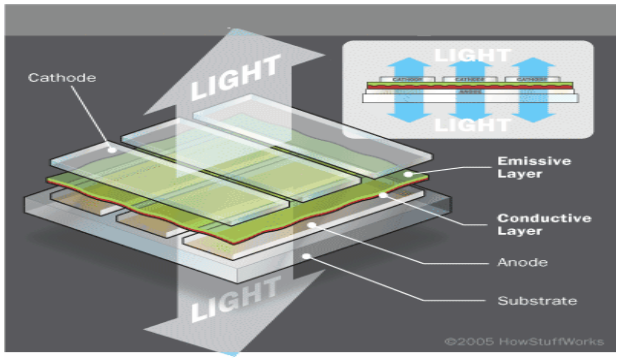


Figure 1.10 Transparent OLED

1.13.4 Top-emitting OLED

Top-emitting OLEDs have a substrate that is either opaque or reflective. They are best suited to active-matrix design. Manufacturers may use top-emitting OLED displays in smart cards[19-22].

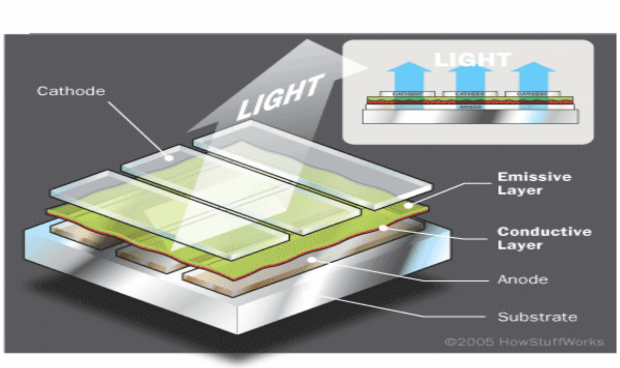


Figure 1.11 Top-Emitting OLED

1.13.5 Foldable OLED

Foldable OLEDs have substrates made of very flexible metallic foils or plastics. Foldable OLEDs have very lightweight and durable. Their use in devices such as cell phones and PDAs can reduce breakage, a major cause for return or repair. Potentially, foldable OLED displays can be sewn into fabrics for "smart" clothing, such as outdoor survival clothing with an integrated computer chip, cell phone, GPS receiver and OLED display sewn into it [19].

1.13.5 White OLED

White OLEDs emit white light have brighter, more uniform and more energy efficient than that emitted by fluorescent lights. White OLEDs also have the true-color qualities of incandescent lighting. Because OLEDs can be made in large sheets, they can replace fluorescent lights which currently used in homes and buildings[19-21]. Their use could potentially reduce energy costs for lighting.

1.14 MAKING OLEDs

Technological Background

1.14.1 Hole Conducting Electrode

For polymeric devices which combine electronics with optics, e.g. OLED's or OSC's, at least one transparent electrode desired in order to couple light into or out of the device. This specification fulfilled for thin semi-transparent metal layers or other transparent layers with similar properties.

1.14.1 (a) Indium Tin Oxide (ITO)

Commonly used as the transparent and hole injecting contact (anode) is indium-tin-oxide (ITO, (In_2O_3)) [23]. The material transparent, conductive and has a reasonably high work function (4.5 to 5 eV). Indium oxide has a wide band-gap semiconductor. To modify the conductivity of the material, indium oxide is degenerately doped with tin. To obtain films, In_2O_3 and SnO_2 usually simultaneously sputtered onto transparent substrates such as glass in a molar ratio of 91%: 9%. Because ITO is non-stoichiometric, the electronic properties depend on the preparation and cleaning processes used. An oxygen plasma treatment can increase the work function by as much as 0.5 eV and thus increase the efficiency of the device. But beside the advantages of outstanding conductivity and optical transparency ITO had also a few disadvantages. ITO has the strong ability to shorten the lifetime of organic semiconducting devices and it has a comparatively rough surface, which leads to an inhomogeneous E-field in the devices. Furthermore, ITO has an ill-defined work function and, therefore, it causes an unpredictable hole injection. Thus, optimization of these devices was required.

1.14.1 (b) Polymeric Anodes

By covering the ITO layer with a p-type conducting polymers, e.g., PEDOT, PANI, the properties of the devices could be enhanced. The surface smoothened, the diffusion of lifetime limiting ITO particles blocked, and a roughly predictable hole injection could be achieved [24].

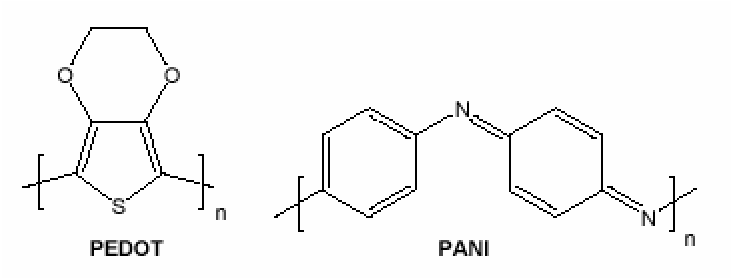


Figure1.12: Materials often used as hole injection layer: Poly-3, 4-ethylenedioxythiophene (PEDOT) and polyaniline (PANI)

1.14.1 (C) Deposition of PEDOT

Usually PEDOT (poly-3, 4-ethylenedioxythiophene) as the mostly used hole conducting material spincoated from suspension forming a thin film of about 40 nm. For our investigations we used the same polymer with spin casting from solution.

But instead of spin casting from solution sometimes it has polymerized electrochemically from its monomer EDOT. As shown in Figure below the polymerization is started by an anodic oxidation of the monomer EDOT.

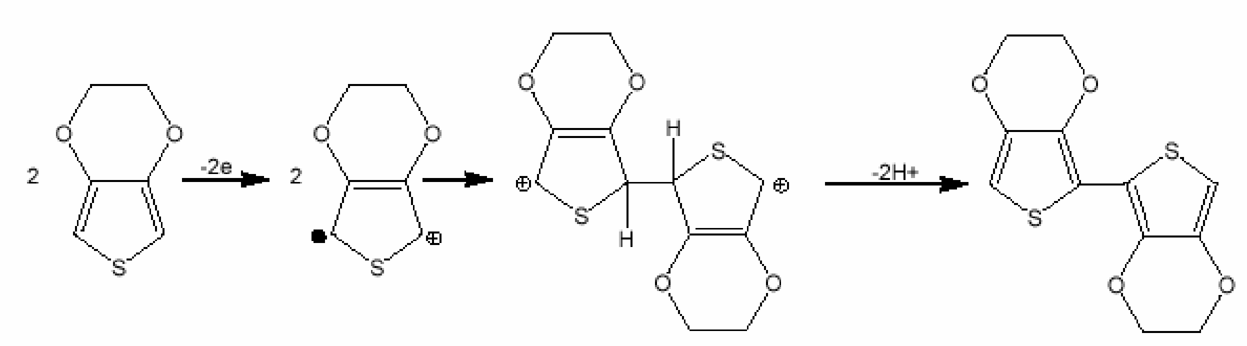


Figure1.13: Dimerization mechanism of 3, 4-ethylenedioxythiophene (EDOT).

Films of electrochemically deposited polymers were mechanically more stable than their spincoated counterparts and therefore better suited for the following doping treatment. In principle doping of conducting polymers realized by oxidation or reduction of the polymer chain. Besides other possible techniques electrochemical doping has the most reliable alternative due to its unique ability to measure the resulting electrochemical potential E_{eq} as an evaluation.

1.14.1. (d) **Active Layer Deposition**

The biggest part of manufacturing OLEDs is applying the organic layers to the substrate. This can be done in four ways:

- Vacuum deposition or vacuum thermal evaporation (VTE) - In a vacuum chamber, the organic molecules gently heated (evaporated) and allowed to condense as thin films onto cooled substrates. This process is expensive and inefficient.
- Organic vapor phase deposition (OVPD) - In a low-pressure, hot-walled reactor chamber, a carrier gas transports evaporated organic molecules onto cooled substrates, where they condense into thin films. Using a carrier gas increases the efficiency and reduces the cost of making OLEDs.
- Inkjet printing - With inkjet technology, OLEDs are sprayed onto substrates just like inks are sprayed onto paper during printing. Inkjet technology greatly reduces the cost of OLED manufacturing and allows OLEDs to be printed onto very large films for large displays like 80-inch TV screens or electronic billboards.

- Spin Coating: It is a preferred method for application of thin, uniform films to flat substrates. An excess amount of polymer solution is placed on the substrate. The substrate is then rotated at speed in order to spun off the edges of the substrate, until the desired film thickness is achieved. The solvent is usually volatile, providing for its simultaneous evaporation.

1.14.1. (e) Cathode Materials

The material used as a cathode should have a low work function, like alkali metals, for good electron-injecting properties. However, all of these metals, for example lithium [25], are also more likely to react with either the emissive material or with the surrounding atmosphere leading to device degradation. The device stability can be enhanced by using alloys containing these metals in a matrix of more stable metals like silver or aluminum [26]. The cathode metal layer is deposited by thermal evaporation. In this project, however, the metal was evaporated through shadow masks to form the desired pattern.

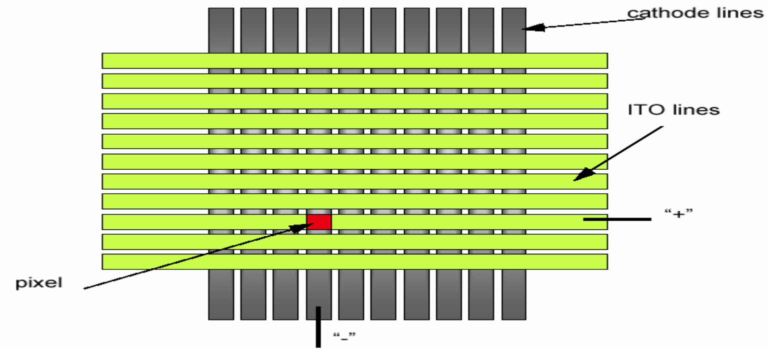


Figure1.14 Devices are formed where the ITO strip intersects with the cathode metal strip.

1.15 OLEDs vs. LEDs- ADVANTAGES AND DISADVANTAGES

The LCD is currently the display of choice in small devices and is also popular in large-screen TVs. Regular LEDs often form the digits on digital clocks and other electronic devices. OLEDs offer many advantages over both LCDs and LEDs which are as follows:

- The plastic, organic layers of an OLED are thinner, lighter and more flexible than the crystalline layers in an LED or LCD [27].
- Because the light-emitting layers of an OLED are lighter, the substrate of an OLED can be flexible instead of rigid. OLED substrates can be plastic rather than the glass used for LEDs and LCDs.
- OLEDs are brighter than LEDs. Because the organic layers of an OLED are much thinner than the corresponding inorganic crystal layers of an LED, the conductive and emissive layers of an OLED can be multi-layered. Also, LEDs and LCDs require glass for support, and glass absorbs some light. OLEDs do not require glass[28].
- OLEDs do not require backlighting like LCDs. LCDs work by selectively blocking areas of the backlight to make the images that you sees, while OLEDs generate light themselves. Because OLEDs do not require backlighting, they consume much less power than LCDs (most of the LCD power goes to the backlighting). This is especially important for battery-operated devices such as cell phones.
- OLEDs are easier to produce and can be made to larger sizes. Because OLEDs are essentially plastics, they can be made into large, thin sheets. It is much more difficult to grow and lay down so many liquid crystals.
- OLEDs have large fields of view, about 170 degrees. Because LCDs work by blocking light, they have an inherent viewing obstacle from certain angles. OLEDs produce their own light, so they have a much wider viewing range.

1.16 CHALLENGES AND SHORTCOMINGS OF OLED's

- Huge driving currents are needed to achieve adequate average brightness in Passive Matrix addressing displays. Such large currents cause problems such as large drive voltages leading to increased power dissipation, excess flicker and shortened lifetimes [27].

  Active Matrix addressing can be used to overcome such problems.
- State of art OLED brightness and lifetime: 100 nits and 40,000 hours (50% initial luminance)
- High brightness level requires the display driving voltage levels to be increased which trades off expected lifetime. For most OLED materials, the relationship between driving voltage level and lifetime is nearly linear.
- Over time, moisture can react with the organic layers and cause degradation and defects in an OLED display.
- Sealing techniques
- Inserting desiccants

Chapter-II

Objective and Scope

2.1 INTRODUCTION

For the last decade, conjugated polymers have attracted a sustained interest. The current level of research in the field of conducting and electroactive polymers was sparked by the discovery in 1977 by MacDiarmid, Shirakawa and Heeger (Nobel prize 2000 in Chemistry), who found that chemical doping of polyacetylene increased its conductivity by 7 orders of magnitude, up to 10^3 S/cm. More recent advances have improved its conductivity to 10^5 S/cm, comparable to the conductivity of copper and silver of ~10^6 S/cm. Knowing that conductivity can be adjusted from insulating to conducting it becomes obvious that semiconducting properties can also be expected which are well known from inorganic semiconductors. Now, the same polymers in the undoped, nonconductive state have become attractive as active components in light-emitting diodes LEDs, field-effect transistors, or nonlinear optical devices.

2.2 Objective

Poly (p–phenylene) (PPP) is particularly interesting because of it exhibits a unique combination of physical properties, namely high mechanical strength, excellent thermal stability and chemical resistance, as well as electroluminescence and high conductivity upon doping. In particular, it is known for its exceptional thermal stability in the neutral sate, its resistance to environmental oxidation and irradiation, its very wide conductivity range (from 10^{-18} S cm $^{-1}$ in the pristine form to more than 10^2 S cm^{-1} in the doped state), the possibility of carrying out chemical or electrochemical n- or p-doping of the polymer similar to that of polyacetylenes and, therefore, its suitability for the realization of all-plastic high energy-density batteries, and lastly, recently discovered, applications of this material for electroluminescent devices. However, its commercial use has been hampered; mainly because of the difficulty to solublized and process high-molecular weight regular PPPs.

In the present work, We try to solve the problems of solubilization, processability and device fabrication for the PPPs. We synthesized the copolymer of benzene and substituted benzene with aromatic compounds which have PL in the visible region like

Anthracene, Naphthalene and Perylene etc.The copolymers have to be shifted in the PL Spectra Correspond to the monomers. The property of the PPPs polymer like solubility, processability, quite improvised.

2.3 Scope And Applications

- Flexible displays
- Replacing incandescent and fluorescent light bulbs

Research and development in the field of OLEDs is proceeding rapidly and may lead to future applications in heads-up displays, automotive dashboards, billboard-type displays, home and office lighting and flexible displays [27]. Because OLEDs refresh faster than LCDs almost 1,000 times faster a device with an OLED display could change information almost in real time. Video images could be much more realistic and constantly updated. The newspaper of the future might be an OLED display that refreshes with breaking news (think "Minority Report") and like a regular newspaper; you could fold it up when you're done reading it and stick it in your backpack or briefcase.

Current main commercial applications

- Mobile phone screen (Samsung/ NEC, Motorola, LG)
- Car radio
- Digital camera (Kodak)
- Car stereo (Pioneer, TDK, Kenwood)
- Razor (Philips)

2.4 BAND GAPS IN CONJUGATED POLYMERS

The origin of the band gap in conjugated polymers is best understood in terms of the bonding and anti-bonding of carbon-carbon double bonds. In these compounds, electrons are delocalized from their parent atoms and form two molecular orbitals of different energies, which act as a highest occupied molecular orbital (HOMO, “valence band”) and a lowest unoccupied molecular orbital (LUMO , “conduction band”). Carbon-carbon double bonds are formed when two of the three 2p orbitals on each carbon atom combine with the 2s orbital to form three 2sp^2 hybrid orbitals. These lie in a plane directed at 120° to each other, and form σ molecular orbitals with neighboring atoms. The third p orbital on the carbon atom, the 2p$_z$, points perpendicularly to this plane, and overlaps with a 2p$_z$ orbital on a neighboring carbon atom, to form a pair of π bonding and π* antibonding molecular orbitals. As equivalent π orbitals are formed between nearby atoms along the chain, the wave-functions overlap, resulting in a delocalisation over the polymer chain.

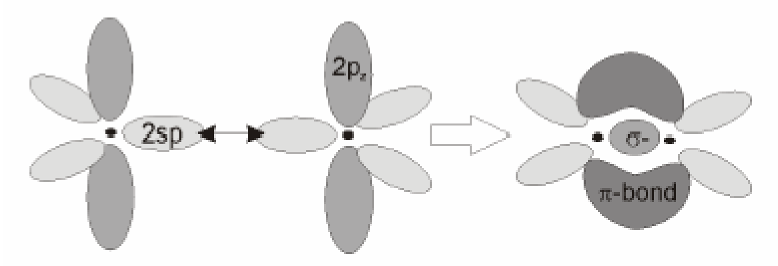


Figure 2.1: The overlapping of 2s ^{2} and 2p$_z$ orbitals forms ð and π bonds respectively.

The difference in energy between the highest occupied molecular orbital (HOMO) in the valence band and the lowest unoccupied molecular orbital (LUMO) in the conduction band gives the energy gap E$_{gap}$. Poly (p-phenylene vinylene) or PPV, poly (p-phenylene) or PPP and their derivatives have been the basis for much of past research in semiconducting polymer devices. The band-gap of these polymers can be altered by adding different side groups to the polymer, which can push (pull) charges to (from) the backbone. This process alters the “absorption edge” and therefore the band gap. Another duty of side chains is an improved solubility.

2.5 WHY DO WE NEED SUBSTITUTED PPPs?

PPP have attracted a great deal of attention with respect to their applications in displays, light-emitting devices, and batteries. The outstanding chemical stability of undoped PPP, their ability to resist treatment at very high temperatures and, recently, the exceptional mechanical properties found for long substituted poly (I, 4-phenylene) chains, are strong arguments in favour of intensive research development in this area. Despite these extremely promising properties, PPPs consist of very rigid rod-like polymers and are therefore insoluble in all organic or mineral solvents, a characteristic that renders the processing of this material very difficult, and which probably explains why direct synthetic routes using benzene or its derivatives as the starting reagent do not produce PPPs with high molecular weights and long linear chains. One solution is to synthesize a more tractable precursor which can be converted to PPP. The other is to add substituents to aromatic rings.

Copolymers have been prepared from combinations of homo cyclic aromatic substrates with Lewis acid catalyst-oxidant combinations. For example, mixtures of m-terphenyl and naphthalene, benzene, or bi-phenyl afforded soluble, fusible copolymers from reaction with $AlCl_3/CuCl_2$ or $AlCl_3/O_2$.Similarly, soluble copolymers of naphthalene and benzene were obtained via oxidative coupling with $AlCl_3/CuCl_2$ .The copolymers generally retain the good thermal stability of PPP, but are more processable. More highly condensed aromatics (anthracene, phenanthrene, pyrene) were also copolymerized with benzene in the presence of $AlCl_3/CuCl_2$ to yield tractable products. An alternating copolymer with a structure of dodecyl disubstituted terphenylene and unsubstituted phenylene units exhibits a PL maximum at about 400 nm and a band gap of 3.5 eV that is substantially larger than that of PPP (2.7 eV). The two adjacent bulky alkyl side groups repulse each other forming a larger tilt angle between the adjacent phenylene units than those without the side groups.

2.6 COLOR TUNING IN PPP COPOLYMERS

Colors generated from light emitting polymers can be tuned by combinations of various chromophores in the polymer backbones. Copolymers are designed to give specific properties concerning band gaps, HOMO, LUMO, QE, solubility, stability, etc. Transfer of energy from one chromophore to another longer wavelength emitting chromophore presents a way to tune the emission of conjugated polymers by the incorporation of a suitable chromophore as a comonomer. The dyes may be incorporated into the main chain, or as end capping units at the chain terminal. Efficient energy transfer in the solid state means that the emission comes solely from the dye. The introduction of functional groups may therefore be used to fine-tune the luminescence of the electrolumophore. This approach may be successfully used to change a color of OLED elements. For example, the green emission of AlQ_3 complex turns to red when an electron-donating substituents are introduced. Likewise, introduction of an electron withdrawing substituent may change the emission of the complex to blue.

Through careful selection of suitable co-monomers, considering their effect on HOMO/LUMO levels of the polymer, one can achieve a whole range of emission colors from PPP based materials. The high-energy blue emission of PPP polymers can be changed into virtually any color by adding small amount of low-energy emitting materials. This approach, based on energy transfer is of prime importance for PLEDs. Thus, efficient energy transfer from blue to red (typical for pure PPPs) color was demonstrated for copolymer based LED. The material instability is one of major limitations of the polymer LEDs. In this light, a very high thermal stability of poly (p–phenylenes) combined with high PL quantum yield, renders them as attractive materials for device applications. Changing the length of the phenylene block and separating bridges, the polymer absorption (336–406nm) and PL maxima (401–480 nm) can be varied over a wide range. The electroluminescence can be tuned over an even wider range (423–650 nm) in multilayer PLEDs and, varying the polymer composition and the device structure.

2.7 TOLUENE

Toluene, also known as methylbenzene or phenylmethane is a clear, water-insoluble liquid with the typical smell of paint thinners, reminiscent of the sweet smell of the related compound benzene. It is an aromatic hydrocarbon that is widely used as an industrial feedstock and as a solvent. Toluene reacts as a normal aromatic hydrocarbon towards electrophilic aromatic substitution. The methyl group makes it around 25 times more reactive than benzene in such reactions.

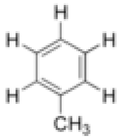


Figure 2.2: Structure of Toluene

2.7 (a) Physical and Chemical Properties

Description: Colorless liquid

Molecular formula: C_7H_8

Molecular weight: 92.13 g/mol

Density: 0.8661 g/cm^3 at 20°C

Boiling point: 110.6 °C

Melting point: -94.9° C

Vapor pressure: 28.1 torr at 25°C

Solubility: miscible in most organic solvents

Conversion factor: 1 ppm = 3.76 mg/m^3 at 25°C

Viscosity: 0.590 cP at 20°C/ 68°F

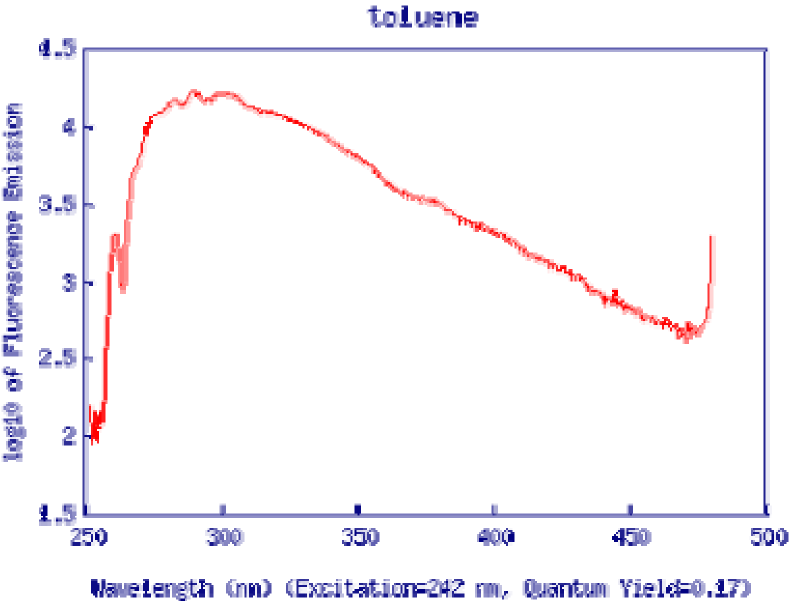


Figure 2.3: This is the fluorescence emission spectrum of toluene dissolved in cyclohexane

2.7 (b) Major Uses or Sources

Toluene occurs naturally as a component of crude oil and is produced in petroleum refining and coke oven operations; toluene is a major aromatic constituent of gasoline. Benzene and other poly cyclic aromatic hydrocarbons are common contaminants of toluene. Toluene is used as an octane booster in fuel, as a solvent in paints, paint thinners, chemical reactions, rubber, printing, adhesives, lacquers, leather tanning, disinfectants, and to produce phenol and TNT. It is also used as a raw material for toluene diisocyanate, which is used in the manufacture of polyurethane foam.

2.8 PERYLENE

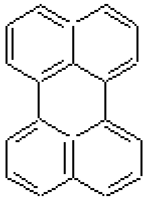


Figure 2.4: Structure of perylene

Perylene or perilene is a polycyclic aromatic hydrocarbon with chemical formula $C_{20}H_{12}$ and occurring as a brown solid. It or its derivatives may be carcinogenic, and it is considered to be a hazardous pollutant. In cell membrane cytochemistry, perylene is used as a fluorescent lipid probe. Perylene displays blue fluorescence. It is used as a blue-emitting dopant material in OLEDs, either pure or substituted. Perylene can be also used as an organic photoconductor.

2.8 (a) Physical and Chemical Properties

Chemical Formula: $C_{20}H_{12}$
Molecular weight: 252.32
Melting point: 277.5 °C
Boiling point: 497 °C
Resonance energy: 2.651 eV
Heat of vaporization: 71.3 KJ / mol

The absorption and fluorescence emission spectra are shown below:

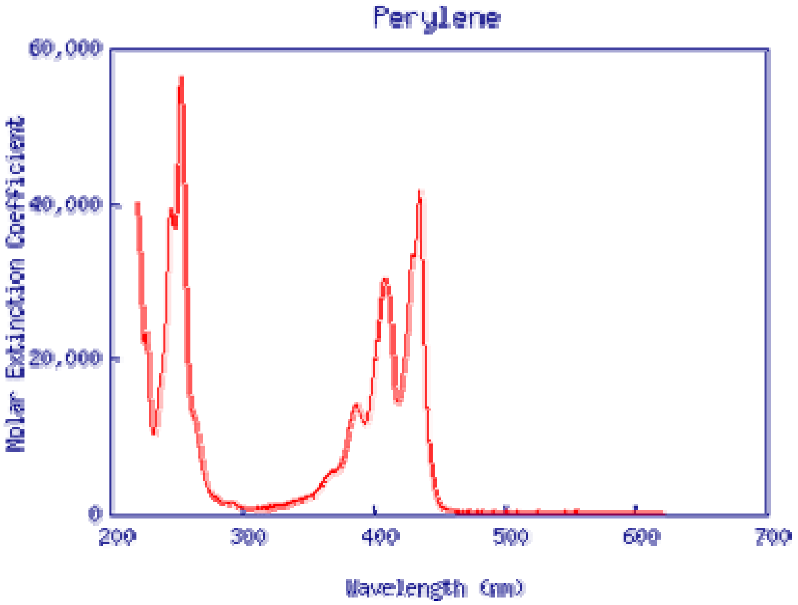


Figure 2.5: This is a graph of the molar extinction coefficient of Perylene dissolved in cyclohexane.

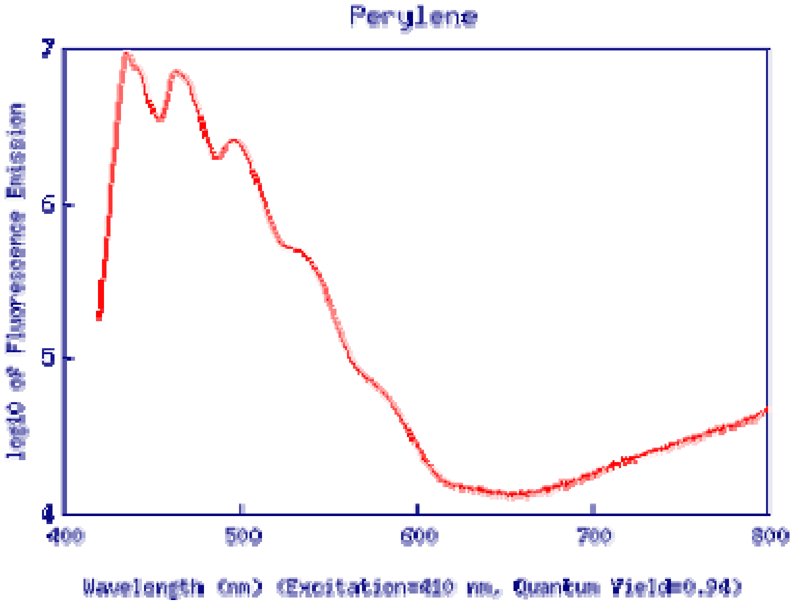


Figure 2.6: This is the fluorescence emission spectrum of Perylene dissolved in cyclohexane.

CHAPTER-III

MATERIAL CHARACTERIZATION TECHNIQUES

3. MATERIAL CHARACTERIZATION TECHNIQUES

In material characterization basically we try to characterize the synthesized material by variety of techniques to assure that the appropriate material with suitable properties is synthesized. Some of the instruments utilized for the characterization of the polymers are given below:

1. Scanning electron microscope (SEM)
2. Ultraviolet and visible spectrophotometer
3. Thermal analysis instruments
    a. Differential Scanning Calorimetry (DSC)
    b. Thermogravimetric Analysis (TGA)
4. Vacuum Thermal Deposition

3.1 SCANNING ELECTRON MICROSCOPE (SEM)

In order to study the surface structure and morphology of the copolymers a high performance scanning electron microscope LEO-440 has been used. It is a software controlled SEM.

Figure 3.1 LEO-440 Scanning Electron Microscope

The electron gun has ionic emitter, as source of source electrons .The normal source is a tungsten hairpin filament, although the LEO-440 may have the lanthanum hex boride LaB_6 option fitted.

Three electromagnetic lenses beneath the gun, focus and shape the electron beam before it strikes the specimen in a scanned or rastered, fashion. The energy of the beam is adjustable from 300 volts to 40 kilovolts in 10 volt steps and the electron beam current is continuously adjustable from 1 pico-amp to micro-amp to suit the type of examination in progress.

The specimen chamber of the LEO-440 holds the specimen to be viewed in such a way that it may be freely maneuvered during examination. The specimen stage that holds the specimen is attached to the door of the chamber and may be of the normal cartesian type. The cartesian stage permits movement of 120 mm in the y direction, 100 mm in x direction, 58 mm in z direction, 0 to 90° tilt and 360° rotation. Control of the motorized stage movements may be achieved either by a joystick controller or via the LEO software. The stage may be opened for examination once the vacuum within the chamber is released. The instrument has a resolution 3.5 nm SEI mode and 5.5 nm BEI mode at variable working distances. The magnification on the computer screen can be varied from 5x to 300000x. Specimen with 10 cm × 10 cm × 5 cm or 10 cm diameter and 5 cm thickness distances.

It is complete software controlled instrument and operates like a desktop computer i.e. all operations are controlled through the mouse and the keyboard. In the present work the SEM was operated at 25 kV (unless otherwise mentioned) in the secondary electron imaged 4 mode. In the case of conducting sample the surface morphology and surface structure were examined directly. However, in the specimen was coated with a very thin layer (10 nm).

3.1 (a) Principle of SEM

When the beam of electrons strikes the surface of the specimen, a large number of signals are emitted from the specimen as a result of electron beam matter interaction. It interesting to mention here that the different signals generated in the specimen as a result of electron beam matter interaction are emitted from the different depth of the specimen. The secondary electrons emitted from various regions of the specimen surface, when it scanned by electron probe, are detected by the secondary electron detector (located near the specimen).

The detector output is amplified, level controlled and converted into video signal by video amplifier. These video signals used for z-modulation in the raster on a TV or oscilloscope screen to display a scanning image, synchronized with probe scan.

The resolution power of the microscope depends on the diameter of the probe and the quality of the signals obtained from the specimen. The magnification of the scanning image is given by the ratio of the image width of the CRT picture to the scanning width of the electron probe.

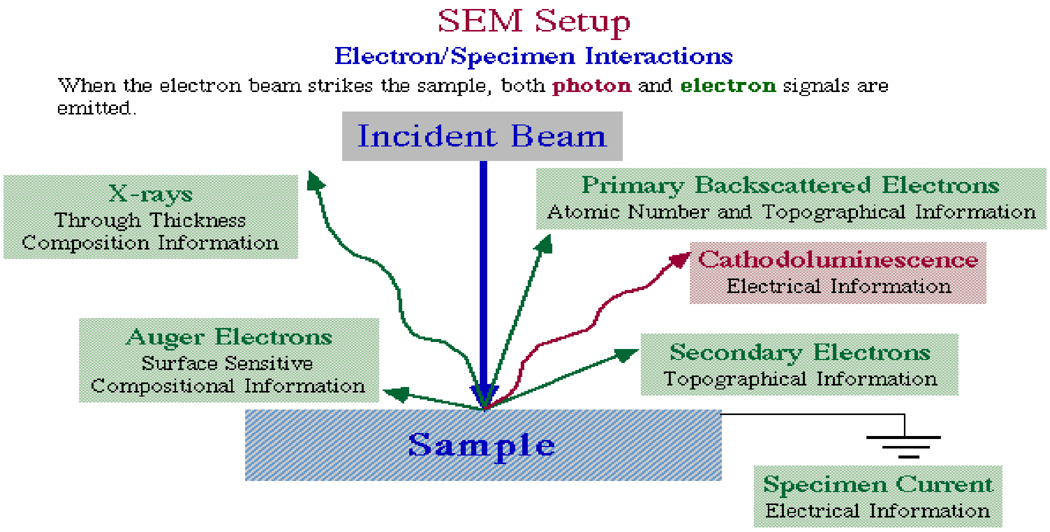


Figure 3.2 Setup for SEM

3.2 UV-VISIBLE SPECTROSCOPY

Ultraviolet-visible spectroscopy (UV = 200-400 nm, visible = 400-800 nm) measures electronic excitations between the energy levels that correspond to the molecular orbitals of the systems. In particular, transitions involving π orbitals and lone pairs are important and so UV-VIS spectroscopy is of most use for identifying conjugated systems, which tend to have sufficient absorptions. Ultraviolet and visible lights are energetic enough to promote outer electrons to higher energy levels. UV-VIS spectroscopy is usually applied to molecules and inorganic ions or complexes in solution. The UV-VIS spectra have broad features that are of limited use for sample identification but are very useful for quantitative measurements. The concentration of an analyst in solution can be determined by measuring the absorbance at some wavelength and applying the Beer-Lambert Law.

Since the UV-VIS range spans the range of human visual acuity of approximately 380 - 780 nm, UV-VIS spectroscopy is useful to characterize the absorption, transmission, and reflectivity of a variety of technologically important materials, such as pigments, coatings, windows, and filters. In this project we used shimadzu UV-1601 UV-VIS spectrophotometer for absorption measurements.

Figure 3.3 Shimadzu UV-1601 UV-VIS Spectrophotometer

3.2 (a) Instrumentation

Most commercial UV-VIS absorption spectrometers use one of three overall optical designs: a fixed or scanning spectrometer with a single light beam and sample holder, a scanning spectrometer with dual light beams and dual sample holders for simultaneous measurement of I and I_o, or a non-scanning spectrometer with an array detector for simultaneous measurement of multiple wavelengths. In single-beam and dual-beam spectrometers, the light from a lamp is dispersed before reaching the sample cell. In an array-detector instrument, all wavelengths pass through the sample and the dispersing element is between the sample and the array detector.

The wavelength range of UV 1601 UV-VIS spectrophotometer is 190 to 1100 nm with a spectral bandwidth of 2 nm. It is a double beam spectrophotometer. The short-wavelength limit for simple UV-VIS spectrometers is the absorption of ultraviolet wavelengths less than 180 nm by atmospheric gases. Purging a spectrometer with nitrogen gas extends this limit to 175 nm. There are two light sources in this instrument: a 50 W halogen lamp having a life of 2000 hrs life for visible and NIR measurements and a deuterium lamp for UV measurements. The instruments automatically swap lamps when scanning between the UV and visible regions. The wavelengths of these continuous light sources are typically dispersed by a aberration corrected concave blazed holographic grating in a single or double monochromator or spectrograph. The spectral bandpass is then determined by the monochromator slit width. Spectrometer designs and optical components are optimized to reject stray light, which is one of the limiting factors in quantitative absorbance measurements. Silicon photodiode is used as a detector in this spectrometer. The diffraction grating and instrument parameters such as slit width can also change.

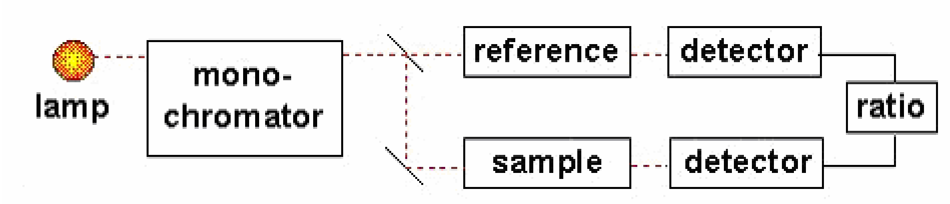


Figure 3.4 Schematic diagram of a dual-beam UV-VIS spectrophotometer

3.2 (b) Working Principle

A beam of light from a visible and/or UV light source is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic (single wavelength) beam in turn is split into two equal intensity beams by a half- mirror device. One beam, the sample beam, passes through a small transparent container (cuvette) containing a solution of the compound being studied in a transparent solvent. The other beam, the reference, passes through an identical cuvette containing only the solvent.

The intensities of these light beams are then measured by electronic detectors and compared. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as I_o. The intensity of the sample beam is defined as I. Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm.

If the sample compound does not absorb light of a given wavelength, $I = I_{o.}$ However, if the sample compound absorbs light then I is less than I_o, and this difference may be plotted on a graph versus wavelength. Absorption may be presented as transmittance ($T = I / I_o$) or absorbance ($A= \log I_o /I$). If no absorption has occurred, T = 1.0 and A= 0. This spectrometers display absorbance on the vertical axis, and the range is from -3.99 (100% transmittance) to +3.99 (1 % transmittance). The wavelength of maximum absorbance is a characteristic value, designated as λ_{max}. Different compounds may have very different absorption maxima and absorbance. Intensely absorbing compounds must be examined in dilute solution, so that the detector receives significant light energy, and this requires the use of completely transparent (non-absorbing) solvents. The most commonly used solvents are water, ethanol, hexane and cyclohexane. Solvents having double or triple bonds, or heavy atoms (e.g. S, Br & I) are generally avoided. Because the absorbance of a sample will be proportional to its molar concentration in the sample cuvette, a corrected absorption value known as the molar absorptivity is used when comparing the spectra of different compounds.

3.3 THERMAL ANALYSIS

3.3 (a) DIFFERENTIAL SCANNING CALORIMETRY (DSC)

A differential scanning calorimeter measures the difference between the heat flows to a sample and a reference pan that are exposed to the same temperature. A heat flow corresponds to a transmitted power and thus is measured in Watts or mW. Integrating power with respect to the time results in an amount of energy expressed in mWs=mJ. The transmitted energy corresponds to an equal change in enthalpy of the sample. When the sample absorbs energy the enthalpy change is called endothermal. When the sample releases energy the process is called exothermal.

DSC provides information about:

Thermal effects shaped as peaks, characterized by their enthalpy change and temperature range. Examples of such thermal effects are: melting, crystallization, solid-solid transition, chemical reaction.

In addition the specific heat capacity is obtained, therefore DSC also observes thermal effects caused by a change in heat capacity, e.g. at the glass transition.

3.3 (B) THERMOGRAVIMETERIC ANALYSIS

Thermogravimetric Analysis (TGA) is a thermal analysis technique used to measure changes in the weight (mass) of a sample as a function of temperature and/or time. TGA is commonly used to determine polymer degradation temperatures, residual solvent levels, absorbed moisture content, and the amount of inorganic (noncombustible) filler in polymer or composite material compositions. A simplified explanation of a TGA sample evaluation may be described as follows. A sample is placed into a tared TGA sample pan, which is attached to a sensitive microbalance assembly. The sample holder portion of the TGA balance assembly is subsequently placed into a high temperature furnace. The balance assembly measures the initial sample weight at room temperature and then continuously monitors changes in sample weight (losses or gains) as heat is applied to the sample. TGA tests may be run in a heating mode at some controlled heating rate, or isothermally. Typical weight loss profiles are analyzed for the amount or percent of weight loss at any given temperature, the amount or percent of noncombusted residue at some final temperature, and the temperatures of various sample degradation processes.

TGA is a useful technique for assessing the effectiveness of oven drying solution polymerized polymer samples. The volatilization of residual solvent is typically associated with the initial weight loss process in a TGA heating run. In some cases, absorbed moisture may be liberated over this same temperature range, though. After the initial solvent (or moisture) weight loss process, TGA profiles will typically plateau to some constant weight level until the polymer degradation temperature range is reached. The weight fraction of residual solvent (or moisture) and the onset and maximum rate weight loss degradation temperatures are readily determined by TGA.

The glass fiber content of composite samples is also readily analyzed by TGA. The polymer resin is degraded and burned off in heating these types of composite specimens to high temperatures in an air atmosphere. The noncombustible glass fiber is left behind as a residue. The weight fraction of glass fiber in the composite is determined using the TGA residue analysis routine.

3.3 (b). 1 Applications of TGA:

TGA measures the weight change in materials as a function of time and temperature. The Measurements provide basic information about the thermal stability of a chemical and its composition. TGA is one of the most commonly requested thermal techniques and it is used to characterize both inorganic and organic materials, including polymers. The measurement is typically carried out on milligram size samples with a heat rate of 10°C/min from 20° to 800°C in a nitrogen atmosphere.

3.3 (b) 2. Specific Measurement of TGA Analysis:

1. Moisture and volatiles content.
2. Composition of multicomponent Systems
3. Thermal stability
4. Oxidative stability
5. Shelf-Life studies using kinetic analysis.
6. Decomposition kinetics
7. Effect of reactive atmospheres

3.4 VACUUM THERMAL DEPOSITION

Thermal vacuum deposition of the copolymer and cathode is realized in the evaporation chamber. Vacuum evaporation (including sublimation) is a Physical Vapor Deposition (PVD) process where material from a thermal vaporization source reaches the substrate without collision with gas molecules in the space between the source and substrate. The pumping system consists from a rotation pump, high-speed diffusion pump and liquid nitrogen trap. The pressure at the Pyrex Glass Bell Jar is 10^{-6} Torr during deposition. The vacuum thermal evaporation deposition technique consists in heating until evaporation of the material to be deposited. The material vapor finally condenses in form of thin film on the cold substrate surface and on the vacuum chamber walls. Usually low pressures are used, about 10^{-6} or 10^{-5} Torr, to avoid reaction between the vapor and atmosphere. At these low pressures, the mean free path of vapor atoms is the same order as the vacuum chamber dimensions, so these particles travel in straight lines from the evaporation source towards the substrate. This originates 'shadowing' phenomena with 3D objects, especially in those regions not directly accessible from the evaporation source (crucible). Besides, in thermal evaporation techniques the average energy of vapor atoms reaching the substrate surface is generally low. This affects seriously the morphology of the films, often resulting in a porous and little adherent material. In thermal evaporation techniques, different methods can be applied to heat the material. These equipments generally use either resistance heating (Joule effect) or bombardment with a high-energy electron beam, usually several KeV, from an electron beam gun (electron beam heating). But here in our case we used resistance heating.

In the evaporation deposition technique, the material is heated until fusion by means of an electrical current passing through a filament or metal plate where the material is placed (Joule effect). The evaporated material is then condensed on the substrate. The assembly of the technique is simple and results appropriate for depositing metals and some polymeric compounds with low fusion temperature. Typical metals used as heating resistance are tantalum (Ta), Molybdenum (Mo) and Tungsten (W), with vapor pressure practically zero at the evaporation temperature (T_{evap} = 1000-2000 °C). When a helicoidally filament surrounds the material it is convenient that the evaporate material wets the metal. A scheme of the deposition equipment used in the laboratory is showed in the figure:

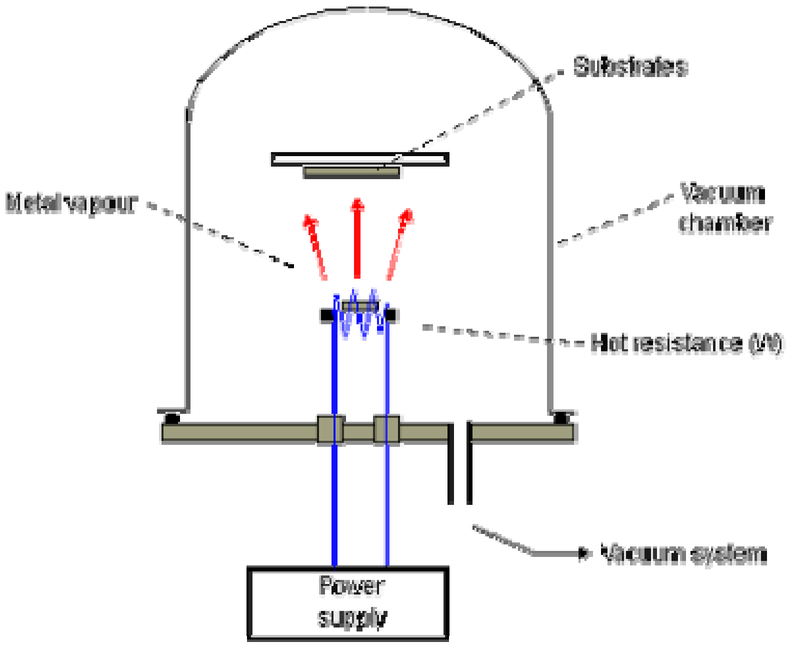


Figure 3.6 Set up for Vacuum Thermal Deposition

Typically, vacuum evaporation takes place in a gas pressure range of 10^{-5} to 10^{-9} Torr, depending on the level of contamination that can be tolerated in the deposited film. For an appreciable deposition rate to be attained, the material vaporized must reach a temperature where its vapor pressure is 10 mTorr or higher.

3.4 (A) Advantages of vacuum evaporation:

- High-purity films can be deposited from high-purity source material.
- Source of material to be vaporized may be a solid in any form and purity.
- The line-of-sight trajectory and "limited-area sources" allow the use of masks to define areas of deposition on the substrate and shutters between the source and substrate to prevent deposition when not desired.
- Deposition rate monitoring and control are relatively easy.
- It is the least expensive of the PVD processes.

CHAPTER-IV

General Method of synthesis of Poly (p-phenylene)

4. General Method of synthesis of Poly (p-phenylene) (PPP)

4.1. Kovacic's Method

The procedure involves the dehydro-coupling of benzene nuclei by catalyst-oxidant systems, leading to the formation of C-C bonds, and provides poly (p–phenylene) in high yield. The reagent used to carry out the polymerization was either a binary system consisting of a Lewis acid and an oxidant or a single reagent with both Lewis acid and oxidizing properties.

4.1.1 (a) Binary catalyst-oxidant systems

Aluminium chloride ($AlCl_3$) as the Lewis acid (catalyst) with cupric chloride ($CuCl_2$) as the oxidizing agent was the best catalyst-oxidant combination used by Kovacic et al. for the polymerization of benzene. Polymerization occurred under mild conditions (36-37°C, 15 minutes), with water as a co-catalyst, and the yield of poly (p-phenylene) was found to depend on the aluminium chloride to cupric chloride ratio.

Two main mechanisms involved are:

- Protonation reactions and
- Deprotonation reactions

Protonation Reactions

Here the initiation step is associated with the protonation of the aromatic nucleus and yields a σ-complex (1) which in turn reacts with the monomer and gives a first unstable cationic dimmer (2). It is considered that cationic dimer is then chemically oxidized to a new cationic aromatic dimmer (3) and that chain propagation occurs, leading to a cationic polymer (4) which, after loss of a proton, gives the PPP chain [29-30] (5). As shown in Fig 4.1

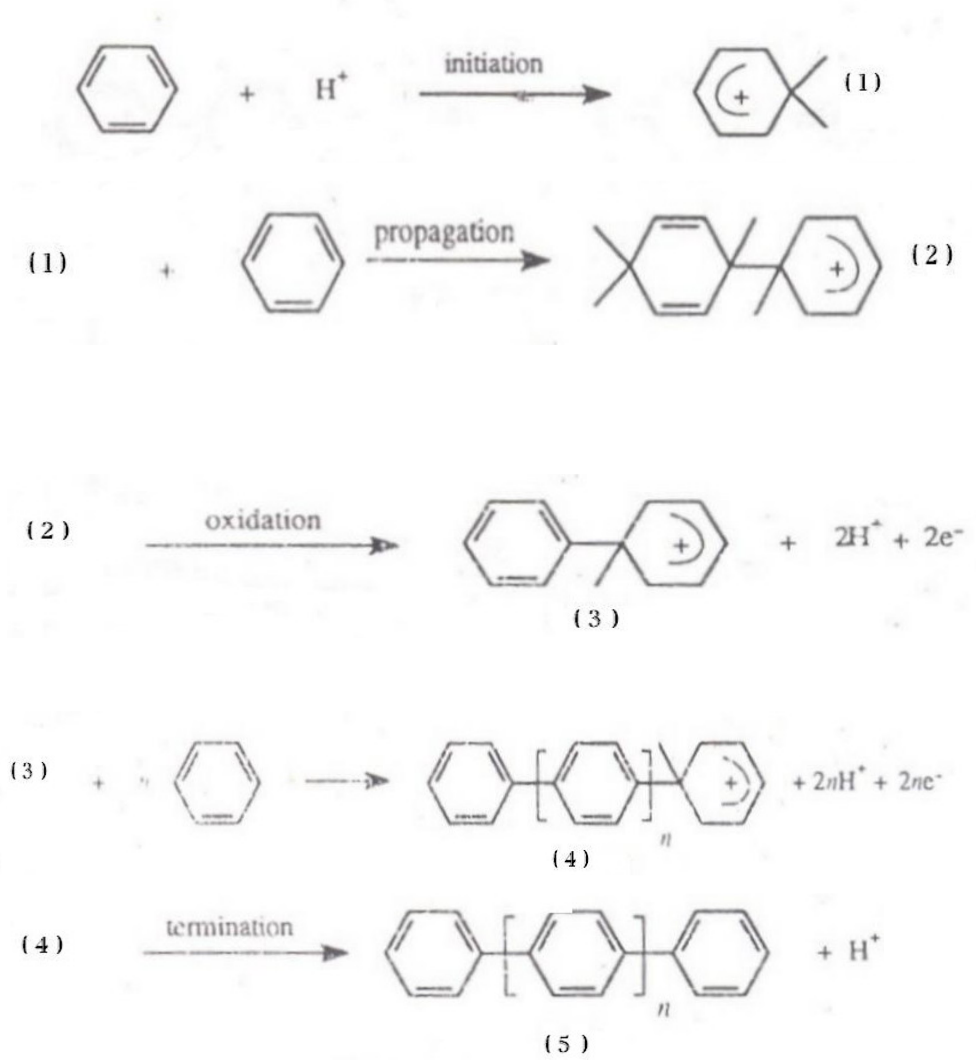


Figure 4.1: Protonation Mechanism of PPP Synthesis

Deprotoation Reactions

This mechanism was proposed as an alternative to the previous one. Here radical-cations are involved as active intermediate species [31]. In this case it is postulated that a Lewis acid (A), considered as an electron acceptor, reacts with the aromatic hydrocarbon and its derivatives to give a radical-cation species (1), which couples with another aromatic substrate to produce a dimmer (2). As shown in Fig. 4.2

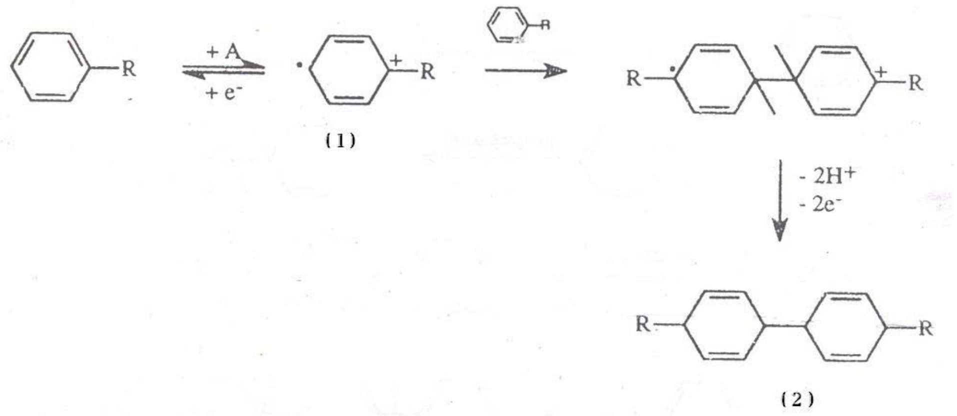


Figure 4.2: Deprotonation Mechanism for PPP Synthesis

A wide variety of catalyst systems are suitable for the polymerization of benzene to poly (p–phenylene). Typically, various oxidizing agents such as manganese dioxide (MnO_2), lead dioxide (PbO_2) **[30]**, nitrogen dioxide (NO_2) **[32]**, p-benzoquinone, chloranil **[30]**, air, N_2O_3 or Nitrobenzene **[29-30]** can be associated with a Lewis acid such as aluminium chloride **[33]**.

4.1 (b) Factors affecting the reaction

In the case of binary catalysts it was found that the Lewis acid-oxidant ratio had an important effect on benzene polymerization. With the $AlCl_3$-$CuCl_2$ system the polymer yield increased considerably as the $AlCl_3/CuCl_2$ ratio increased, and an almost quantitative yield of 98% was attained with a ratio of 2: 1. In contrast, the addition of large amounts of $CuCl_2$ inhibited polymerization completely and the presence of water was also detrimental **[29-30]**.

4.1 (c) Modifications in Kovacic Method

A slight modification of the procedure was made recently by using the cuprous chloride CuCl-$AlCl_3$ system in the presence of oxygen for the polymerization of benzene **[34]** according to the reaction below:

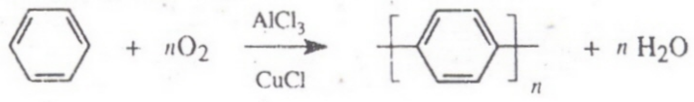


Figure 4.3: Reaction showing polymerization of benzene using CuCl-AlCl$_3$ system

Under these conditions, a soluble double aluminium-copper (I) chloride salt ($AlCuCl_4$) was formed and polymerization is initiated by a benzene radical-cation species. The polymerization was slow and PPP is obtained as a dark brown solid, insoluble in all organic solvents, with a molecular weight lower than that of PPP obtained by the usual Kovavic route.

Generally, poly (p-phenylenes) obtained under Kovacic's conditions are powdery materials which exhibit more or less crystallinity. Thus, in the case of PPP synthesis from benzene with $AlCl_3$-$CuCl_2$[35], the powder was found to consist of small fibrils associated in heterogeneous microdomains corresponding to rods or globules surrounded with micropowder. The rods ranged from 300 to 500 µm in length and 50 and 100 µm in diameter while the fibrils were only 100 nm in diameter. The globular structures, a few nm in diameter, resulted from a packing of the fibrils, and the crystallinity of the whole powder could be increased by annealing at 400°C [35].

Another interesting improvement on the Kovacic method was proposed by Arnautov et al. [36] who synthesized poly (p-phenylenes) with controlled molecular weights by using an ionic liquid as the solvent. In a typical procedure the $AlCl_3$-butylpyridinium chloride mixture (molar ratio 2: 1) constituted an ionic medium in which $CuCl_2$ was dissolved. By the addition of controlled amounts of benzene and reaction of the mixture at room temperature for one day, PPPs with DPs ranging up to 25 were obtained. These relatively high molecular weights were attributed to the fact that the solubility of poly (p-phenylene) is higher than in the usual organic solvents [36].

4.2.2 Single catalyst systems

This type of catalyst the reagent used to polymerize benzene has the properties both of a Lewis acid and of an oxidizing agent. The most usual catalysts are: $FeCl_3$ [37-39], $MoCl_5$ [39, 40], AsF_5 [41] and SbF_5 [42] associated with water as a co-catalyst, which appears to determine the polymerization kinetics. In particular, with $FeCl_3$ as the catalyst and for short reaction times, the rate of polymerization was enhanced when the molar ratio of H_2O to $FeCl_3$ was about unity. For long reaction times, this ratio was less important and polymers were obtained in high yield, but mixed with polynuclear structures and significant amounts of chlorine.[37]

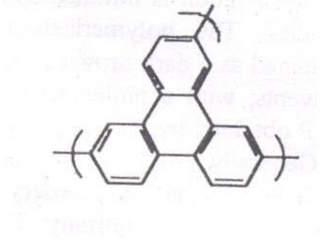


Figure 4.4: Polynuclear Structures

Well-developed fibrillar structures were formed when the polymerization was carried out with $MoCl_5$ [40], whereas PPP aggregates of indefinite shapes were observed with $FeCl_3$ as catalyst. The formation of the fibrils was interpreted as resulting from simultaneous polymerization and crystallization, and was attributed to the fact that benzene reacts with poly (p-phenylene) chain ends aligned on the crystalline surface of already precipitated PPP [40]. In the case of $FeCl_3$ the crystallinity of the PPP is less pronounced and it was suggested that benzene could form polyphenyl sidechains or polynuclear structures, which would prevent the formation of the fibrillar structures [37].

Poly (p-phenylene) was found to be processible when the polymerization was carried out in an arsenic trifluoride (AsF_3) solution, using AsF_5 gas as the polymerizing reagent. At a temperature between 25°C and 90°C, benzene or its derivatives polymerize and yield a homogeneous solution.

Thin conducting metallic poly (p-phenylene) films can be produced directly from oligomer films consisting of biphenyl, p-terphenyl, p-quaterphenyl, p-quinquephenyl or sexiphenyl by using Lewis acid gases such as AsF_5. In the case of terphenyl, it was found that after exposure to AsF_5 gas (400 Torr AsF_5 at room temperature for periods up to 24 hours) a highly conducting material (50 S cm^{-1}) resulted. After compensation with $(CH_3)_2NH$ and annealing at 400°C, the IR spectrum revealed a mean DP of 9 corresponding to a mixture of three oligomers with DPs of 6, 9 and 12. This confirmed that solid-state polymerization had occured. Under certain conditions poly (p-phenylene) with oriented chains can be obtained by solid-state polymerization of epitaxially grown poly (p–phenylene) oligomers.

To summarize, of all these different catalyst systems, it appears that the $AlCl_3$-$CuCl_2$ combination (Kovacic route) is probably the most suitable for obtaining poly (p-phenylene) with a low yield of polynuclear structures. Nevertheless, the method has some disadvantages.

4.2.2 (a) Limitations of Kovacic's Method

The molecular weights are low (the DP is not higher than 15), and, moreover, the PPPs contain large amounts of impurities such as oxygen, chlorine and catalyst residues [33, 43].

4.2 Catalytic and Thermal Aromatization of Poly (1, 3-Cyclohexadiene)

This reaction was based on the aromatization of the soluble poly (1, 3-cyctohexadiene) (PCHD) precursor, which is heated to give the PPP. The dehydrogenation reaction was run in the presence of a mild oxidant, at a temperature, which was selected with regard to the medium [44-45] and the nature of substituents attached to the cyclohexadiene moiety [46].

The key problem was to obtain the PCHD with the highest molecular weight (MW) and with the smallest number of defects. Among the early attempts, polymerization of 1, 3-cyc1ohexadiene to a linear polymer containing cyclohexene units was achieved by using a Ziegler catalyst consisting of a mixture of tri-isobutyl aluminium and titanium tetrachloride [44-45]. The best results were obtained at room temperature by using n--heptane or cyclohexane as the solvent but the polymers had low MWs ranging from 5000 to 10000. Treatment of this polymer with chloranil as the dehydrogenating agent led to a insoluble tan-brown powder, almost identical to p-quaterphenyl. Heating at 450°C for several hours under nitrogen yielded a black powder containing 90% poly (p–phenylene) and 10% carbon.

In comparison to several more or less efficient initiators (peroxides, Lewis acids, Ziegler catalysts), organolithium compounds were found to lead to PCHD with higher MWs. With n-butyllithium in heptane, 1, 3-cyclohexadiene polymerized with high conversion yields, and aromatization or partial dehydrogenation was performed either by reaction with chloranil or by bromination followed by dehydrobromination [45].

4.2 (a) Modifications

A quite different route was developed by Francois et al. with the view to obtaining soluble block copolymers containing long PPP chains [47-48]. Their method is based on the synthesis of a soluble polystyrene-poly (1, 3-cyclohexadiene) precursor (PS-PCHD) which is first aromatized to a soluble polystyrene (PS)-PPP block copolymer. In a further thermal treatment the PS sequences are decomposed, leaving pure PPP films or powders [49].

The PS-PCHD block copolymer was prepared by anionic polymerization. Methyl-lithium was used in a first step to polymerize styrene to PS and then 1, 3–cyclohexadiene was introduced and polymerized to the PCHD sequence. The 1, 2 polymerization of CHD was found to be negligible, and the 1, 4 units exceeded 99%.

Interestingly, films could be cast on quartz plates or KBr crystals from PS-PPP solutions, and after heating at 420°C for a few minutes in nitrogen atmosphere. PS was destroyed and PPP remained on the plate. The IR spectra indicated that the PPPs prepared by this procedure were similar to Kovacic's PPP. i.e. with DPs of not more than 10-15 [49].

This method seems to be of wide application and was extended to block polymers with poly (Thiophene) (PTh) sequences, (PS-PTh) and to poly (methylmethacrylate) blocks (PMMA) associated with PPP. The fact that these copolymer blocks have a micellar structure led to new organized polymers, with unexpected morphologies in the solid state, as for instance the regular honey-comb morphology, obtained with PS-PPP block copolymers [48].

4.3 Metal-Catalyzed Coupling Reactions

A great variety of reactions based on the coupling of 1, 4-disubstituted aromatic monomers in the presence of various metals have been investigated in order to generate high molecular weight all Para-linked poly (p-phenylene). Several new routes, based upon the use of transition metal catalysts, have been proposed. They can be classified into two main groups:

- In the first, Ni compounds promote the coupling of various 1, 4-disubstituted aromatic monomers such as dihalides, bistriflates and bisalkylsulfonates.
- The second route is based on the Suzuki reaction which consists in coupling aromatic boronic acids with halogenated aromatic compounds in the presence of a Pd (0) catalyst. Mild conditions, high selectivity, quantitative yields and high molecular weights are obtained. Structures and materials that were only dreamt of a few years ago are now available on a large scale and will soon be used in numerous applications.

4.4 Earlier Syntheses Using Metal-Calalyzed Coupling Reactions

4.4 (a) Wurtz-Fittig Reaction

One of the first synthesis of PPP was reported in 1949 by Goldfinger[50] who used a Wurtz-Fittig reaction shown below:

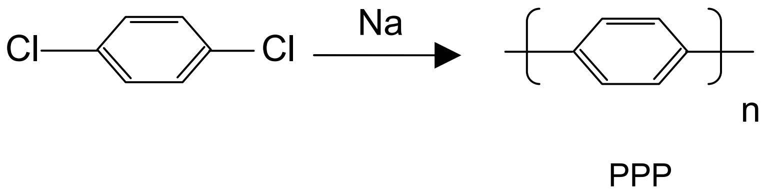


Figure 4.5: Wurtz-Fittig reaction for PPP

Goldfinger obtained a benzene-soluble polymer which had a molecular weight of 2700±500 (DP~34). The structure was considered to consist of phenyl and quinoid groups linked in the para position. This latter point was not proved and was in contradiction to the observed solubility, which does not indicate an all-para-linked polymer.

4.4 (b) Ullmann Reaction

The Ullmann reaction was also attempted for the synthesis of high molecular weight all-para-linked PPPs. Unfortunately, only low molecular weight products with structural irregularities were obtained, but generally the molecular weights and melting points were higher than those obtained by the Wurtz-Fittig reaction[51].

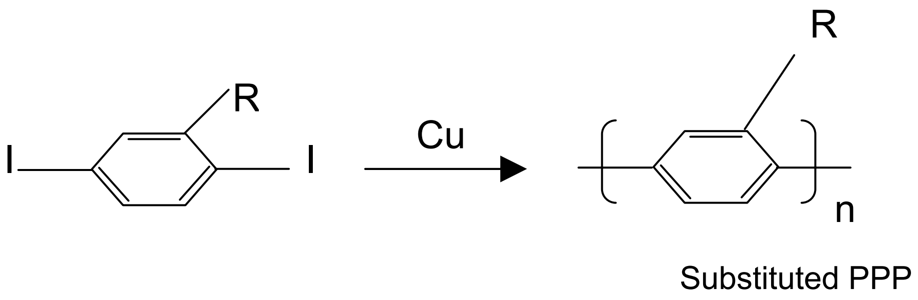


Figure 4.6: Ullmann reaction

The Ullmann reaction was found suitable for the polymerization of substituted phenylenes such as methyl [52]-, nitro [53]- and perfluorophenylene [54]. For instance, 3, 3' -dinitro-4, 4' -diodobiphenyl treated under Ullmann [53] conditions produced a bright yellow polymer with an average degree of polymerization of 52 as determined. Nitro substituents along the polymer back-bone increased the solubility in polar solvents, such as nitrobenzene and dimethylformamide, but the polymer remained insoluble in all other solvents.

4.4 (c) Grignard Method

The Grignard method of polymerization has also been used in the preparation of both meta-linked and substituted poly p–phenylenes [55-56]:

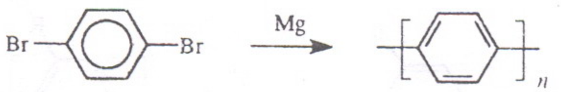


Figure 4.7: Grignard Method of Polymerization

This reaction usually yields higher molecular weight polymers than those obtained by the Wurtz-Fittig method but appears less efficient than the Ullmann synthesis. Recently, Taylor et al. [57] reported the coupling of the Grignard reagent of diaryl bromides in high yields using cis-l, 4-dichloro-2-butene as catalyst. PPP was produced but high molecular weights were not reached.

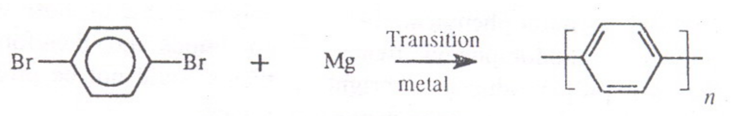
4.4 (d) Limitations

Other attempts to obtain high molecular weight PPP through the metal-catalyzed coupling route generally failed. The molecular weights were low and para linking was not observed, probably due to the high temperature required for dehalogenation by metals. The severe reaction conditions introduced some structural irregularities and branching in the final products. Moreover, the choice of substituent groups on the PPP backbones was restricted to those which could resist the reaction conditions and, therefore, PPPs with sensitive substituents could not be produced through these synthetic routes.

4.5 Ni-based catalytic systems/Yamamoto Method

The need for a more efficient and a more versatile synthetic route to PPP was filled by Yamamoto et al.[59] in the late 1970s. Results, indicating that transition metals or their complexes catalyze the coupling of Grignard reagents with aryl halides [58], were adapted to the coupling of dihalogen aromatic compounds. Mild conditions, high selectivity and quantitative yields were reported to be achieved when transition metal catalysts[58] were applied to the preparation of various organic aromatic compounds.

Indeed, p-dibromobenzene was readily dehalogenated and coupled in the presence of magnesium and transition metal compounds, yielding PPP with strictly linear chains:



PPP

Figure 4.8: Yamamoto Polymerization for PPP

A variety of transition metal complexes catalyze the reaction but the most efficient catalysts seem to be Ni (II) complexes [59]. In particular, the use of $NiCl_2$ (bpy) (bpy= 2, 2'-bipyridinc) leads to high yields under mild conditions. Four hours in refluxing THF produced a light-yellow material in 94% yield of which 20% was soluble in hot toluene. The polymer did not melt up to 550°C where it begins to decompose. $NiBr_2 (PPh_3)_2$ and $PbCl_2$ (bpy) also show high catalytic activities. Of the dihalobenzenes, p-dibromobenzene proved to be better than

p-diiodobenzene or p-dichlorobenzene.

4.5 (a) Kovacic vs. Yamamoto Method

The PPP obtained from Yamamoto method is much less colored than that prepared by the Kovacic method. The IR spectra present the main absorption bands of PPP. Molecular weights, based upon IR analysis, were initially estimated to be comparable to that of PPP prepared by Kovacic. The X-ray diffraction spectrum of the material showed strong, sharp peaks, indicating high crystallinity.

Elemental analysis showed that the Br content was between 6% and 8%, which is significantly higher than the halogen content of the Kovacic polymer (2% Cl) [33]. Neither polynuclear nor meta- or ortho-linked phenylene moieties were detected but the insolubility of the material prevents a full characterization of the structural defects. Although the polymer seems to be all-para-linked, the molecular weight remains low and the UV spectrum indicates a large distribution of chain lengths. IR spectroscopy suggests a DP of 9 which is significantly less than that estimated for the Kovacic material.

The Yamamoto procedure has been used to obtain substituted PPPs. In contrast to the Kovacic method, for which side-groups on the benzene unit induce electronic and steric perturbations that lead to a higher degree of defects in the PPP backbone, the metal-catalyzed procedure is very regiospecific and proves and interesting route to well defined all-para-linked substituted PPPs. Furthermore, it can be extended to phenyl nuclei bearing various organic substituents.

Although this procedure has been widely used and the material produced is often referred to as the Yamamoto PPP, there are no specific studies related to the mechanism or Yamamoto PPP synthesis, in marked contrast to mechanism of PPP synthesis by the Kovacic route. The mechanism postulated for the reaction is an extension of that proposed for the catalytic action of a transition metal on the coupling of a Grignard reagent RMgX with an aryl halide R´X [58], consisting of the following steps:

(a) Formation of NiR_2L_2 by reaction of NiX_2L_2 and RMgX

(b) Reaction of NiR_2L_2 with R'X to yield R-R and $NiR'XL_2$

(c) Alkylation of $NiR'XL_2$ with RMgX to yield $NiRR'L_2$ and MgX_2

(d) Elimination of R-R' with formation of $NiR'XL_2$ in the reaction of $NiRR'L_2$ with RX

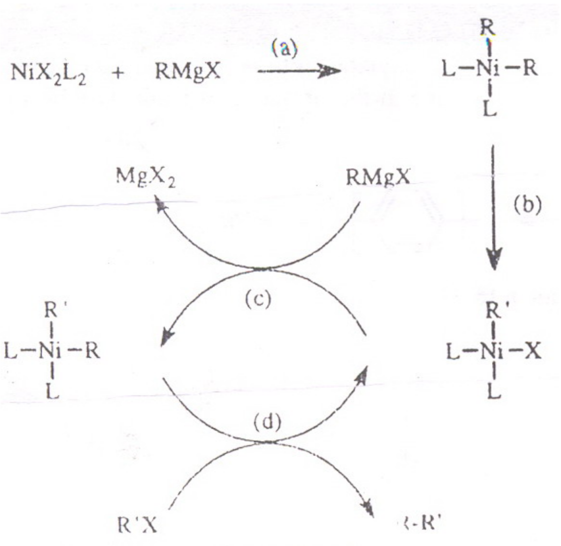


Figure 4.9: Mechanism of Yamamoto polymerization

Yamamoto et al. presented in their original study an adaptation of this reaction scheme to the polymerization of dihalobenzene [59] and noted that it was not fully compatible with experimental observations, since C_6H_5MgBr terminal units were not evidenced during the work-up of the polymer. This fact was attributed to the presence of trace amounts of water. They also reported that introducing C_6H_5MgBr or C_6H_5Br into the reaction vessel reduced the chain length of the material.

Maxdem Inc has patented several substituted PPPs [60]. Poly (2, 5-aniline) with a chain of more than 25 monomer units was produced after protection of the amino groups. The syntheses were apparently performed by the Yamamoto procedure. Poly (2-decyloxy-l, 4-phenylene) and poly (2-hydroxy-1, 4-phenylene) have been obtained using Yamamoto's procedure. The latter can be transformed into its sodium and tetrabutylammonium salts, which were described as self-doped n-type conducting polymers. Deprotonation strongly modifies the photoluminescent properties of the material but the electrical conductivity is only slightly affected.

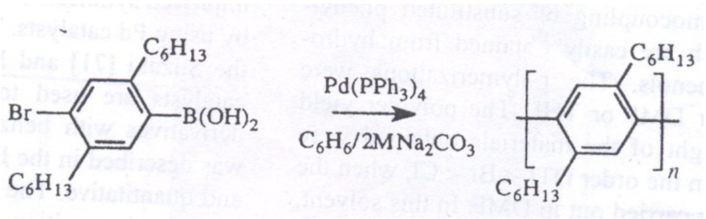
Recently, Yamamoto et al. presented a new route to PPP using the zero-valent nickel complex itself as a dehalogenation reagent. This reaction proceeds under mild conditions and can be applied to a wide range of aromatic compounds including those with carbonyl and cyano groups.

Among the substituted PPPs generated by Maxdem Inc., poly (benzoyl-l, 4-phenylene) [38] and poly (phenoxybenzoyl-l, 4-phenylene) [39] have been presented as the first thermoplastic poly (p-phenylene) [40] derivatives. These polymers can be moulded by injection or compression and can be cast as films from organic solvents. They have outstanding mechanical properties, considerably better than those of the best polymeric materials, and can even be compared to structural metals. Applications in the design and construction of military and commercial aircraft, sports and industrial equipment and automobile & components are proposed. Ni (0)-catalyzed polymerization by the Colon or Yamamoto procedure seems to be an easy and economically feasible synthetic route to a wide range of heterocyclic and phenyl-based polymers. High molecular weights are obtained and the past years have been rich in the synthesis of new materials and PPP subunits. Nevertheless, side.-groups such as halides, acids, alcohols, primary and secondary amines and nitro groups may interfere with the reaction and should be avoided or introduced in protected forms.

4.6 Pd-based catalytic systems/Suzuki Method

Looking for other transition metal-catalyzed coupling reactions, the Mainz research group achieved an improved synthesis of poly (p-2, 5-di-n-hexylphenylene) by using Pd catalysts. This procedure was adapted from the Suzuki [61] and Miller [62] reactions in which Pd catalysts are used to couple various bromo benzene derivatives with benzene boronic acid. This reaction was described as being highly selective and quantitative. The influence of substituents attached at the ortho position was reported to be negligible.

The 4-bromo-2,5-di-n-hexylbenzene boronic acid (1) was synthesized and allowed to react in a heterogeneous system of aqueous Na_2CO_3 and benzene in the presence of $Pd(PPh_3)_4$ under reflux for 2 days. A colorless polymer (2) was produced in 100% yield. The ^{13}C NMR spectrum was compared to that of the same material obtained by the Yamamoto procedure. It established clearly the all-para-linked polymer structure and indicated, by the absence of end-group signals, a high molecular weight, which constitutes a clear improvement upon the Yamamoto procedure. Osmometry and GPC experiments indicated a DP of over 28.It shown in the scheme below:



(1) (2)

Figure 4.10: Suzuki Polymerization for substituted PPP

Since this publication, the Suzuki route to substituted PPPs has been extensively used and new polymeric materials have been synthesized. It has been recognized as a very efficient means of coupling starting materials with a wide variety of ortho functional groups. Monomers containing nitro, keto or ether functions can be condensed without any complication. Relatively high degrees of polymerization can be achieved and keto substituents appear to increase the rate of aryl-aryl coupling considerably.

Copolymerization of substituted and unsubstituted monomers was also investigated [63]. The density of side-chains along the PPP backbone was slowly decreased by varying the ratio of substituted to nonsubstituted monomers in the reaction mixture. Copolymers exhibit statistically distributed repeating units; no evidence for alternation or for block-sequences was found. There was a marked effect on the UV spectra, indicative of a modification in the extent of conjugation between adjacent benzene rings induced by side-chains. This effect is linked to steric hindrance and it shows that a disubstituted benzene unit acts as an electronic insulator between unsubstituted blocks of PPP. DPs of 50 were reported for these copolymers.

PPP derivatives with a controlled number of side chains have been obtained by copolymerization of functionalized telomers. This approach allows the construction of PPP derivatives with well defined blocks of unsubstituted units of variable length linked to each other by only one alkyl-substituted aromatic unit.

Several new polymeric structures were obtained by means of the Suzuki reaction. They combine terphenyl subunits with other organic functional groups, thus illustrating the versatility of this reaction.

The Suzuki reactions and the substituted PPP produced by this route have also been used in order to obtain ladder-type polymers [64]. These polymers possess a two-dimensional structure and incorporation of the π chain into a rigid ladder allows full conjugation. π-Extended systems of the ladder type are expected to show small HOMO /LUMO energy differences and high hyperpolarizability. The optical, electrical, photoelectrical and non-linear optical properties of these materials appear to show great promise. The organic electroluminescent diode is an example of the expected future applications of such materials. The availability of substituted PPP has notably influenced research towards ladder-type polymers. The ladder-type frame is obtained in a two-step process consisting of:

(1) Formation of a suitable functionalized open-chain precursor
(2) Subsequent intramolecular ring closure

As an example, tetra (tert-butyl) ter-, quater- and quinquenaphythyls were obtained via Suzuki coupling of naphthalene containing bromo and boronic acid functions [65-66]. The Suzuki reaction has also been used to prepare a water-soluble hyperbranched poly (p-phenylene).

4.7 Conclusion

Within only a few years, Ni (0) and Pd (0) catalysts have proved to be outstanding tools for the synthesis of various kinds of polyarylenes. Polymers that were only dreamt of some years ago are now reality. In metal-catalyzed couplings, it is important to control and minimize side reactions in order to achieve higher molecular weights.

Technological applications in areas as diverse as military aircraft components and light-emitting diodes are predicted. One of the most striking and appealing features of these coupling reactions is the perfect structure control that is achieved by means of a simple synthetic procedure. This, associated with the versatility of the method, promises an extensive use of these reactions in the future. Furthermore, the catalytic activity of the Ni (0) and Pd (0) compounds is generally high. In most cases good results are obtained with 0.5% or less of the metal complex. This drastically reduces the impact of the use of relatively expensive metal complexes on the overall cost of the process.

CHAPTER V

EXPERIMENTAL WORK

5. EXPERIMENTAL WORK

5. 1 SYNTHESIS OF POLY (p-PHENYLENE) (PPP) POLYMER

Cupric Chloride ($CuCl_2.5H_2O$) was made anhydrous by heating at around 120°C temperature in a Vacuum oven for the 24 hours. Benzene (2 moles or156 gram or 178 ml) and Kovacic mixture of $AlCl_3$ (1 mole or 133.34g) and $CuCl_2$ (1 mole or 134.48 g) were mixed together to form a homogeneous mixture. The Benzene taken in 1 liter beaker and mechanical stirring used. The Kovacic mixture was added to the Benzene within 1 hour with continuous stirring. With the addition of this mixture intense fumes of HCl comes out. With the addition of $AlCl_3$-$CuCl_2$ mixture the viscosity of the reaction mixture started increasing. Temperature for the reaction required is 35-40°C. The stirring was continued for about 4 hours. The reaction mixture started turning green with the polymerization.

Precautions

(1) The monomer should be dry and should be measure under dry conditions.

(2) The stirring should be maintained adequately

(3) The $AlCl_3$-$CuCl_2$ mixture has to be completely dry. Mixed with monomer continuously and uniformly.

Washing

A warm solution of water and HCl was used to wash the above synthesized polymer. It was washed till it gave a transparent filtrate. After this, wash the polymer with warm water to remove all the HCl and thus to make it neutral.

Drying

The polymer was then dried at a temperature of about 60-70°C. After drying it became dirty green in color.

Solubility

The polymer was Insoluble in all the common organic solvents like chloroform, carbon tetrachloride, toluene, tetrahydrofuran (THF), benzene, NMP, xylene etc.

5.2 SYNTHESIS OF CO-POLYMER OF BENZENE AND PERYLENE (Bpery)

Benzene (2 moles or156 gram or 178 ml) and Perylene (0.002 mole or 0.50464 gram) and Kovacic mixture of $AlCl_3$ (1 mole or 133.34g) and $CuCl_2$ (1 mole or 134.48 g) were mixed together to form a homogeneous mixture. Cupric Chloride ($CuCl_2.5H_2O$) was made anhydrous by heating at around 120°C temperature in a Vacuum oven for the 24 hours. The Benzene and Perylene taken in 1 liter beaker and mechanical stirring used. The perylene completely dissolved in benzene The Kovacic mixture was added to the solution Benzene and Perylene within 1 hour with continuous stirring. With the addition of this mixture intense fumes of HCl comes out and the color of the mixture turns dark blue. With the addition of $AlCl_3$-$CuCl_2$ mixture the viscosity of the reaction mixture started increasing. Temperature for the reaction required is 35-40°C. The stirring was continued for about 4 hours. The reaction mixture started turning green with the polymerization.

Precautions

(1) The monomer should be dry and should be measure under dry conditions.

(2) The stirring should be maintained adequately

(3) The $AlCl_3$-$CuCl_2$ mixture has to be completely dry. Mixed with monomer continuously and uniformly.

Washing

A warm solution of water and HCl (1:1) was used to wash the above synthesized polymer. It was washed till it gave a transparent filtrate. After this, wash the copolymer with warm distilled water to remove all the HCl and thus to make it neutral.

Drying

The copolymer was then dried at a temperature of about 60-70°C. After drying it became Brown in color.

Solubility

The copolymer was Insoluble in all the common organic solvents like chloroform, carbon tetrachloride, toluene, tetrahydrofuran, benzene, NMP, xylene etc.

Purification of the polymer

The polymer reflux in benzene for the 24 hours at 90 ^{o}C and filter the solution with whatman filter paper No.4 Yellow color solution obtained which give green fluorescence under the UV lamp and the red brown residue i.e. polymer. The polymer obtained after the reflux futher reflux with benzene and similar thing was obtained. The fresh polymer was taken and reflux with chloroform for the 24 hours at 80 ^{o}C and filter the solution with Whatman filter paper no.4 dark yellow color solution obtained which give green fluorescence after dilution under the UV lamp and the red brown residue (polymer) on further reflux no color solution obtained

5.3 SYNTHESIS OF COPOLYMER OF TOLUENE AND PERYLENE (TP)

Cupric Chloride ($CuCl_2.5H_2O$) was made anhydrous by heating at around 120°C temperature in a Vacuum oven for the 24 hours. Toluene (2 moles or 186 gram or 210.85 ml) and Perylene (0.002 mole or 0.50464 gram) and Kovacic mixture of $AlCl_3$ (1 mole or 133.34g) and $CuCl_2$ (1 mole or 134.48 g) were mixed together to form a homogeneous mixture. The Toluene and Perylene taken in 1liter beaker and mechanical stirring used. The perylene completely dissolved in Toluene. The Kovacic mixture was added to the solution Toluene and perylene within 1 hour with continuous stirring. With the addition of this mixture intense fumes of HCl comes out. With the addition of $AlCl_3$-$CuCl_2$ mixture the viscosity of the reaction mixture started increasing. Temperature for the reaction required is 35-40°C. The stirring was continued for about 4 hours. The reaction mixture started turning green with the polymerization.

Precautions

(1) The monomer should be dry and should be measure under dry conditions.

(2) The stirring should be maintained adequately

(3) The $AlCl_3$-$CuCl_2$ mixture has to be completely dry. Mixed with monomer continuously and uniformly.

Washing

A warm solution of water and HCl (1:1) was used to wash the above-synthesized polymer. It was washed till it gave a transparent filtrate. After this, wash the copolymer with warm distilled water to remove all the HCl and thus to make it neutral.

Drying

The copolymer was then dried at a temperature of about 60-70°C. After drying it became Dark red brown in color.

Solubility

The copolymer was completely soluble in all the common organic solvents like chloroform, carbon tetrachloride, toluene, THF, benzene, NMP, xylene etc.

Purification of the polymer

The polymer was purified by column chromatography silica used for the column was 60-120 mesh size and the eliuent use for the column was chloroform and cyclo-hexane in the ratio 1:99. The different fractions were reported.

(4) SYNTHESIS OF COPOLYMER OF BENZENE AND PENTACENE (BPent)

Cupric Chloride ($CuCl_2.5H_2O$) was made anhydrous by heating at around 120°C temperature in a Vacuum oven for the 24 hours. Toluene (2 moles or 156 gram or 178 ml) and Pentacene (0.002 mole or 0.5568 gram) and Kovacic mixture of $AlCl_3$ (1 mole or 133.34g) and $CuCl_2$ (1 mole or 134.48 g) were mixed together to form a homogeneous mixture. The Benzene and Pentacene taken in 1liter beaker and mechanical stirring used. The pentacene completely dissolved in Benzene. The Kovacic mixture was added to the solution Benzene and pentacene within 1 hour with continuous stirring. With the addition of this mixture intense fumes of HCl comes out. With the addition of $AlCl_3$-$CuCl_2$ mixture the viscosity of the reaction mixture started increasing. Temperature for the reaction required is 35-40°C. The stirring was continued for about 4 hours. The reaction mixture started turning green with the polymerization.

Precautions

(1) The monomer should be dry and should be measure under dry conditions.

(2) The stirring should be maintained adequately

(3) The $AlCl_3$-$CuCl_2$ mixture has to be completely dry. Mixed with monomer continuously and uniformly.

Washing

A warm solution of water and HCl (1:1) was used to wash the above-synthesized polymer. It was washed till it gave a transparent filtrate. After this, wash the copolymer with warm distilled water to remove all the HCl and thus to make it neutral.

Drying

The copolymer was then dried at a temperature of about 60-70°C. After drying it became dark brown in color.

Solubility

The copolymer was completely Insoluble in all the common organic solvents like chloroform, carbon tetrachloride, toluene, THF, benzene, NMP, xylene etc.

5.5 *Device* Fabrications

5.5 (a) Device fabrication using copolymer of Toluene and Perylene as emitting layer

A double-layered light emitting diode was fabricated using copolymer of toluene and perylene as emitting layer. The device was fabricated on a patterned indium tin oxide (ITO) coated glass substrate having a sheet resistance of 15 ohms/square. The substrate was cleaned in an ultrasonic bath using neutral labogent solution, distilled water, acetone, trichloroethlene and then with isopropyl alcohol. A film of PEDOT was prepared by the spin coating with speed of 2000 rpm and the copolymer was deposited by Vacuum coating machine on ITO coated glass at 200^{o}C and 10^{-4} to 10^{-5} bar. A 200-300 nm thick layer of copolymer and nearly 300 nm aluminium, as cathode, was then vacuum deposited to make the device using a shadow mask. The voltage was applied between these two electrodes using an Alpha Power Supply to get emission under forward bias condition.

5.5 (b) Device fabrication using copolymer of Benzene and Perylene as emitting layer

A mono-layered light emitting diode was fabricated using Copolymer of benzene and perylene as emitting layer. The device was fabricated on a patterned indium tin oxide (ITO) coated glass substrate having a sheet resistance of 15 ohms/square. The substrate was cleaned in an ultrasonic bath using neutral labogent solution, distilled water, acetone, trichloroetlene and then with isopropyl alcohol. The copolymer was deposited on the glass substrate having a layer of ITO by vacuum deposition machine at below 200 ^{o}C and a pressure of 10^{-4} to 10^{-5} barr. The thickness of the copolymer layer was 200-400 nm. The aluminium was deposited by the vacuum deposition the thickness was 200-300 nm as cathode using the shadow mask.

5.5 (c) Device fabrication using copolymer of benzene and pentacene as emitting layer

A double-layered light emitting diode was fabricated using copolymer of benzene and pentacene as emitting layer. The device was fabricated on a patterned indium tin oxide (ITO) coated glass substrate having a sheet resistance of 15 ohms/square. The substrate was cleaned in an ultrasonic bath using neutral labogent solution, distilled water, acetone, trichloroethlene and then with isopropyl alcohol. A film of PEDOT was prepared by the spin coating with speed of 2000 rpm and the copolymer was prepared by Vacuum coating machine on ITO coated glass at 200 ^{o}C and 10^{-4} to 10^{-5}bar. A 200-300 nm thick layer of copolymer and nearly 300 nm aluminium, as cathode, was then vacuum deposited to make the device using a shadow mask. The voltage was applied between these two electrodes using an Alpha Power Supply to get emission under forward bias condition.

CHAPTER-VI

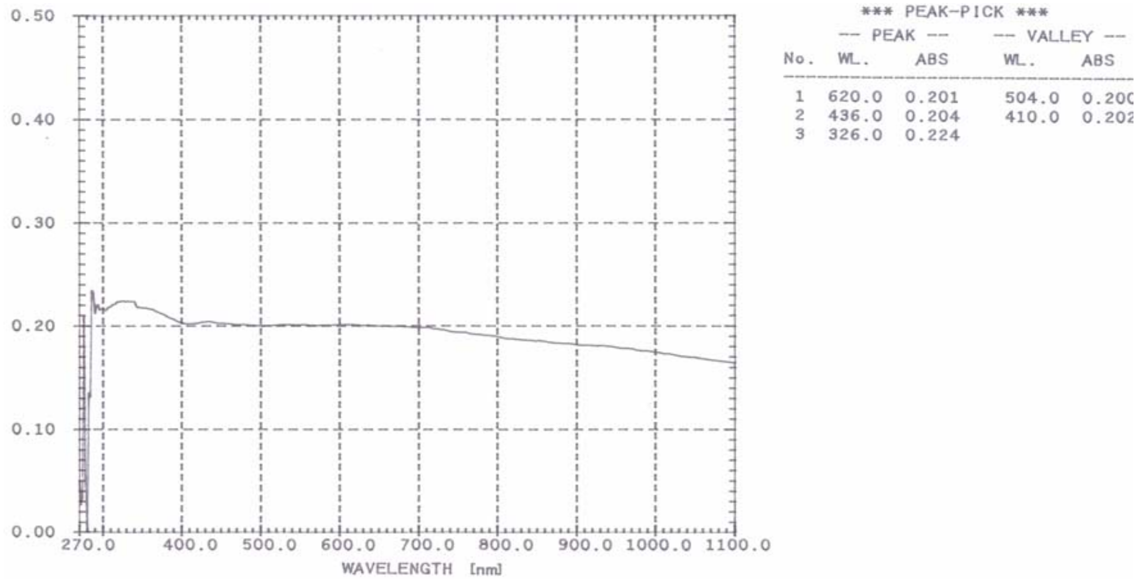
RESULTS AND DISCUSSION

6 RESULTS AND DISCUSSION

6.1 Poly p- Phenylene (PPP)

6.1 (a) UV-VIS Absorption Spectra of Poly (p-phenylene) polymer

UV-VIS Spectra of the Poly (p-phenylene) polymer was recorded on a Shimadzu UV-2401 Spectrophotometer. The sample was prepared in chloroform. The absorption peak was observed centred at 386 nm as shown in fig. (6.1)



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        *** PEAK-PICK ***
     -- PEAK --      -- VALLEY --
No.  WL.    ABS      WL.    ABS
---------------------------------
 1  620.0  0.201    504.0  0.20
 2  436.0  0.204    410.0  0.20
 3  326.0  0.224
```

Fig. 6.1 UV Spectra of Poly (p-phenylene)

6.1 (b) Themogravimetric analysis (TGA) of Poly (p-phenylene):

Thermogravimetric Analysis (TGA) of the synthesized Poly (p-phenylene) was carried out on Mettler Toledo Star System and shown in fig. (6.2) The TGA plot of the material shows loss in mass started at 320 ^{0}C due to the degradation of the polymer chain.The degradation of the polymer continues up to 680 ^{0}C.The total lose in the mass was 23.8975 %.

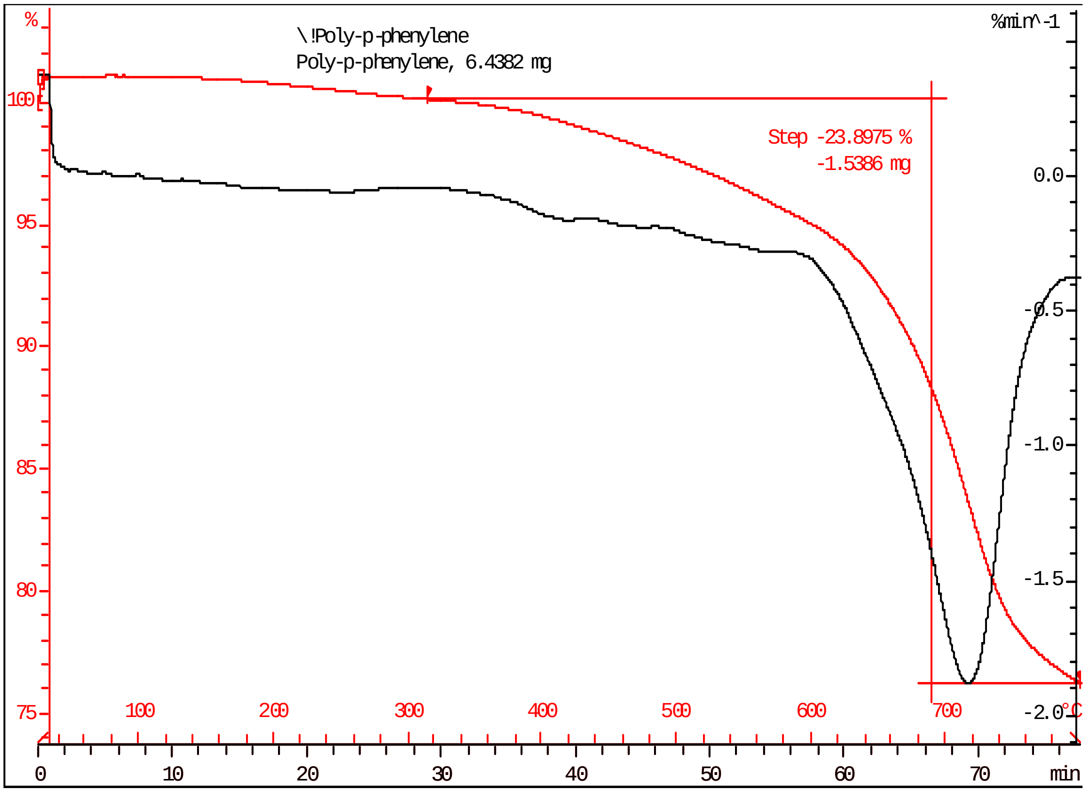

Fig 6.2 TGA graph for poly (p-phenylene)

6.1 (c) Morphology of the poly (p-phenylene) by Scanning Electron Microscope

The Scanning Electron Microscope microphotographs of the poly (p-phenylene) as can be seen from fig.6.3. The SEM morphology of the poly (p-phenylene) taken at different resolution from 1μm to 10μm.It can be concluded that poly (p-phenylene) is spherical in shape As the particle accumulated to form round sphere which was clearly shown in SEM picture. These spheres may be solid or hollow.

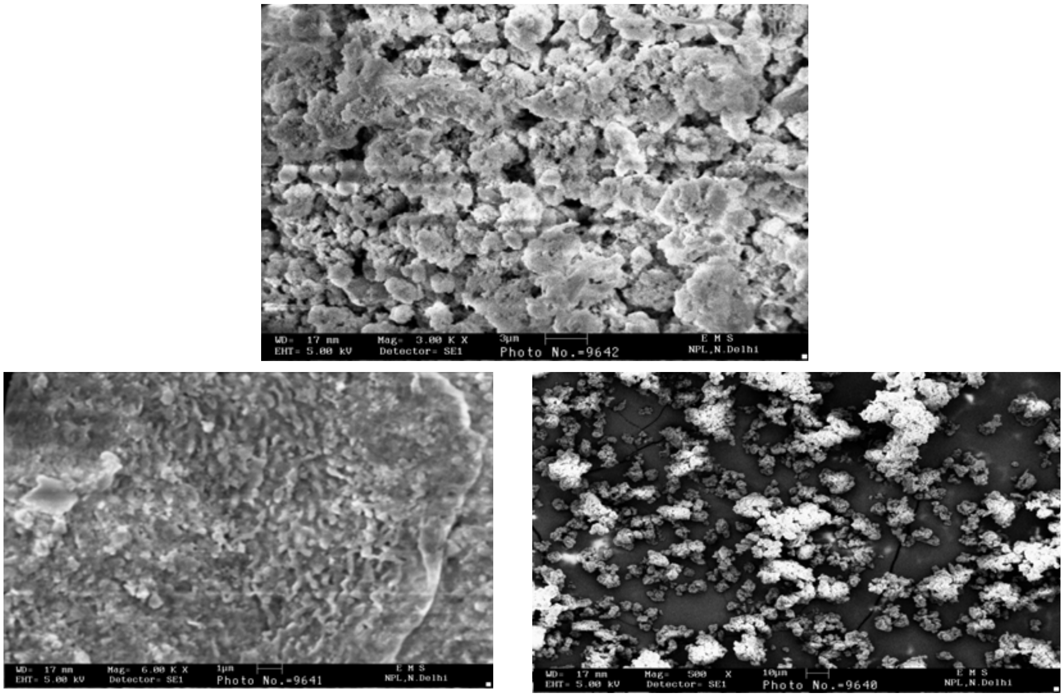

Fig.6.3 Scanning electron microscope for the poly (p-phenylene).

6.1 (d) FTIR Spectra of Poly (p-phenylene)

The sample of the polymer for FTIR was prepared in freshly cleaned dry KBr and the pellet of the sample was prepared by the hydraulic press. The FTIR spectrum was recorded as shown in fig. 6.4. The peak at 3027 and 2923 cm^{-1} was due to C—H Stretching vibrations of ring. The peaks at 1651, 1479 and 1400 cm^{-1} were due to quadrant and semi-circle stretching vibrations of rings. The C-H stretching in rings is also seen at 1116 and 999 cm^{-1}. The peak at 806 cm^{-1} shows the para substitution of the polymer. The C-H out of plane bending was present at 765 and 694 cm^{-1}.

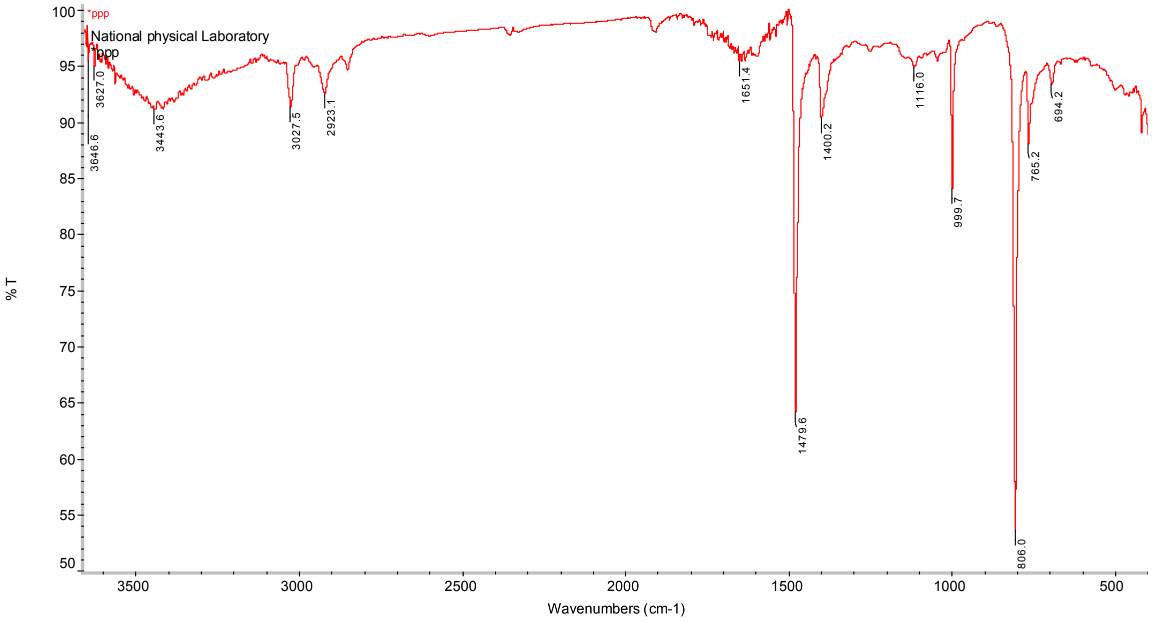

Fig. 6.4 FTIR spectra of Poly (p-Phenylene).

6.2 Copolymer of Benzene and Perylene (Bpery)

6.2 (a) UV-VIS Absorption Spectra of Copolymer of Benzene and perylene

UV-VIS Spectra of the Copolymer of benzene and perylene was recorded on a Shimadzu UV-2401 Spectrophotometer. The sample was prepared in chloroform of the fraction of the reflux Ist and IInd. In the Ist fraction absorption peak was observed centred at 455, 366 and 286 nm as shown in figure (6.5) .The absorption peak in the fraction IInd was also similar.

The absorption peaks of the polymer were obtained at the 454,429 and 280 nm in fig. (6.5)

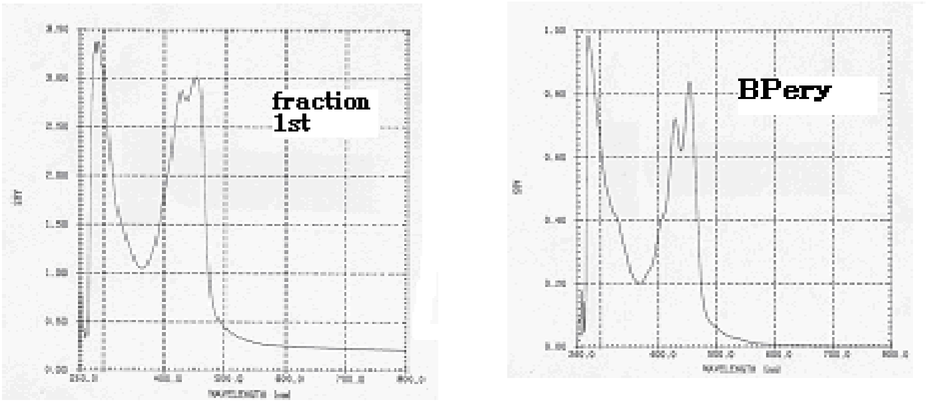

Fig. 6.5 UV spectra of the copolymer Benzene and perylene.

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6.2 (b) Themogravimetric analysis (TGA) of Co-polymer of Benzene and perylene

The Thermogravimetric Analysis (TGA) of the Co-polymer of Benzene and perylene was carried out on Mettler Toledo Star System and shown in fig. (6.6) The TGA plot of the material shows loss in mass started at 300 ^{0}C due to the degradation of the polymer chain.The degradation of the polymer continues up to 680 ^{0}C.The total lose in the mass was 22.8498 %.

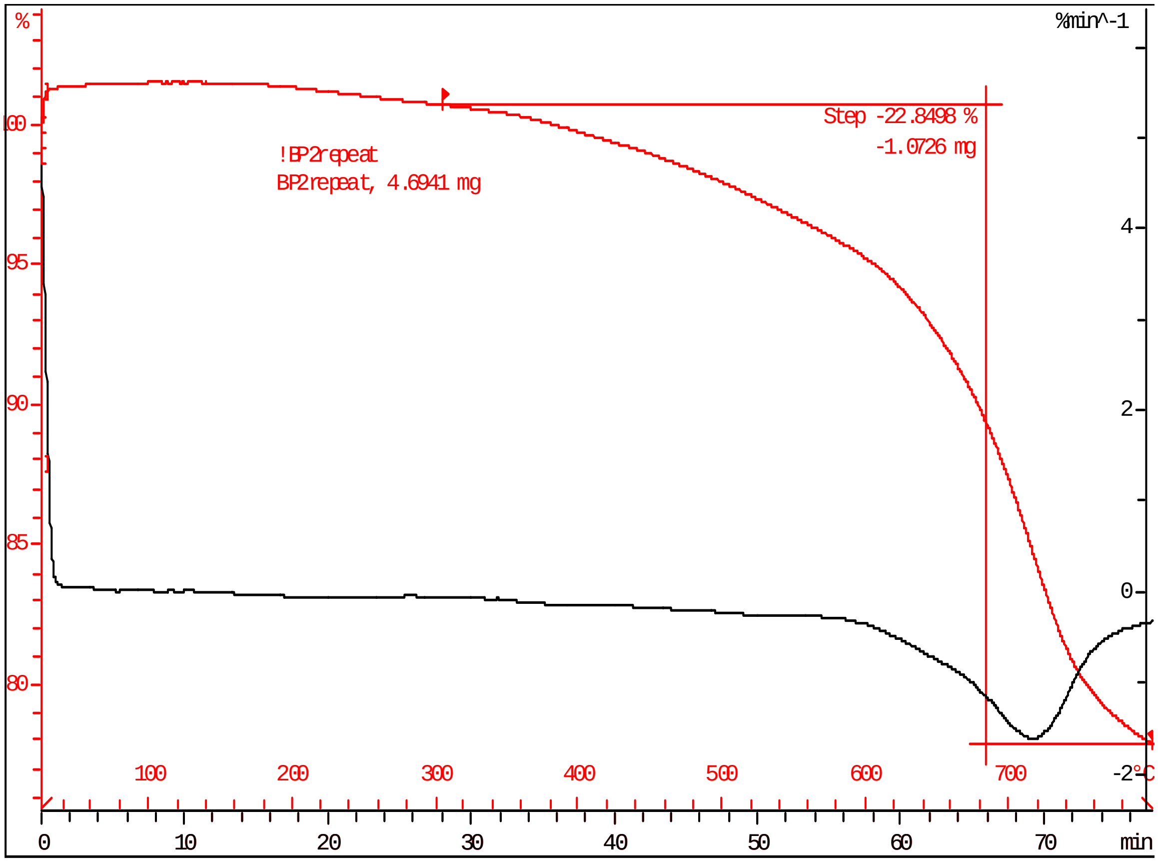


Fig.6.6 TGA graph of copolymer of Benzene and Perylene

6.2(c) Photoluminescence (PL) spectra of Copolymer of Benzene and Perylene

Under UV illumination, Copolymer of Benzene and perylene shows photoluminescence in the visible region. The sample was illuminated with strong 290 nm radiations from a strong UV source. Two characteristic peaks at 500 and 470 nm were observed as shown in figure (6.7). The absorption peaks at peak at 474 and 499 nm in fraction Ist **(B)** and adsorption peak at 452, 469 and 505 nm in the IInd **(C)** fraction.

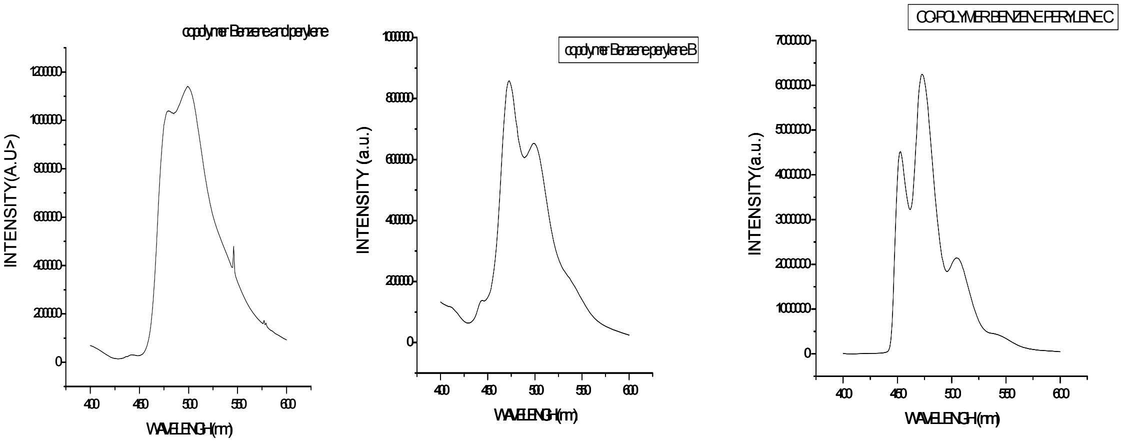


Fig. 6.7 PL spectra of the copolymer of Benzene and perylene

6.2 (d) Morphology of the copolymer of benzene and perylene by Scanning Electron Microscope.

The Scanning Electron Microscope microphotographs of the copolymer of benzene and perylene as can be seen from fig.6.8.The SEM morphology of the copolymer of benzene and perylene taken at different resolution from 1 to 10µm. It can be concluded that polymer was spherical in shape as the particle accumulated to form round sphere which was clearly shown in SEM picture. These spheres may be solid or hollow. The particles was accumulated so the show spherical in shape.

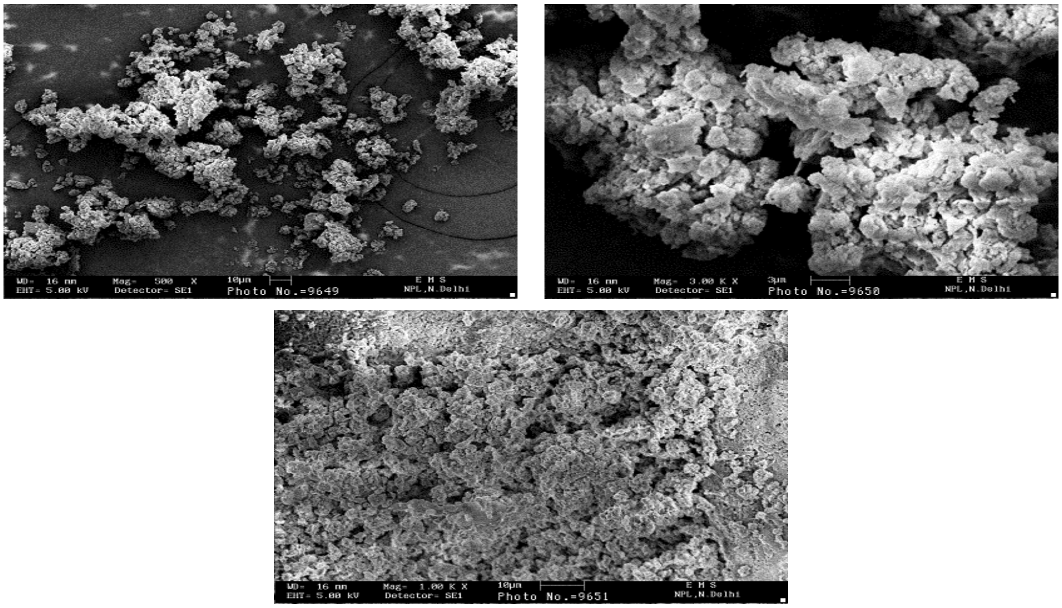


Fig. 6.8 SEM picture for the Copolymer of Benzene and Perylene

6.2 (e) FTIR Spectra of Copolymer of Benzene and Perylene

The sample of the polymer for FTIR was prepared in freshly cleaned dry KBr and the pellet of the sample was prepared by the hydraulic press. The FTIR spectrum was recorded as shown in fig. 6.9. The peak at 3027 cm^{-1}was due C-H stretching of Benzene ring in polymer while the peaks at 2923 and 2852 cm^{-1} was due to C—H Stretching vibrations of Perylene ring in the polymer. The band occurs in the 2000 to1700 cm^{-1} aromatic region. The peaks at 1634, 1541, 1507 and 1480 cm^{-1} were due to Quadrant and semi-circle stretching vibrations of rings. The C-C in plane stretching of aromatic ring present at 1118 and 1000 cm^{-1}. The peak at 806 cm^{-1} shows the para substitution of the polymer. The C-H out of plane bending present at 765 and 669 cm^{-1}.

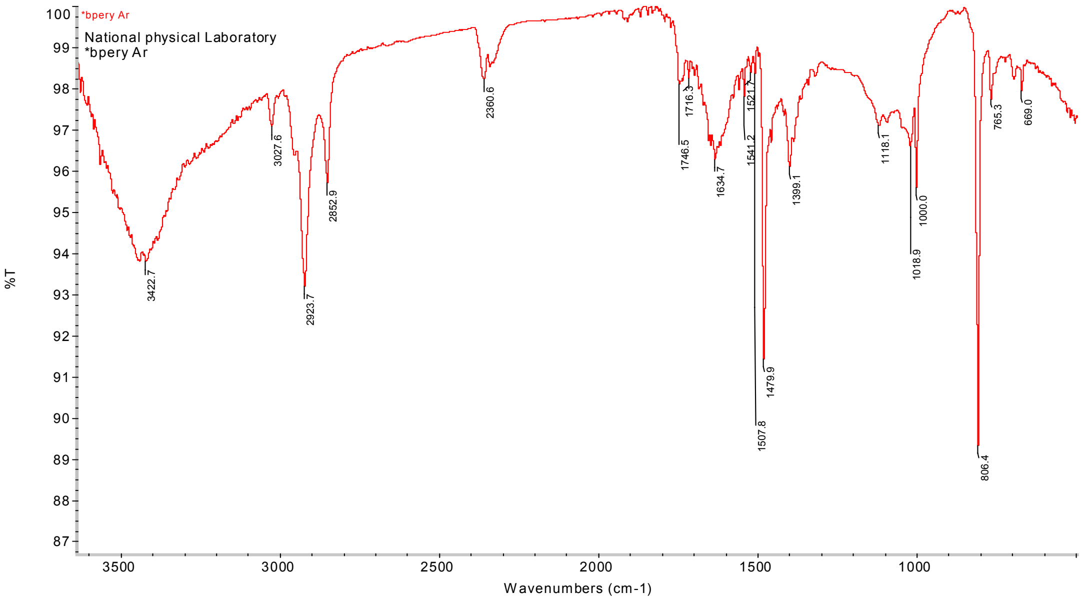


Fig.6.9 FTIR Spectra of Copolymer of Benzene and Perylene

6.3 Copolymer of Toluene and Perylene (TP)

6.3 (a) UV-VIS Absorption Spectra of Copolymer of Toluene and perylene

UV-VIS Spectra of the Copolymer of Toluene and perylene was recorded on a Shimadzu UV-2401 Spectrophotometer.

Fraction A The absorption peaks present at the 535, 420, 332 and 296 nm in the U.V. Spectra of fraction A was similar to the perylene monomer. As shown in the fig. (6.10)

Fraction B The absorption peaks were present at 529, 512, 492, 452 and 334 nm

Fraction C The absorption peaks were present at 530, 512, 496, 455 and 344 nm.

Fraction D The absorption peaks were present at 534, 513, 496, 438, 426, 416, 402 and 325 nm.

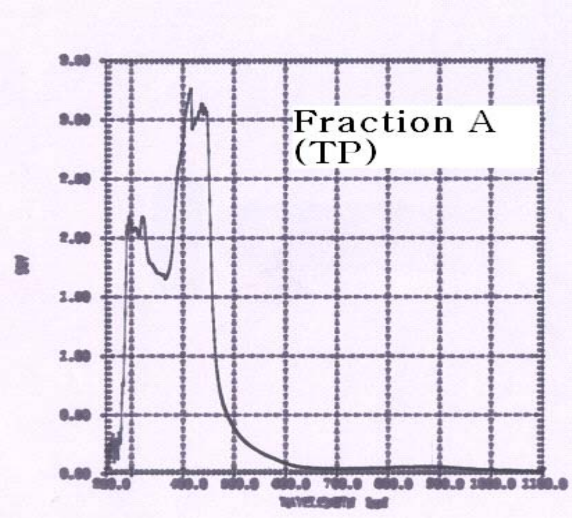
Fraction E The absorption peaks were present at 540, 528, 505, 488, 435, 423, 410, 399 and 338 nm.

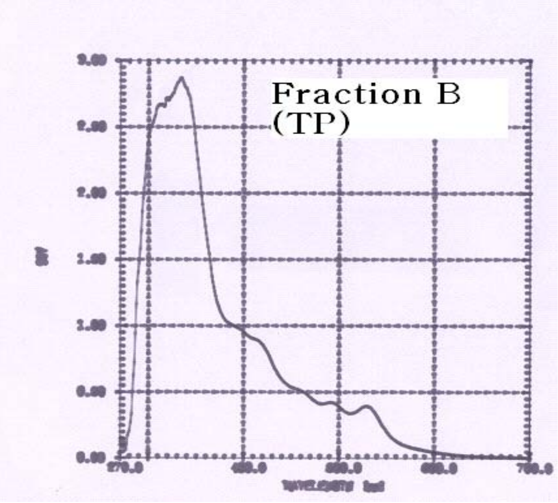
Fraction F The absorption peaks were present at 509, 494, 401, 389, 379, 370 and 295 nm.

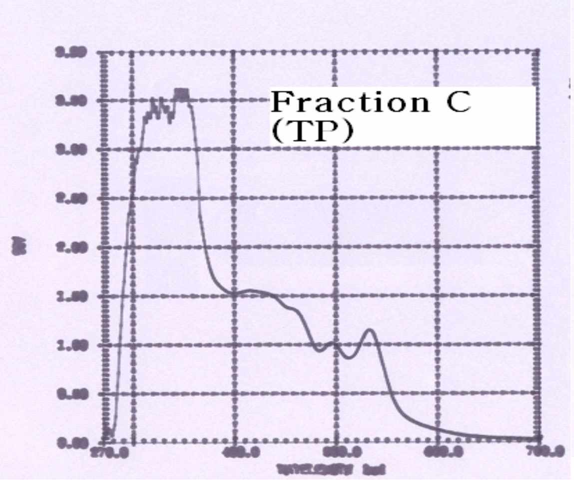
Fraction G The absorption peaks were present at 383, 373 and 296 nm.

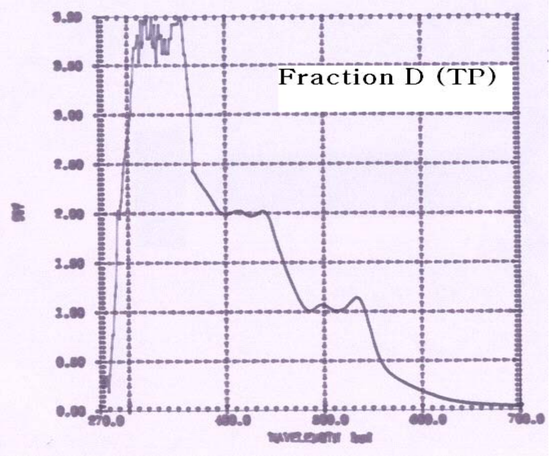
Fraction H The single absorption peak was present at 302 nm that means it was the purest form of the polymer.

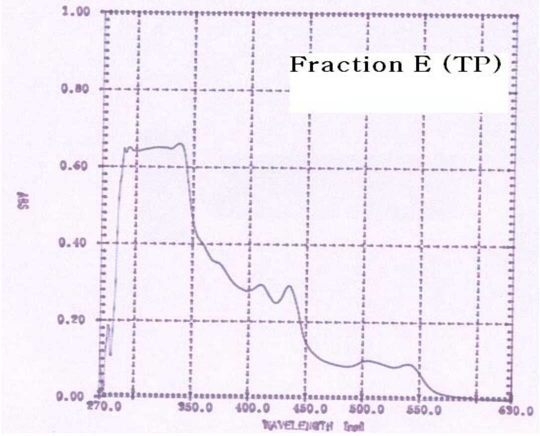
The U.V.-VIS Spectra of polymer was also taken after the vacuum deposition on glass plate.

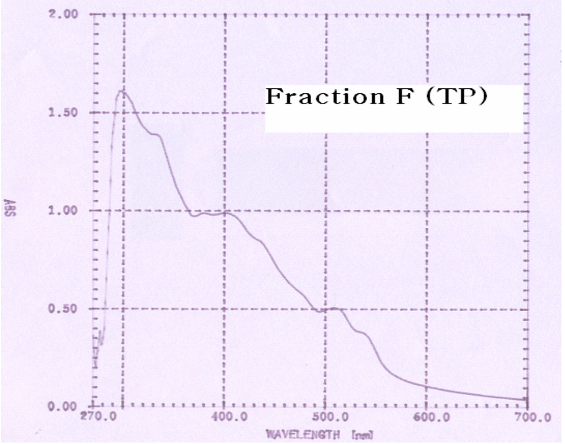

Fraction A (TP)


Fraction B (TP)


Fraction C (TP)


Fraction D (TP)


Fraction E (TP)


Fraction F (TP)

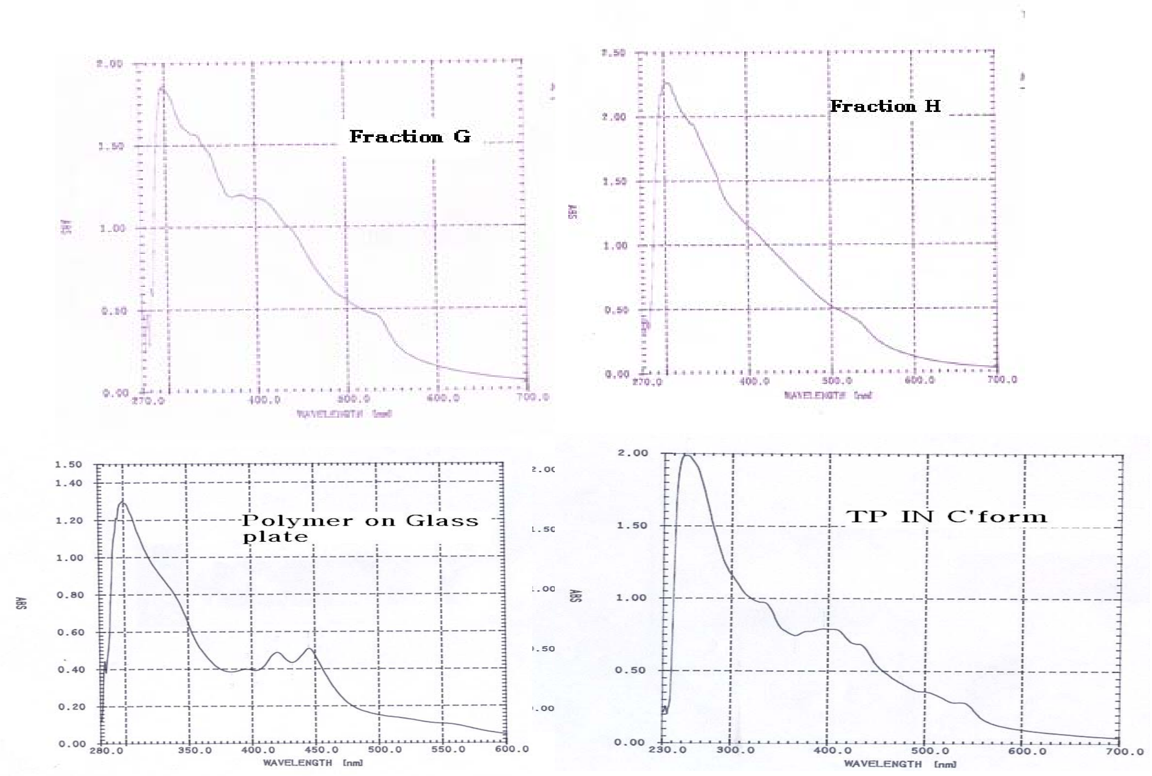


Fig.6.10 UV-VIS spectra of copolymer of Toluene and Perylene

6.3 (b) Themogravimetric analysis (TGA) of Copolymer of Toluene and Perylene

The Thermogravimetric Analysis (TGA) of the Co-polymer of toluene and perylene was carried out on Mettler Toledo Star System and shown in fig. 6.11. The TGA plot of the material shows loss in mass started at 180 ^{0}C due to small the degradation of the polymer chain substitute and moisure. The total loss in the mass was 4.0983 %.

The degradation of the polymer start at 400 ^{0}C continues up to 750 ^{0}C.The total lose in the mass was 14.9926 % in this step.

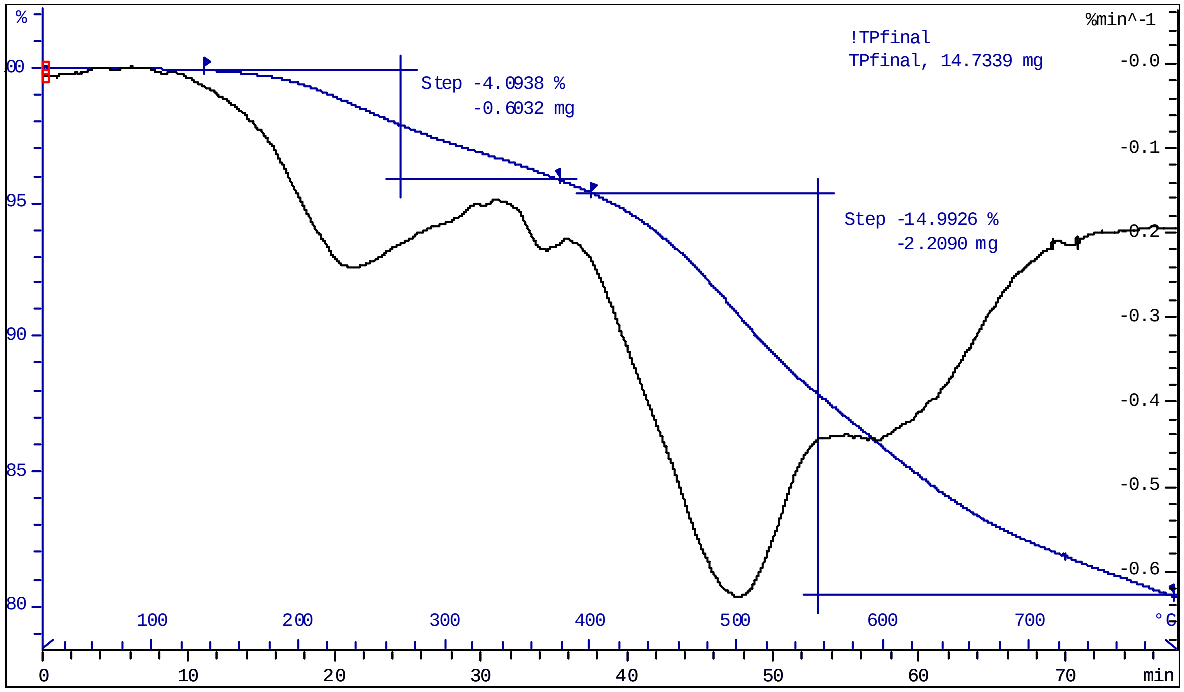


Fig.6.11 TGA graph of Copolymer of Toluene and Perylene

6.3 (c) Morphology of the Copolymer of toluene and perylene by Scanning Electron Microscope

The Scanning Electron Microscope microphotographs of the copolymer of toluene and perylene as can be seen from fig 6.12. The SEM morphology of the copolymer of toluene and perylene taken at different resolution from 1 to 10μm. It can be concluded that polymer was spherical in shape as the particle accumulated to form round sphere which was clearly shown in SEM picture. These spheres may be solid or hollow. The particles was accumulated so the show spherical in shape.

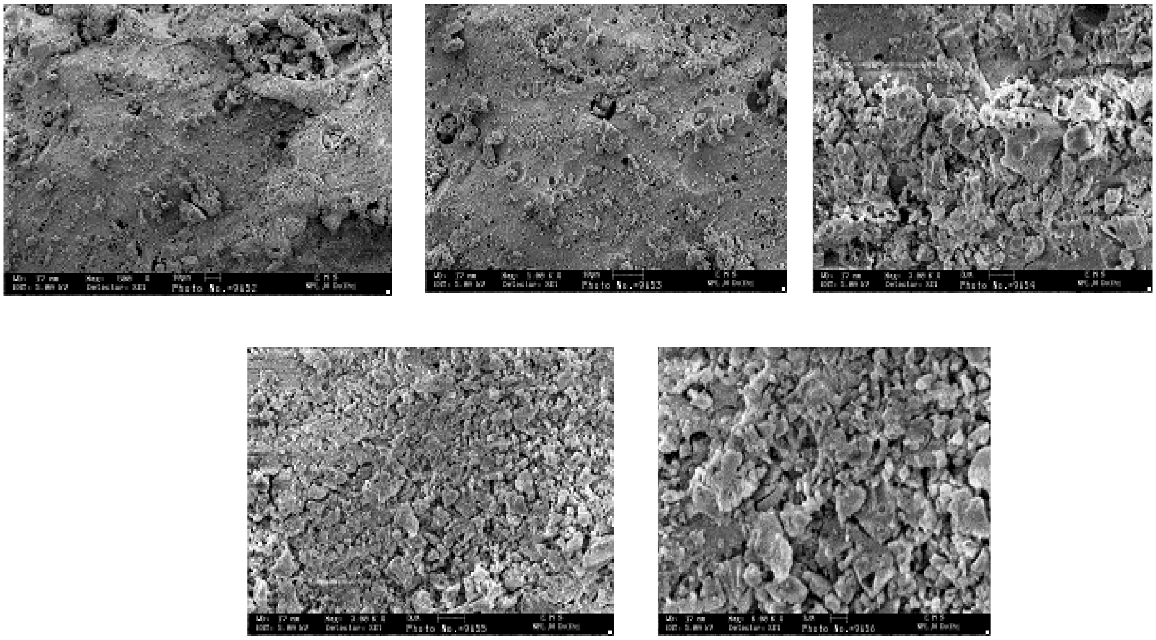


Fig. 6.12 SEM Picture of Copolymer of Toluene and Perylene

6.3 (d) Photoluminescence (PL) spectra of Copolymer of Toluene and Perylene

The photoluminescence was taken by HORIBA JOBIN YVON Instrument. The copolymer of the toluene and perylene shows photoluminescence in the visible region. The sample was illuminated by strong UV source with Xenon lamp. Photoluminescence of copolymer was carried out in chloroform solution and on film. The photoluminescence spectra of the different fractions were taken.

FRACTION A The peaks were come at 397, 423, 452, 472 and 505 nm.

FRACTION B The peaks of this fraction was a broad peak maxima came at 560 nm.

FRACTION C The peaks were come at 519 and 574 nm.

FRACTION D The peaks were come at 523 and 586 nm.

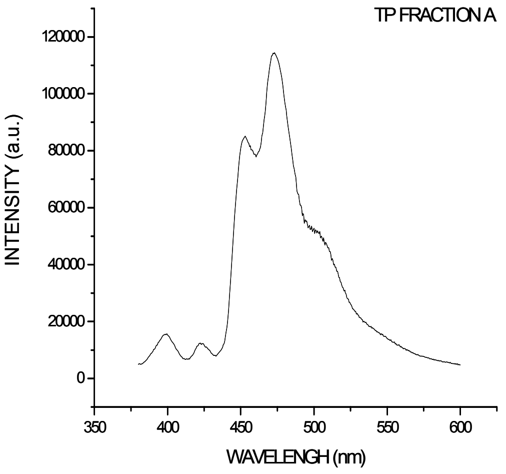
FRACTION E The peaks were at 493, 517 and 556 nm.

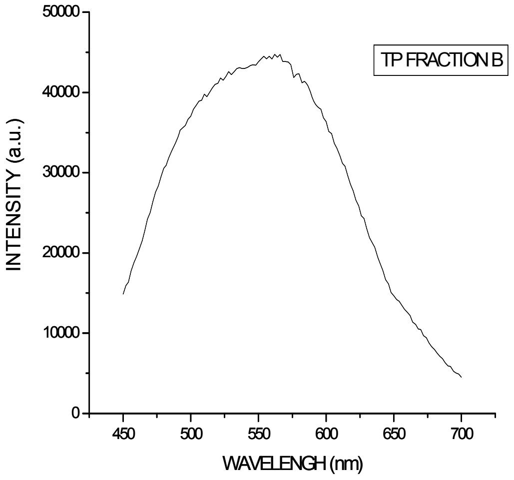
FRACTION F The peaks were at 455, 526, 567 and 601 nm.

FRACTION G The peaks were at 492, 524, 565, 582, 605, 623 and 657 nm.

FRACTION H The peaks were at 617 and 663 nm.

SPECTRA OF COPOLYMER ON GLASS PLATE The single peaks present at the 613 nm.


TP FRACTION A
INTENSITY (a.u.)
0
20000
40000
60000
80000
100000
120000
350
400
450
500
550
600
WAVELENGH (nm)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INTENSITY (a.u.)
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20000
30000
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600
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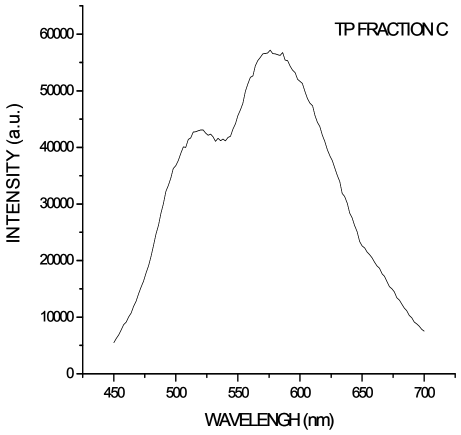
WAVELENGH (nm)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INTENSITY (a.u.)
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30000
40000
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60000
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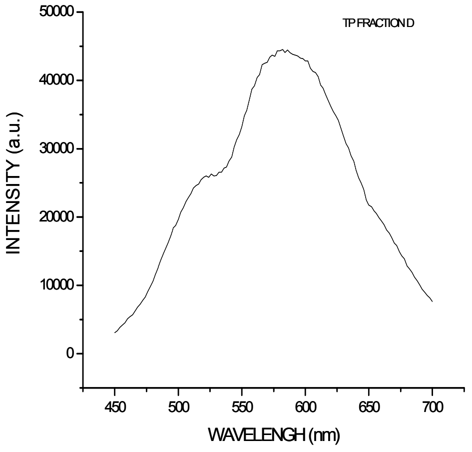
550
600
650
700
WAVELENGH (nm)


TP FRACTION D
INTENSITY (a.u.)
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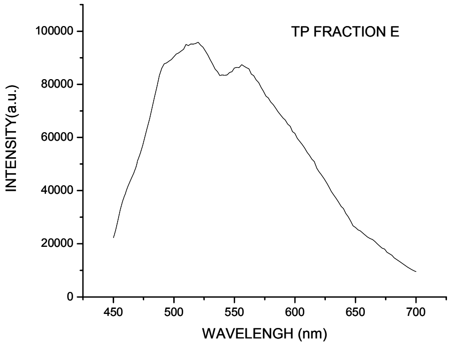
10000
20000
30000
40000
50000
450
500
550
600
650
700
WAVELENGH (nm)


TP FRACTION E
INTENSITY(a.u.)
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40000
60000
80000
100000
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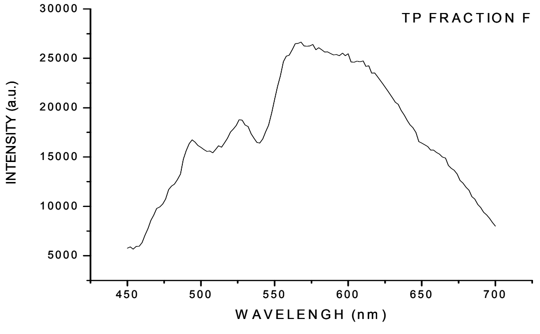
500
550
600
650
700
WAVELENGH (nm)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20000
25000
30000
450
500
550
600
650
700
WAVELENGH (nm)

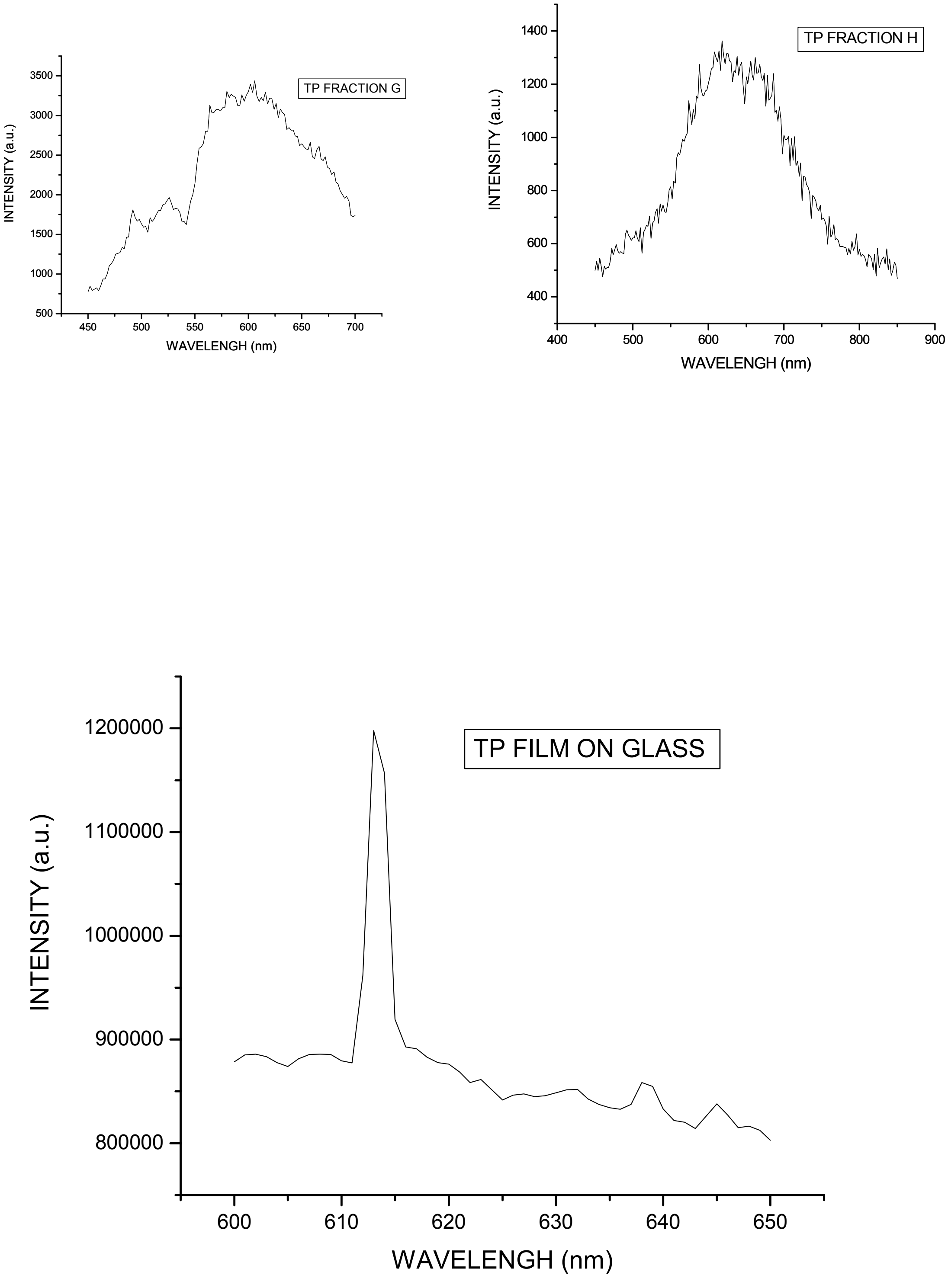


Fig. 6.13 Photoluminescent spectra of Copolymer of Toluene and Perylene.

6.3 (e) FTIR Spectra of Copolymer of Toluene and Perylene

The sample of the polymer for FTIR was prepared in freshly cleaned dry KBr and the pellet of the sample was prepared by the hydraulic press. The FTIR spectrum was recorded as shown in fig. 6.14. The peak at 3019 cm^{-1} was due to C—H Stretching vibrations of ring. The strong peaks at the 2918 and 2851 cm^{-1} show C—H stretching of methyl group asymmetric and symmetric vibration respectively. The peaks at 1651, 1613 and 1557 cm^{-1} were due to Quadrant and semi-circle stretching vibrations of rings. The C-H in plane stretching of methyl group also seen at 1448 and 1375 cm^{-1} asymmetric and symmetric peaks respectively. The peaks in the region of 1212 to 1020 cm^{-1} was due to the C-C stretching vibrations. The peak at 818 cm^{-1} shows the para substitution of the polymer. The C-H out of plane bending present at 752 and 667 cm^{-1}.

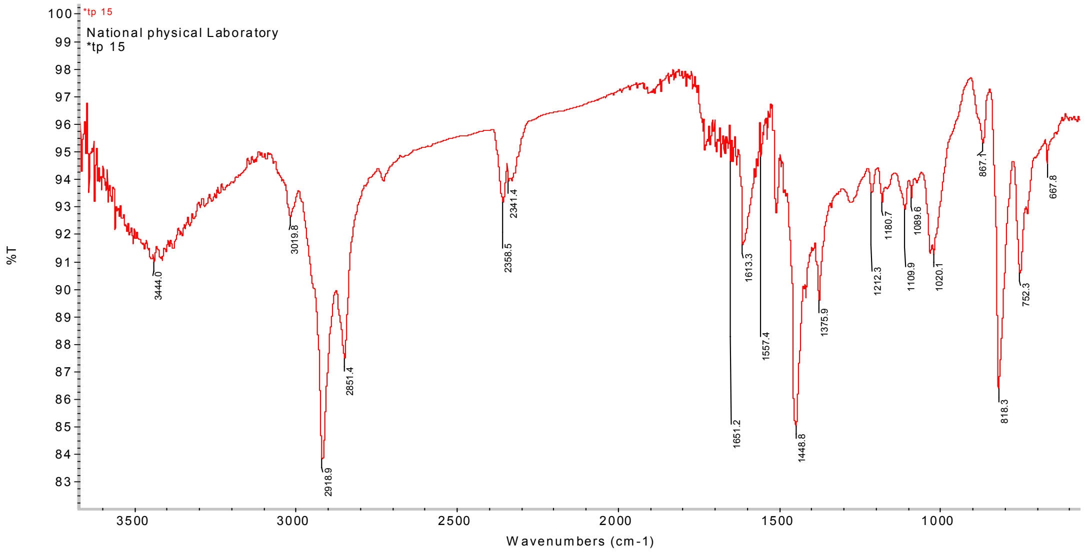
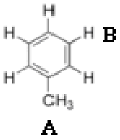
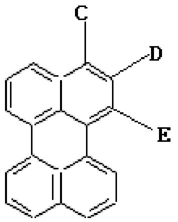


Fig. 6.14 FTIR Spectra of Copolymer of toluene and Perylene.

6.3 (f) NMR Spectra of Copolymer of Toluene and Perylene

The ^{1}H NMR spectrum of the polymer was taken on 400 MHz instrument in the $CDCl_3$ solvent. The peaks of the monomer toluene came at (a) (singlet) δ 2.34 and (b) (singlet) δ 7.17 and the perylene shows the peak at (C) δ 7.656 (D) δ 7.466 and (E) δ 8.196





The polymer show the peaks at (quintet) δ 7.52 due to proton on the perylene in the polymer and at (multiplet) δ 7.262 due to protons of the toluene in the polymer. The peak present at (multiplet) δ 1.66 due to methyl group present in the toluene.There were no peak of monomer found in the NMR Spectra.

6.3 (g) Electroluminescence (EL) Spectra of Co-polymer of Toluene and perylene

The Electroluminescent (EL) spectrum of ITO\PEDOT\TP\Al device was recorded applying a potential of 9 V across it. The photoluminescence maximum for copolymer of Toluene and perylene occurs at 613 nm, and the Electroluminescence emission maximum is found Red shifted and occurs at 698 nm as shown in fig. 6.15 and results in orange-red emission from the device. It was observed that the EL emission maximum was not dependent on the applied voltage and stayed fixed at 698 nm. Therefore the material could be used for orange red emitting device.

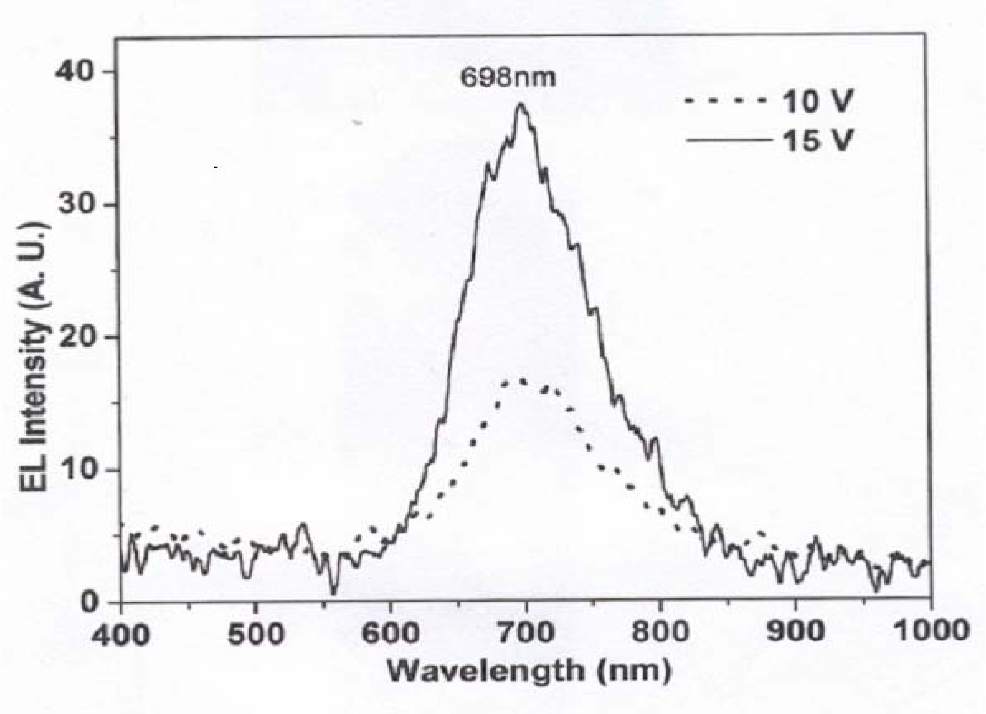


Fig.6.15. Electroluminescent Spectra of Copolymer of Toluene and Perylene.

6.3 (h) I-V Characterisation of copolymer of Toluene and Perylene

The current voltage (I-V) characteristics of the fabricated device were recorded by applying a dc voltage across the device with ITO as positive electrode and the aluminium as negative electrode (forward bias) as shown in Figure 6.16. The current voltage (I-V) characteristics show that the current start rising above 4V indicates the onset of light emission (threshold voltage). The I-V characteristics of the device show highly non-linear nature with ohmic conduction at low voltage and trap limited conduction at high voltage. An intense Red emission was observed from the device on applying a voltage of 11 V across it.

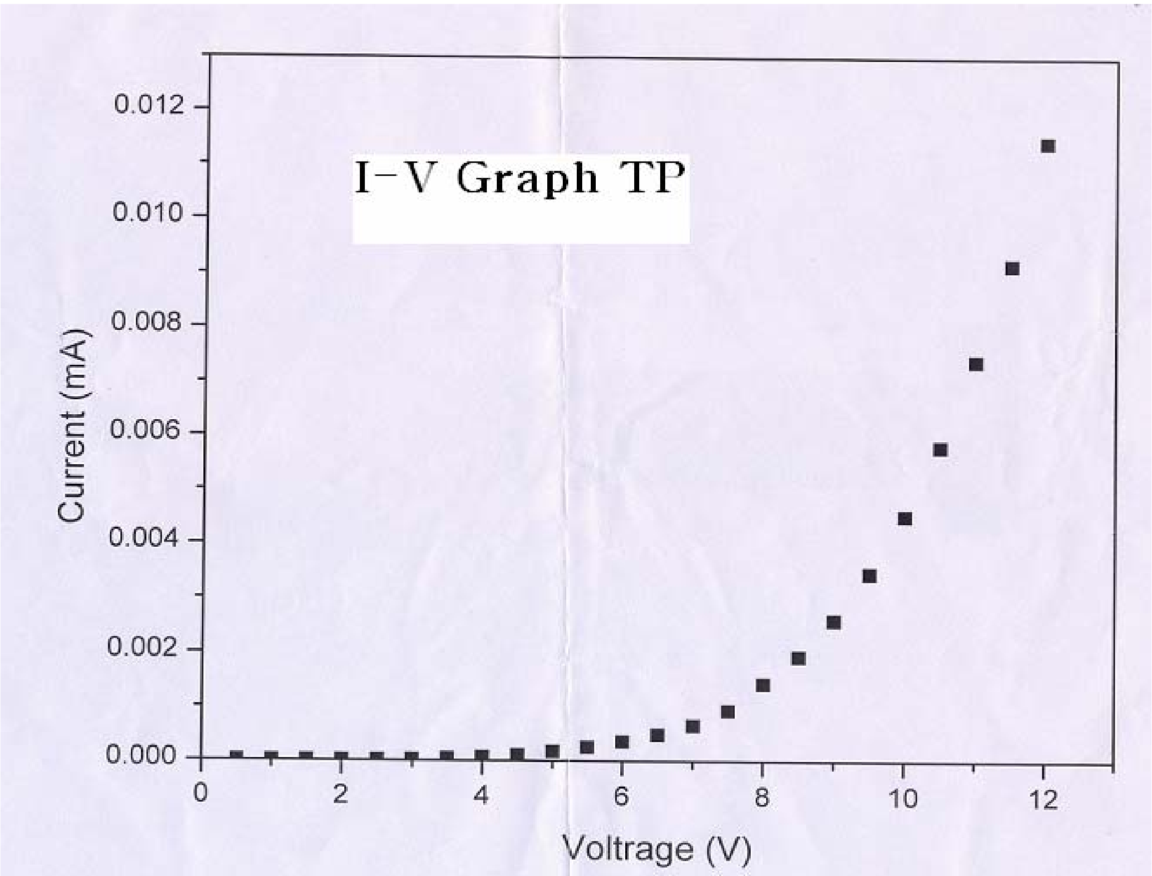


Fig.6.16 I-V Graph of the Copolymer of Toluene and Perylene.

6.4 Copolymer of Benzene and Pentacene (BPent)

6.4 (a) UV-VIS Absorption Spectra of Copolymer of Benzene and pentacene

UV-VIS Spectra of the Copolymer of benzene and pentacene was recorded on a Shimadzu UV-2401 Spectrophotometer. The sample was prepared in chloroform the absorption peak was observed centred at 436, 336 and 770 nm as shown in fig. 6.17.

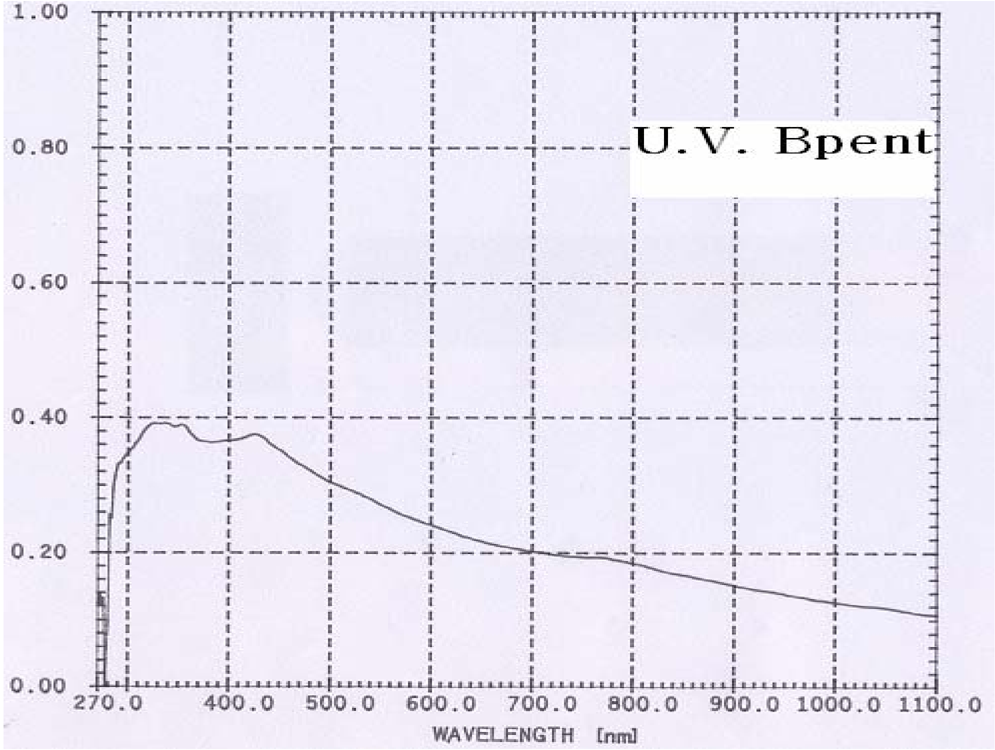


Fig. 6.17 UV-VIS Spectra of copolymer of Benzene and Pentacene

6.4 (b) *Themogravimetric analysis (TGA) of Copolymer of Benzene and pentacene*

The Thermogravimetric Analysis (TGA) of the Copolymer of Benzene and pentacene was carried out on Mettler Toledo Star System and shown in fig. 6.18. The TGA plot of the material shows loss in mass started at 200 ^{0}C due to the degradation of the polymer chain and continues up to 620 ^{o}C and loss of mass was 7.8221. The degradation of the polymer continues up to 750 ^{0}C. The further lose in the mass was 12.3427 %.

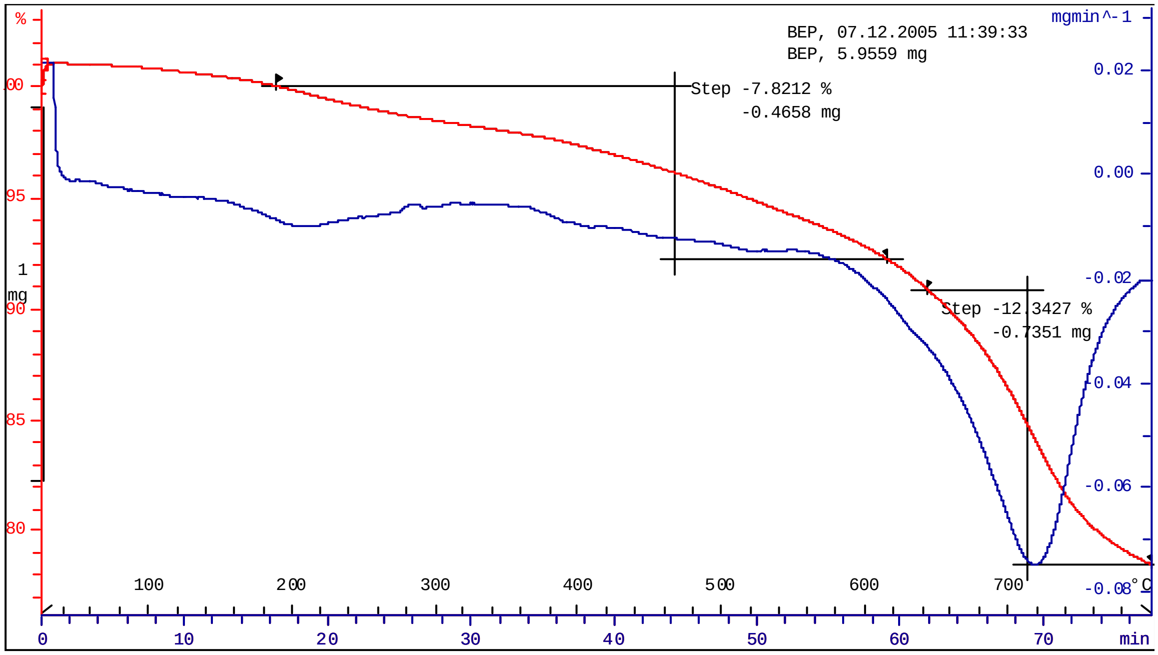


Fig. 6.18 TGA- Graph of copolymer of Benzene and Pentacene.

6.4 (c) Morphology of the Copolymer of Benzene and Pentacene by Scanning Electron Microscope

The Scanning Electron Microscope microphotographs of the copolymer of Benzene and pentacene as can be seen from fig 6.19. The SEM morphology of the copolymer of benzene and pentacene taken at different resolution from 1 to 10µm. It can be concluded that polymer is spherical in shape as the particles accumulated to form round sphere which was clearly shown in SEM picture. These spheres may be solid or hollow. The particles was accumulated so the show spherical in shape

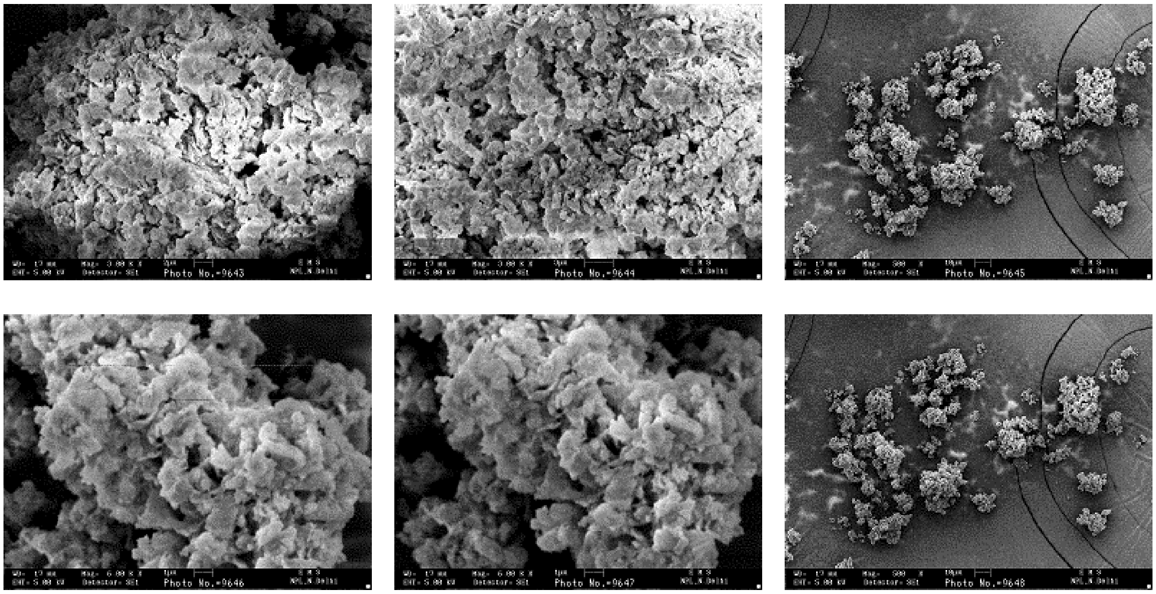


Fig 6.19 SEM Picture of Copolymer of Benzene and Pentacene

6.4 (d) FTIR Spectra of Copolymer of Benzene and Pentacene

The sample of the polymer for FTIR was prepared in freshly cleaned dry KBr and the pellet of the sample was prepared by the hydraulic press. The FTIR spectrum was recorded as shown in fig. 6.20. The peak at 3027 cm^{-1} was due C-H stretching of Benzene ring in polymer while the peaks at 2924 and 2853 cm^{-1} was due to C—H Stretching vibrations of Pentacene ring in the polymer. The band occurs in the 2000 to1700 cm^{-1} aromatic region. The peaks at 1628 and 1480 cm^{-1} were due to Quadrant and semi-circle stretching vibrations of rings. The C-C in plane stretching of aromatic ring present at 1117 and 1000 cm^{-1}. The peak at 806 cm^{-1} shows the para substitution of the polymer. The C-H out of plane bending present at 764 and 668 cm^{-1}.

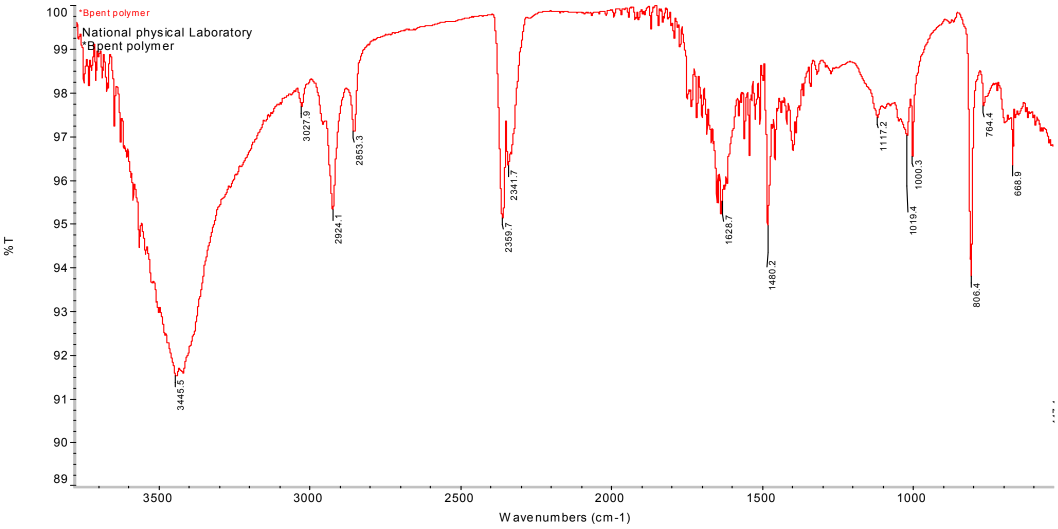


Fig.6.20 FTIR Spectra of Copolymer of Benzene and Pentacene

6.4 (e) Photoluminescence (PL) spectra of Co-polymer of Benzene and Perylene

Under UV illumination, Co-polymer of Benzene and pentacene shows photoluminescence in the Infra red. The sample was illuminated with strong 360 nm radiations from a strong UV source. Only single peak at 791 nm was observed as shown in fig. 6.21. The peak at this region comes in IR region.

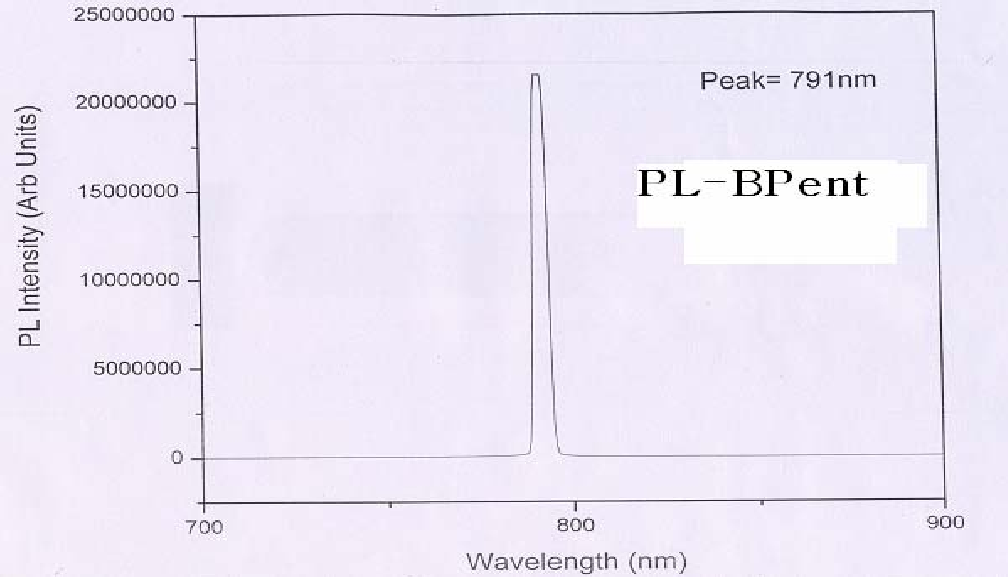


Fig. 6.21 Photoluminescent Spectra of Copolymer of Benzene and Pentacene.

Conclusions

1) Poly p-Phenylene (PPP), Copolymer of Benzene and Perylene (Bpery), Copolymer of Toluene and Perylene(TP) and Copolymer of Benzene and Pentacene (Bpent) were synthesised by Kovacic method and polymers were characterized by taking UV-VIS Absorption Spectra, Fourier Transform Infra Red Spectra, Photoluminescene (PL) Spectra and Thermo-gravimetric Analysis (TGA).

2) The results of UV-VIS Absorption Spectra and Photoluminescene (PL) Spectra of these materials show that materials synthesised were of good purity.

3) According to the Thermo-Gravimetric Analysis (TGA) of polymers, the thermal stability of the polymers was found up to 300^oC which is enough for the OLEDs.

4) Three devices of the following configurations ITO/Bpery/Al, ITO/PEDOT/TP/Al and ITO/PEDOT/BPent/Al were fabricated and there Electroluminescence (EL) spectra and Current Voltage (I -V) characteristics were measured.

5) From the Electroluminescence (EL) spectra and Current Voltage (I -V) studies of the devices, the following results were obtained.

   i) The device with configuration ITO/Bpery/Al comparatively large Voltage nearly 18 V for the device functions and produced light yellow-red Electroluminescent. The photoluminescent spectra show at 500 nm but not able to take Electroluminescence spectra due to spark. The electroluminescence may be improved by using the electron injecting layers.

  - ii) The device with configuration ITO/PEDOT/TP/Al shows bright red Electroluminescence at 698 nm on applying the threshold voltage of 15 V. The material shows Photoluminescent at 614 nm.
  - iii) The device with configuration ITO/PEDOT/BPent/Al shows the photoluminescence spectra in IR region at 719 nm.

6) The materials synthesised have shown a very good results in application of OLEDs. Therefore, the synthesised materials have good prospects for the Industrial applications as electroluminescent materials in coming days.

Paper Communicated

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"Synthesis of soluble π-Conjugated poly p-phenylenes for OLED's Application"

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Abstract

Light-emitting diodes (LEDs) based on π-conjugated polymers have drawn a lot of attention due to some merits from material development to device fabrication. The emissive color of a π-conjugated polymer is fine-tunable by controlling the effective π-conjugation. Electroluminescent efficiency can be improved by balancing the hole/electron mobility through chemical modifications like incorporating electron-donating or electron-withdrawing groups with in the polymer backbone or the side-chain. In order to develop an emissive polymer showing desired LED performance, it is

important to design the segments of a polymer. In the present work, we have synthesized the copolymers for red-light emission with high LED performances. Conjugated polymer, poly-p-phenylene (PPP) has attracted great deal of attention from the material scientists. However, the polymer is intractable and difficult to process. Hence it has not been extensively used in the fabrication of organic light emitting diodes (OLEDs). In order to solve the unprocessibility and solubilization problem, we have co-polymerized substituted benzene and perylene using Kovacic's method, which uses the mechanism of propagation of oxidative coupling occurring through a dehydrogenation step via radical cations. The resulting co-polymer is soluble in common organic solvents like toluene, benzene, chloroform, acetone, THF and NMP. The copolymer has an optical absorption doublet band at 420 nm and 445 nm and the corresponding photoluminescence maximum at 613 nm. The copolymer has been characterized using spectroscopic and thermo gravimetric techniques. OLED device has been fabricated using ITO/PEDOT/Copolymer/Al. The devices give bright red electro luminescence at 698 nm on applying a threshold voltage of ~ 10V.

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