CHAPTER - 2

DETAILS OF EXPERIMENTAL TECHNIQUES USED

In this chapter, preparation process for conjugated polymer film, Selection of solvent, Preparation of MEH-PPVs Samples, Spin-coating system, sheet resistance, Vacuum Deposition of Electrode, Absorption Studies, Photoluminescence, Electroluminescence, Refractive Indices, Conductivity Studies, I-V characteristics, j-V characteristics, Hole mobilities, Differential Thermal Analysis, Dielectric Studies, Deep Level Transient Spectroscopy (DLTS), Thermochromic studies, X-ray studies, Scanning electron microscopy (SEM) etc. will be described.

2.0 Preparation of MEH-PPV Films

2.0.1 Characteristics of MEH-PPVs

The conjugated polymer used in this study was poly (2-methoxy-5-(2'-ethylhexyloxy)-1, 4-phenylene vinylene) (MEH-PPV). MEH-PPV is an amissive amorphous polymer used in orange-yellow LEDs\textsuperscript{1, 2}. The MEH-PPVs was obtained from the Aldrich Chemistry Corporation, it is poly(para-phenylene vinylene) (PPV) derivative p-type amorphous polymer with glass transition temperature (T\textsubscript{g}) of 65 °C and melting point (m.p.) of 190~200 °C\textsuperscript{3}. The molecular formula of MEH-PPV is (C\textsubscript{18}H\textsubscript{28}O\textsubscript{2})\textsubscript{n} and its molecular structure and spectral analysis are shown in fig 2-1\textsuperscript{4}. Shows the chemical structures\textsuperscript{5} of MEH-PPV, M3EH-PPV and MEH-DOO-PPV synthesized by Wudl and Srdanov in 1993.
Figure 2.0  (a) Structure of MEH-PPV, (b) Structure of M3EH-PPV 
(c) Structure of MEH-DOO-PPV.
2.0.2 Selection of solvent:

MEH-PPV is particularly attractive for LED fabrication due to being soluble in the conjugated form with common organic solvents which are nonaromatic or aromatic. The common aromatic solvents are chlorobenzene (CB), 1,2-dichlorobenzene (DCB), toluene and p-xylene. The common nonaromatic solvents are tetrahydrofuran (THF) and CHCl₃. Here toluene was used as a solvent for all the three PPVs.

In contrast, the aggregation style of MEH-PPV solute is different between nonaromatic and aromatic solvents. When the powder of MEH-PPV is in an aromatic solvent, the aggregation is formed with the aromatic polymer backbone facing the solvent and the side chains point inwards and towards each other. But the nonaromatic solvents result in the twisted aggregation of
the MEH-PPV molecules. Using aromatic solvent will cause a better π-π overlapping, therefore favors the formation of the interchain species. Also, the conducting polymer backbones arranged outside is also expected to be more conductive than the twisted aggregation which happens in the nonaromatic solvent. Besides, the film used aromatic solvent could yield a better contact with electrodes. This prediction was observed in experiment. It was found that films used aromatic solvents exhibit a higher current than those used THF at the same applied voltage and film thickness[6].

Because of the above-mentioned phenomena, aromatic solvent was used in this study. Moreover, toluene is cheaper and easier to obtain, therefore, the standard toluene was used to dissolve MEH-PPV in this study. The boiling point (b.p.) of the toluene is 110 °C.

2.0.3 Preparation of MEH-PPVs Samples:
The primary species studied was MEH-PPV. This polymer is an orange-red luminescent powder easily soluble in common organic solvents, other polymers includes M3EH-PPV[7], (poly[2-methoxy-5-(2-ethylhexyloxy)-1,4 - phenylene-ethylene-2,5 - dimethoxy-1,4-phenylene -ethenylene) and MEH-DOO-PPV[8] (poly [2 methoxy.5.(2. ethylhexyloxy) -1, 4-phenylene-ethenylene -2,5 - dioctyloxy-1,4 – phenylene - ethylene). The polymers are dissolved in a solvent (Toluene) and poured over an Indium Tin Oxide (ITO) coated borosilicate glass slide. It is then kept in a desiccator or a vacuum oven for few hours so that the solvent get evaporated and a solid film is formed on the glass slide. The films can also be spin cast on the n+ Silicon wafer. The film on conducting glass substrate is then vacuum coated with aluminum or silver using suitable masks. Then samples which are spin coated can attain a thickness of the order of nanometers. The samples are ready for investigation.
2.0.4 Spin-coating system:
Spin-coating is a technique that utilizes centrifugal force created to spread solution coating over a surface. This coating technique is widely used in thin-film depositions for quick and efficient responses. The variation of concentration of solution, spin speed and spin duration etc. could determine the thickness of coated film. The MEH-PPV film was deposited with a spin-coating system (ACE 200) in the present study.

![Figure 2.2 ACE 200 Spin Coater.](image)

Spin coated samples of MEHPPVs mentioned above were made with various thicknesses and concentration using the spin coating arrangement and prepared solutions. The spinning was carried out at 1000 rpm for 1 min. The substrates were then subjected to annealing in vacuum in order to
ensure the entire solvent removal.

2.0.5 Vacuum Deposition of Electrode:
Thermal evaporation is used for the deposition of the cathode layer. The evaporation system consists of a diffusion pump backed by a rotary pump. The base pressure was of the order of $4 \times 10^{-6}$ to $3 \times 10^{-6}$ mbar. The deposition of the electrode was achieved by the application of current through a filament or crucible. This then cause the filament or crucible to heat up and allows the material to simply evaporate and is then deposited upon the polymer coated ITO substrate\cite{9}.

2.1 Absorption Studies:
Absorption spectra are taken on a Varian optical spectrometer. The instrument baseline is set once every hour using blank quartz slide. Subsequent measurements are automatically corrected for this baseline. Transmission intensity is collected as the excitation wavelength is increased in 1 nm steps.

2.2 Photoluminescence
Perkin Elmer LS-50B luminescence spectrophotometer, The LS-50B Luminescence Spectrometer has been designed and tested in accordance with Perkin Elmer Specifications and IEC 61010-1, 'Safety requirements for electrical equipment for measurement, control and laboratory use'. A white light source (Xenon lamp) was used to photo excite the sample.
2.3 Electroluminescence:
The electroluminescent studies were also conducted using the same spectrophotometer mentioned in the previous section except that instead of the activating xenon light a constant voltage source was used to bias the polymer layer in the device.

2.4 Refractive Indices:
The spectra of the refractive index of the films were evaluated using an ATAGO Model DR-A1 Digital Abbe Refractometer. This is a standard refractometer used by researchers all over.

2.5 Conductivity Studies:
Conductivity studies were carried out using a set up mentioned below (Fig.2.3). The arrangement shown below is used to measure bulk conductivities of the sample as well as the device\textsuperscript{[10, 11]}. Since the sample used here are in the form of thin film the power supply mentioned in figure 2.3 viz Aplab (0.5 to 5 kV) was replaced with Keithley 6517A, whose built constant voltage source was used. This way one of the Keithley Electrometer can be reduced. Here for this study we had carried out conductivity measurements\textsuperscript{[12]} in two different methods and corroborated the data.

2.5.1 I-V Characteristics:
Constant voltage was supplied by Keithley 6517A (built in voltatage source) and the resulting current was measured by another Keithley 6517A.
2.5.2 J-V characteristics: The current density vs bias voltage (j-V) curve was recorded using the above mentioned configuration, but under standard illumination (AM 1.5) using a standard xenon source (solar spectrum simulator) and an area of 2mm x 2mm. The illumination was normal to the film surface when the current densities were measured for different bias voltage.

2.5.3 Hole mobilities:
The hole mobilities were determined using a standard hall effect set up. From the hall voltage and applied magnetic field the mobility $\mu$ for the particular temperature and bias voltage was calculated. It is expected that for MEHPPV the mobility $\mu$ follows a relation as mentioned in the equation below.
\[ \mu = \mu_0 \exp(\alpha E^{1/2}) \]

where \( \mu_0 \) and \( \alpha \) are constants.

### 2.6 Differential Thermal Analysis:

Differential thermal analysis is carried out by heating the sample together with a reference standard under identical thermal conditions in the same oven and measuring the temperature difference between the sample and reference substance during the period of heating. As soon as the sample changes state, crystal form, melts, etc. the latent heat of phase transition will be absorbed and the temperature of the sample will lag behind that of the reference material. In this way any change in state will be shown and the temperature at which it occurs will be recorded. The differential thermogram of the material gives the softening temperature, melting point etc. which is the limit at which these materials can be used for device application.

Figure 2.4 Differential Thermal Analysis (DTA)
In the present study differential scanning calorimetry (DSC) was used to study the melting point as well as the other phase transitions in the polymer.

The above figure shows the actual working of a DSC thermograph. Differential scanning calorimetry (DSC) monitors heat effects associated with phase transitions and chemical reactions as a function of temperature\cite{13}. In a DSC the difference in heat flow to the sample and a reference at the same temperature, is recorded as a function of temperature. The reference is an inert material such as alumina, or just an empty aluminum pan. The temperature of both the sample and reference are increased at a constant rate. Since the DSC is at constant pressure, heat flow is equivalent to enthalpy changes:
Here $\frac{dH}{dt}$ is the heat flow measured in mcal sec$^{-1}$. The heat flow difference between the sample and the reference is:

$$\left(\frac{dq}{dt}\right)_p = \frac{dH}{dt}$$

and can be either positive or negative. In an endothermic process, such as most phase transitions, heat is absorbed and, therefore, heat flow to the sample is higher than that to the reference. Hence $dH/dt$ is positive. Other endothermic processes include helix-coil transitions in DNA, protein denaturation, dehydrations, reduction reactions, and some decomposition reactions. In an exothermic process, such as crystallization, some cross-linking processes, oxidation reactions, and some decomposition reactions, the opposite is true and $dH/dt$ is negative.
Figure 2.6 Photograph of Labsys evo DSC thermograph used in the present study.
2.7 Dielectric Studies:

![Diagram of dielectric setup](image)

**Figure 2.7** A Set up for measuring the dielectric constant of the samples at various temperatures and frequencies.

In the current study the dielectric constant and loss tangent was calculated directly from the values of the capacitance measured using HP 4192A impedance bridge. The capacitance was measured at different temperatures and frequencies. Since the allowed frequency of the bridge was only from 10 Hz to 10 MHz which, is in fact a useful range for the material to be used in devices. The schematic diagram of the set up used for measuring the dielectric constant (Sample holder with temperature controller) is given in the Figure above. The sample holder was taken through a high frequency coaxial cable and a BNC connector to the impedance bridge.
2.8 Deep Level Transient Spectroscopy (DLTS):
A successful DLTS, like experiment was performed on MEH-PPV, a measurement technique design in the lines of classical semiconductors (Si, GaAs, etc) for conjugate polymers although the transients chosen were in minutes rather than seconds unlike in inorganic semiconductors. An electroluminescent transient study was carried on the samples by suddenly changing the bias voltage of the device (square electric pulse for for less than one ms duration) and the emitted light intensity was monitored over time. The intensity depends on the recombination rate. Most of the injected charge carriers recombining from HOMO and LUMO levels emits photons while trapped charge carriers from deeper levels can be recognized by a slow decay of intensity. The emission rate $\varepsilon_n$, the reciprocal of transient time $\tau$, depends on the levels depth $E_a$ and the temperature $T$ as given in equation
Thermochromic studies:
In the temperature range between 25 and 100 °C, MEHPPV films undergo a transition from red to yellow. To understand more qualitatively the observed color change, temperature-dependent absorption spectra were obtained. Transmission spectra for thermochromic films were taken on a Varian 3 spectrophotometer. Samples were heated in situ by securing a nichrome wire against the film with a conductive tape as close as possible to the substrate center so as to avoid interference with the measurement, and passing current through the wire. The temperature was allowed to equilibrate prior to scanning, taking approximately 5–10 min depending on the step size. Heating of the film was achieved through conduction in the substrate and therefore suffered a minor level of nonuniformity. However, temperatures were tested immediately prior to the scan at the film center and thus accurately correlate with the temperature of the part of the film where the transmission was measured. The high-temperature limit of such a setup appeared to be the breakdown of the tape adhesive occurring at around 80 °C. As the temperature is increased the films undergo a continuous blue shift and decrease in overall absorption. The blue shift of the absorption of MEH-PPV in the temperature range of 25–80 °C was measured. Similarly M3EH-PPV and MEH-DOO-PPV respectively were subjected to spectral studies. A blue shift of the photoluminescence was also observed in MEH-PPV at increased temperature.
2.10 X-ray studies
The X-ray diffractogram of the samples were taken on a Shimadzu XD-5 X-ray diffraction (XRD; 45 kV, 30 mA) with copper target and Ni filter. The basal spacing (n = 1) and ionic channel size were calculated according to Bragg’s law, \( n\lambda = 2d \sin \theta \), the scanning speed was maintained at 2°/min.

2.11 Scanning electron microscopy (SEM):

![Schematic diagram of a Scanning Electron Microscope (SEM).](image)

**Figure 2.9** Schematic diagram of a Scanning Electron Microscope (SEM).
Polymer structure and morphology are greatly affected by synthesis conditions such as electrode materials for electrosynthesis, solvent and electrolyte salts, oxygen and water content of the system and the current density used for electropolymerization. To estimate the morphology and microtexture Scanning Electron Microscopy (SEM), is the best option. SEM was used for the analysis of the polymer samples in its film and pellet form\textsuperscript{[14]}. Films appear generally smooth, while pellets show uneven surfaces and the possible existence of macroscopic defects such as cracks.
REFERENCES:


