Chapter 2

EXPERIMENTAL TECHNIQUES
AND THEORY

2.1 Introduction

The common feature of conducting polymers is their \( \Pi \) conjugated structure. Three of the four electrons from one \( s \) and two \( p \) states in the outermost shell of carbon occupy \( sp^2 \) hybridized states. These electrons form three strong \( \sigma \) bonds that play a key role in forming the polymer structure. The remaining valence electron occupies a \( p \) orbital and is called a \( \Pi \) electron. The \( \Pi \) electron wave functions from different carbon atoms overlap to form a \( \Pi \) band. Sigma bonds are strong and localized, while the \( \Pi \) bonds are weak and thus delocalized. The delocalized \( \Pi \) electrons are responsible for the high electrical conductivity of conducting polymers [1, 2]

But in systems such as polyacetylene, adjacent \( CH \) bonds move towards each other to form alternate short and long bonds, thereby
lowering the electronic energy of the system. This is called Peierls distortion. The resulting ground state can be described in terms of the inequality of the transfer integrals for the single and double bonds $t_1$ and $t_2$, which opens up an energy gap, $2\Delta = 2(t_1 - t_2)$, separating the Highest Occupied Molecular Orbital (HOMO) from the Lowest Unoccupied Molecular Orbital (LUMO) [3-5].

The value of the symmetry breaking parameter or distortion $U_0$ can be related to the one dimensional energy gap through the relation $2\Delta = 8\beta U_0$, where $\beta$ is the electron phonon coupling constant which describes the modulation of the $\Pi$ electron transfer integral due to the atomic motion. Here, in quasi one-dimensional conjugated systems, the domain walls separating the degenerate ground state structures are called solitons. In such systems (e.g. Polyacetylene), solitons take the place of electrons and holes in semi conductors. They are responsible for the transport of electrons and holes along the polymer chains. In short, solitons are excitations of a system leading from one minimum of the potential to another minimum of the same energy. Solitons can propagate without energy loss. There are three types of solitons—positive, negative and neutral [2].

For conducting polymers other than polyacetylene, different solitonic states have different energies. So solitonic conduction mechanisms are not expected. However, states appear in the band gap due to the formation of polarons (electrons localized in an electric potential minimum formed by lattice distortions). Polarons have both charge and spin and their motion can contribute to charge transport.
Polarons of opposite spin often pair up to form bipolarons with zero spin.

2.2 Non-redox doping

Polyaniline is a mixed oxidation state polymer composed of reduced benzenoid units and oxidized quinonoid units (scheme 2.1a). The average oxidation state is given by $1-y$. It can exist in several oxidation states ranging from the completely reduced leucoemeraldine base state (scheme 2.1b), where $1-y=0$, to the completely oxidized pernigraniline base state (scheme 2.1c), where $1-y=1$. The "half" oxidized ($1-y=0.5$) emeraldine base state (scheme 2.1d) is an insulator and is composed of an alternating sequence of two benzenoid units and one quinonoid unit.

\[
\begin{align*}
\text{(a)} & \quad \left[ \left( \begin{array}{c}
\text{H} \\
\text{N} \\
\text{H} \\
\text{N} \\
\text{H} \\
\text{N} \\
\text{H} \\
\text{N} \\
\text{H} \\
\text{N} \\
\text{H} \\
\end{array} \right) \right]_y \left( \begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\end{array} \right)_x \\
\text{(b)} & \quad \left( \begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\end{array} \right)_{n-x} \\
\text{(c)} & \quad \left( \begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\end{array} \right)_{n-x} \\
\text{(d)} & \quad \left( \begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{N} \\
\end{array} \right)_{n-x}
\end{align*}
\]

Fig. 2.1 Different oxidation states of polyaniline
However, emeraldine base can be non-redox doped with acid[6] to yield the conductive emeraldine salt state of polyaniline as shown in fig 2.2.

![Diagram of polyaniline doping](image)

**Fig. 2.2** Protonic acid doping of polyaniline (emeraldine base) to polyaniline (emeraldine salt)

This non-redox doping differs from redox doping in that it does not involve the addition or removal of electrons from the polymer backbone.

### 2.3 Electronic conduction mechanisms

Employment of the above described doping techniques and sophisticated synthesis methods provide a conceptual framework for understanding the electronic structure of these novel polymer semiconductors at low doping levels [7-11]. The origin of metallic nature in conducting polymers is still controversial[12,13].

Though such systems exhibit a Pauli spin susceptibility[12], a quasilinear temperature dependence of thermo power[14] and a linear term in the specific heat[15], the real fingerprints of metallic
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behaviour (e.g.- finite D.C conductivity as $T \to 0$, a positive temperature co-efficient of resistivity and metallic reflectivity in the infrared) are absent. Nowadays new methods of synthesis and processing of conducting polymers have resulted in systems with improved homogeneity and long range order, providing opportunities for investigating the metallic state through transport and optical measurements [16-26].

2.3.1 Disorder induced metal-insulator transition

Anderson [27] reported that the localization of electronic wave functions can occur if the random component of disorder potential is large enough compared to the band width. The mean free path ($\lambda$) in such systems is given by,

$$\frac{1}{\lambda} = 0.7(1/a)(V_0/B)^2$$

where $a$ is the interatomic distance, $V_0$ is the random potential, and $B$ is the bandwidth. According to Anderson, the states will become localized throughout the band for a critical value of $V_0/B$ that is estimated to be of the order of unity in three dimensions.

Later on, Mott [28, 29], pointed out that the states in the band tails are more susceptible to localization. The critical energy called the mobility edge ($E_c$) separates the localized states from the non localized states and it plays an important role in cases of significant disorder, even when $V_0/B$ is below the critical value.
In 1970, Anderson [30] proposed that a degenerate electron gas in a random disorder potential tends to localize if the magnitude of the disorder potential is large compared with the bandwidth. Such a system is called a "Fermi glass". It is an insulator with a continuous density of localized states (no energy gap) occupied according to Fermi statistics. If the extent of disorder is sufficiently large so that the Fermi energy ($E_F$) lies in the region of localized states, there is a transition from the metallic state (finite value of conductivity as $T \to 0$) to a nonmetallic state (conductivity $\to 0$ as $T \to 0$). This disorder induced metal-insulator (M-I) transition is called Anderson transition [28, 29]. The critical region is characterized by a universal power law temperature dependence of conductivity, $\sigma_{crit} \propto T^{-\delta}$. The localization length increases as $E_F$ approaches $E_c$.

Mott proposed the concept of minimum metallic conductivity $\sigma_{\text{min}}$, treating M-I transition as discontinuous and employing the Ioffe-Regel criterion that the lower limit of mean free path is the interatomic spacing[31].

$$\sigma_{\text{min}} = 0.03(2 \pi e^2)/(3ha)$$  \hspace{1cm} (2.2)

for $\sigma \sim \sigma_{\text{min}}$, the system is near the M-I transition, whereas systems with $\sigma < \sigma_{\text{min}}$ is on the insulating side of the M-I transition. An important parameter for characterizing the disorder is the product of Fermi wave vector ($K_F$) and the mean free path ($\lambda$).

In short, if $K_F \lambda << 1$, $\sigma << \sigma_{\text{min}}$, the sample is on the insulating side of the M-I transition and if $K_F \lambda \geq 1$, $\sigma \geq \sigma_{\text{min}}$, the sample is on the metallic side of the M-I transition. Though conducting polymers are in general quasi 1D systems, strong interchain coupling suppresses the localization, facilitating the formation of 3D metals[32,33]. When such
a material is oriented (e.g., by tensile drawing), it behaves like an anisotropic 3D metal.

2.3.2 Hopping in disordered semiconductors

For many of the amorphous materials, electronic conduction is governed by Mott's variable range hopping [28]. In disordered semiconductors with localized states in the band gap, conduction occurs by phonon assisted tunneling between electronic localized states centered at different positions.

Mott and Davis have formulated an expression for variable range hopping as,

\[ \sigma(T) = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right] \]  

(2.3)

for hopping in three dimensions, the exponent has the value \( \frac{1}{4} \). It is assumed that the electronic wave functions decay with distance \( r \) as \( \exp(-r/L_{\text{loc}}) \), where \( L_{\text{loc}} \) is the localization length and \( T_0 \) is a constant. According to this model, in three dimensions,

\[ \sigma_0 = e^2 v R^2 N(E) \]  

(2.4)

and

\[ T_0 = \lambda \alpha^3 / K N(E) \]  

(2.5)

where

- \( e \): the electronic charge
- \( \lambda \): a dimensionless constant with its value approximately equal to 18.1
- \( N(E) \): the density of states at the Fermi level.
- \( \alpha \): the inverse rate of fall of the wave function and
- \( K \): the Boltzmann constant
The hopping distance,

\[ R = \left[ \frac{9}{8\pi a k N(E)} \right]^{1/4} \]  

The average hopping energy \( W \) can be estimated by knowing \( R \) and \( N(E) \) from the relation,

\[ W = \frac{3}{4} \pi R^3 N(E) \]

\( T_0 \) and \( \sigma_0 \) can be obtained from the slope and intersection with the conductivity axis respectively.

\( \alpha \) is approximated as 10 \( \text{A}^0 \) and the characteristic phonon frequency \( v, 10^{13} \text{ s}^{-1} \).

At sufficiently high temperatures, hopping is to nearest neighbours with \( \gamma = 1 \). This is a case similar to that in a crystalline semiconductor. For 2D hopping, \( \gamma = 1/3 \) and for 1D hopping, \( \gamma = 1/2 \). Quasi 1D hopping plays a key role in conducting polymers where polymer chains traverse disordered regions to connect crystalline islands. Charge carriers would diffuse along such electrically isolated disordered chains as part of the conduction path, but would readily localize owing to the 1D nature of the chains. Quasi 1D variable range hopping along disordered chains dominates the overall resistance of the polymers in such cases.

### 2.3.3 Tunneling between metallic islands

Calculations by Sheng and Klafter (1983) and Sheng (1992) \[34,35\] reveal that, if conduction is by electronic tunneling through non-conducting
material separating mesoscopic metallic islands, rather than between localized states, the expression for the tunneling conductivity approximately takes the form (2.3), with \( \gamma = 1/2 \). This model is appropriate for a granular metal in which small metallic grains are surrounded by non-conducting shells. Here the conductivity is limited by the electrostatic charging energy when an electron is transferred from one island to the next. The inhibition of tunneling when the thermal energy \( kT \) is less than the charging energy is referred to as Coulomb blockade.

If the metallic regions are large enough that the electrostatic charging energy is much smaller than the thermal energy \( kT \), tunneling can occur between metallic states of the same energy on different sides of the barrier without thermal excitation, provided that the wave functions overlap. Fluctuations in the voltage across the tunneling junction can greatly increase the tunneling current as temperature increases according to Sheng (1980) [36].

Conductivity due to this fluctuation assisted tunneling for a simple parabolic barrier shape can be approximated as,

\[
\sigma(T) = \sigma_l \exp \left[-\left(\frac{T_l}{(T+T_s)}\right)\right]
\]

(2.8)

where,

\( T_l \) : The temperature at which the thermal voltage fluctuations become large enough to raise the energy of electronic states to the top of the barrier

\( T_l/T_s \) : determines the tunneling in the absence of fluctuations

\( \sigma(0) \) : low temperature limit
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The prefactor $\sigma_t$ is approximated as independent of temperature.

2.3.4 Space charge limited conduction

In the metal-polymer-metal configuration, where the contacts are ohmic, carriers can be injected from the metal electrode into the conduction band of the polymer under an applied electric field. If the amount of injected carriers is more than that which can be transported across the pellet, a space charge will be build up at the metal polymer interface. So electrons flowing through the system under an electric field will be impeded and controlled by the space charge collected at the metal-polymer interface and this gives rise to the phenomenon known as space charge limited (SCLC) conduction [37]. For a trap free material, the current density under SCL conduction is given by

$$J_{\text{scl}} = \frac{9}{8} \varepsilon \varepsilon_0 \mu \left( \frac{V^2}{D^3} \right) \quad (2.9)$$

$\varepsilon$ : the dielectric constant of the material
$V$ : the applied voltage and
$D$ : the thickness of the sample

SCL currents are important because the injected current is independent of the mechanism of carrier generation and depends only on the transport and trapping of the carriers within the sample. SCLC shows three to four distinct regions in the current-voltage plots. The first region corresponds to the low field conduction region where the variation of current density with voltage is ohmic. As voltage is increased, the injected carriers outnumber the thermally generated ones and SCLC starts. The equation (2.9) shows that $J$ is directly
proportional to $V^2$ and inversely proportional to $d^3$. The transition from ohmic to square law shows the onset of SCLC conduction.

### 2.3.5 Schottky Effect

The potential barrier at the metal-insulator interface region can be overcome by the electrons and they can flow from the metal electrode to the conduction band of an insulator under an applied field. This effect called Schottky effect is a field assisted conduction process. When an electron jumps from the metal surface, the latter becomes polarized and exerts an attractive force on the electron. Due to the resulting image force, the potential step at the metal polymer interface changes smoothly. The potential energy of the electron due to the image force is

$$\Phi = -\frac{e^2}{16 \pi \varepsilon_0 x} \qquad (2.10)$$

Here $x$ is the distance of the electron from the electrode surface.

### 2.3.6 Poole-Frenkel Conduction Process

Upon the application of an electric field to a sample, the potential barrier height caused by Coulombic forces on an atom will be reduced. This phenomenon is known as Poole-Frenkel effect. The potential energy of an electron in the field of a trapping center is given by the usual Coulomb expression,

$$\Phi = -\frac{e^2}{4 \pi \varepsilon_0 x} \qquad (2.11)$$

Here $x$ is the distance from the center.

The potential energy here is four times that due to the image force in Schottky mechanism.
2.4 Experimental Techniques

In this section, a detailed description of the techniques employed for structural, morphological, electrical, optical, thermal and mechanical characterization of the samples investigated in the present work is included.

2.4.1 FTIR spectroscopy

Fourier Transform InfraRed (FTIR) spectroscopy is employed for the identification of functional groups.

Fig 2.3 depicts a schematic diagram of FTIR setup.

![Schematic diagram of FTIR spectrometer]

The basic optical component of Fourier transform spectrometers is the Michelson interferometer. Light from an infrared source—a heated element or a glow bar—is collimated and directed on a beam splitter. An
ideal beam splitter creates two separate optical paths by reflecting 50% of the incident light and transmitting the remaining 50%. In the near and middle infrared region, germanium deposited on a KBr substrate is used as a beam splitter. In one path the beam is reflected back to the beam splitter by a fixed position mirror, where it is partially transmitted to the source and partially reflected to the detector. In the other leg of the interferometer, the beam is reflected by the movable mirror that is translated back and forth, while maintained parallel to itself. The beam from the movable mirror is also returned to the beam splitter where it, too, is partially reflected back to the source and partially transmitted to the detector. Although the light from the source is incoherent, when it is split into two components by the beam splitter, the components are coherent and can produce interference phenomenon when the beams are combined. The detector is usually a deuterated triglycine sulfate pyroelectric detector and the movable mirror rides on air bearing for good stability. Other detectors such as cooled HgCdTe are also used.

Different functional groups in the sample absorb characteristic frequencies of I.R radiation. IR spectrometers could analyze gases, liquids and solids using various sampling accessories. Thus FTIR spectroscopy is an important and popular tool for structural elucidation and compound identification. The spectrum obtained, representing the molecular absorption and transmission is a molecular fingerprint of the sample. Different functional groups absorb at their unique characteristic frequencies. This makes infrared spectroscopy useful for several types of analysis [38-41].
In the present work, FTIR spectrum is taken using an Avatar 370 spectrometer employing a DTGS KBr detector. The resolution of the instrument is 4 cm\(^{-1}\).

2.4.2 X-ray diffraction

X-ray topography or X-ray diffraction is a non-destructive technique for structural study[42-45]. Though it is not a high resolution technique, it gives microscopic information. The schematic diagram corresponding to crystal diffraction is given below.

Monochromatic X-rays impinge on a crystal with lattice spacing 'd'. They emerge out at twice the Bragg diffraction angle \(\theta\).
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The Bragg equation is,

\[ 2d \sin \theta = \lambda \ldots \ldots (2.12) \]

Or \[ \theta = \sin^{-1}(\frac{\lambda}{2d}) \ldots \ldots (2.13) \]

The diffracted X-rays are made to fall on a photographic plate or film, placed as close to the sample as possible. The film must be perpendicular to secondary X-rays to get a good image. Dislocations or defects produce a highly intense diffracted beam than that from a perfect plane.

\[ \text{Strain}(S) = \frac{(d_{\text{unstrained}} - d_{\text{strained}})}{(d_{\text{unstrained}})} \ldots \ldots \ldots \ldots \ldots (2.14) \]

Topography is generated when the sample and film are scanned in synchronism with the screen.

X-ray topography is of two types—reflection X-ray topography and transmission X-ray topography. In reflection X-ray topography, developed by Berg and Barret, X-rays are incident on the crystal plane at small angle \( \alpha \). The reflected X-rays fall on the photographic plate placed close to the sample. Reflection X-ray topography is helpful in the study of crystal dislocations. Transmission X-ray topography is developed by Lang. Monochromatic X-rays are made to fall on the crystal through a slit. The X-rays transmitted through the crystal passes through a slit on the screen and then to the photographic plate. Transmission X-ray topography [46, 47] is used in the study of crystal defects. In section topography, the sample and the film is kept stationary [48, 49]. A small section of the sample—the cross-section is imaged. Section topography provides “defect depth” information.
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The XRD analysis of the samples is carried out using a fully automated Rigaku 1710 X-ray Diffractometer. In our set-up, filtered Cu-K\(_\alpha\) radiation having wavelength \(\lambda = 1.542 \text{ Å}\) is used for diffraction. The accelerating potential applied to the X ray tube is 30KV and the tube current is 20 mA.

2.4.3 D.C electrical conductivity measurements

The four-point probe technique is the most common method for measuring the semiconductor resistivity/conductivity. It is an absolute measurement without recourse to calibrated standards. It is often used to provide standards for other resistivity measurements. Though two-point probe method is easier to implement, the interpretation of measured data is difficult. In two-point probe, each probe serves as a current and as a voltage probe. The total resistance \(R_T\) between the two probes is given by,

\[
R_T = \frac{V}{I} = 2R_P + 2R_C + 2R_{sp} + R_s
\]

(2.15)

Where \(R_P\) is the probe resistance, \(R_C\) the contact resistance at each metal probe/semiconductor contact \(R_{sp}\), the spreading resistance under each probe, and \(R_s\) the semiconductor resistance. We assume \(R_C\) and \(R_{sp}\) to be identical for both the contacts. The contact resistance arises from the mechanical metal probe contacting the semiconductor. The spreading resistance accounts for the resistance encountered by the current when it flows from the small metal probe into the semiconductor and from the semiconductor to the probe. \(R_{sp}\) is a measure of resistivity, because for typical four-point probes \(R_{sp} \gg R_s\).
Neither $R_c$ nor $R_{sp}$ can be accurately calculated for a mechanical probe contact. So they cannot be accurately extracted from the total resistance. $R_p$ can be separately determined by shorting the two probes and measuring the resistance.

The solution to this dilemma is the four point probe technique originally proposed by Wenner [50]. Here two probes carry the current and the other two probes sense the voltage. The two current carrying probes have contact and spreading resistance associated with them. But this is not true for the two voltage probes. The voltage is measured either with a potentiometer which draws no current at all, or with a high impedance voltmeter, which draws very little current. The parasitic resistances $R_c$, $R_p$ and $R_{sp}$ are negligible in either case because the voltage drop across them is negligibly small due to a very small current that flows through them. Such four-contact measurement techniques are frequently referred to as Kelvin techniques.

Let $I$ be the current entering through probe 1 and leaving through probe 4. The potential $V$ at a distance $r$ from an electrode in a material of resistivity $\rho$ is given by,

$$V = \frac{\rho I}{2\pi r}$$

For probes resting in a semi-infinite medium, with current entering probe 1 and leaving probe 4, the voltage $V_0$, measured with respect to zero reference potential becomes,
where \( r_1 \) and \( r_4 \) are the distances from the probes 1 and 4 respectively. The minus sign accounts for current leaving through probe 4. For probe spacing \( s_1, s_2 \) and \( s_3 \), the voltage at probe 2 is,

\[
V_2 = \frac{\rho I}{2\Pi} \left( \frac{1}{s_1} - \frac{1}{s_1 + s_3} \right) \quad \text{(2.18)}
\]

and at probe 3 is

\[
V_2 = \frac{\rho I}{2\Pi} \left( \frac{1}{s_1} - \frac{1}{s_1 + s_2} \right) \quad \text{(2.19)}
\]

The total measured voltage \( V = V_2 - V_3 \) becomes

\[
V = \frac{\rho I}{2\Pi} \left( \frac{1}{s_1} - \frac{1}{s_2 + s_3} - \frac{1}{s_1 + s_2} + \frac{1}{s_3} \right) \quad \text{(2.20)}
\]

The resistivity \( \rho \) is given by,

\[
\rho = \frac{2\Pi V}{\left( \frac{1}{s_1} - \frac{1}{s_2 + s_3} - \frac{1}{s_1 + s_2} + \frac{1}{s_3} \right)} \quad \text{(2.21)}
\]

\( \rho \) is usually expressed in ohm.cm, with \( V \) measured in volts, \( I \) in amperes, and \( s \) in cm. The current is usually such that the resulting voltage is approximately 10mV. For most four-point probes, the probe spacings are equal. With \( s = s_1 = s_2 = s_3 \), the equation becomes,
Smaller probe spacings allow measurements closer to wafer edges.

Semiconductor wafers are not semi-infinite in extent in either the lateral or vertical dimension. So, the equation for resistivity must be corrected for finite geometries.

For an arbitrarily shaped sample, the resistivity is given by,

\[ \rho = \frac{2\pi SV}{I} \]  \hspace{1cm} (2.22)

Conductivity \( \sigma = \frac{1}{2\pi SFV} \) \hspace{1cm} (2.24)

where \( F \) is a correction factor that depends on the sample geometry. \( F \) corrects for probe location near sample edges, for sample thickness, sample diameter, probe placement and sample temperature.

For collinear or in-line probes with equal probe spacing \( s \), the correction factor \( F \) is a product of three separate correction factors \( F_1 \), \( F_2 \) and \( F_3 \).

\[ Ie, F = F_1 \times F_2 \times F_3 \] \hspace{1cm} (2.25)

\( F_1 \) corrects for sample thickness \( F_2 \) corrects for lateral sample dimensions, and \( F_3 \) corrects for placement of probes relative to sample edges.
Sample thickness must be corrected for most measurements since semi conducting wafers are not infinitely thick. Their thickness is usually on the order of the probe spacing, or less, introducing the correction factor [51],

\[ F_{11} = \frac{t}{s/2 \ln \left( \frac{\sinh(t/s)}{\sinh(t/2s)} \right) } \] (2.26)

This is for a non-conducting bottom surface, where \( t \) is the wafer or layer thickness.

For a conducting bottom surface, the correction factor becomes

\[ F_{12} = \frac{t}{s/2 \ln \left( \frac{\cosh(t/s)}{\cosh(t/2s)} \right) } \] (2.27)

Conducting bottom surfaces are difficult to achieve. In most of the cases, four-point probe measurements are taken with insulating bottom boundaries. For thin samples,

\[ F_{11} = \frac{t}{s/2 \ln (2) } \] (2.28)

Conventional four probe measurements are suitable for moderate or low resistivity materials, while minority carrier injection and sample loading by the voltmeter limit the accuracy of measurement in the case of high resistivity samples.

2.4.4 Photoluminescence (P.L) measurements

P.L measurements are performed using a Jobin Yvon Flurolog 3 Spectrofluorometer. (Model FL3-22). The instrument has a 450W Xenon lamp as source and a PMT detector (Model: R928P). The
sample compartment module is T-box type. Double gratings are used for excitation and emission spectrometers.

Photoluminescence is the process by which light energy is absorbed by the material and a fraction of it is emitted in the visible or near visible region. The excitation source is IR, visible, UV or X-rays. Photoluminescence is mainly divided into two-fluorescence and phosphorescence. In fluorescence, emission occurs during excitation or within $10^{-8}$ s after excitation. $10^{-8}$ s is of the order of lifetime of the atomic state corresponding to the allowed electric dipole transitions in the visible region. If emission occurs microseconds or even hours after excitation is removed, it is called phosphorescence. Some samples show characteristic luminescent behaviour. In others activators are mainly responsible for luminescence [52-53].

In polymers, generally excitons are responsible for luminescence. Exciton is a stable, bound electron-hole pair in the sample. An electron from the LUMO of the polymer combines with a hole from the HOMO to form excitons. Generally singlet excitons are delocalized over the polymer chain while the triplet excitons are bound. Obviously singlet excitons are mainly responsible for photoluminescence in conjugated polymers. The singlet exciton formed decays radioactively to the ground state with the emission of light[2]. If emission does not occur, then a non-radiative pathway is dominant and the electronic excitation is converted into rotational or vibrational motion within the polymer and its surroundings. The difference between the absorption and emission maxima of the spectra is called the Stoke’s shift. Stoke’s shift
occurs when the emission from the lowest vibrational excited state relaxes to various vibrational levels of electronic ground state.

![Diagram of various optical processes](image)

**Fig. 2.5** Schematic diagram of various optical processes

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abs</td>
<td>absorption</td>
</tr>
<tr>
<td>ISC</td>
<td>Intersystem crossing</td>
</tr>
<tr>
<td>IC</td>
<td>internal conversion</td>
</tr>
<tr>
<td>VR</td>
<td>vibrational relaxation</td>
</tr>
<tr>
<td>S₀</td>
<td>ground state singlet</td>
</tr>
<tr>
<td>S₁</td>
<td>first excited state</td>
</tr>
<tr>
<td>T₁</td>
<td>first triplet excited state</td>
</tr>
</tbody>
</table>

Based on the processes responsible for photoluminescence, the phenomenon of photoluminescence is mainly divided into two-intrinsic luminescence and extrinsic luminescence. Some samples exhibit intrinsic luminescent behaviour. In others, activators are mainly responsible for luminescence. Activators are impurity atoms present in small concentrations in the host material or stotchiometric excess of certain component in the host material (self-activators).

In extrinsic luminescence, there will be some localized energy levels in the forbidden energy gap of the sample. There are two possibilities.
a) Intermediate level corresponding to the activator atom, A.

b) Intermediate level corresponding to the host material, G which is under the perturbing influence of activators or belonging to lattice defects, whose existence is associated with the incorporation of activator atoms.

There are mainly three possibilities of excitation.

a) A photon of appropriate energy may excite an electron from G to A.

b) Excitons may be formed in some other parts of the sample. They may diffuse to the luminescence center. Under the excitation of the excitons, electrons may be excited from G to A.

c) Due to the bombardment with electron or photon, an electron may be created in the conduction band and a hole in the valence band. Hole from the valence band may occupy the level G and electron from the conduction band the level A. Their recombination and subsequent deexcitation results in photoluminescence.

2.4.5 TEM studies

The TEM images are obtained using a JOEL JEM 2200 FS electron microscope working under an accelerating voltage of 200 KV. Schematic diagram of a Transmission Electron Microscope (TEM) is given in fig 2.6.
In a TEM, electrons from the electron gun are accelerated from 100KV to 400KV and are focused onto the specimen by a combined lens system[54-57]. The sample is kept very thin for effective transmission and is placed on a copper grid. The transmitted and forward scattered electrons produce a diffraction pattern in the back focal plane of the lens and a magnified image on the image plane of the lens. Either of it is projected onto a fluorescent screen for photographing or electronic recording. Formation of diffraction pattern helps to study the structural details.

There are mainly three imaging techniques-bright field, dark field and high resolution imaging [38]. Contrast depends on diffraction and scattering of electrons. Transmitted electrons give rise to bright field
image and specific diffracted beam the dark field image. Contrast depends on the intensity of electrons transmitted through the sample that pass through the imaging lens. Heavier elements lead to greater scattering of electron beam. So, intensity of transmitted electrons is reduced. Contrast comes about by phase contrast, mass contrast, thickness contrast and diffraction contrast. High resolution TEM (HREM) is used to obtain information on the atomic scale and is particularly used in the interface analysis. Here a number of different diffracted beams are combined together to give an interference image.

2.4.6 SEM studies

The SEM images are obtained using a Joel 6390LV scanning electron microscope. The schematic diagram of a scanning Electron Microscope (SEM) is given in figure 2.7.

Fig. 2.7 Schematic diagram of a scanning electron microscope
Scanning Electron Microscopy is similar to optical microscopy. But here electrons are used instead of photons. Electrons of energy 10-30KeV impinge on the sample. Secondary electrons, back scattered electrons, auger electrons and X-ray photons are produced. Secondary electrons form the SEM image. Back scattered electrons also form an image [58]. Absorbed electrons are measured as electron beam induced current.

The secondary electrons are detected and amplified. The image of the specimen is mapped onto a C.R.T screen. There should be one to one correspondence between each point on the specimen and each point on the screen. Magnification is defined as the ratio of the length of C.R.T display to length of sample scan. Using SEM, magnification of the order of $10^6$ could be achieved, which is impossible through optical microscope. Large magnification is possible because electrons have smaller wavelengths and depth of field produced is large. Contrast is an important parameter for SEM imaging. For flat, uniform samples, there is no contrast. But for samples composed of materials with different atomic numbers, contrast is
observed. Contrast is observed mainly due to back scattered electrons because back scattering co-efficient is a strong function of atomic number than secondary electron emission co-efficient. Other factors affecting contrast are sample surface, surface topography and local electric fields. Secondary electrons are emitted from the top 10nm of the sample surface. When the sample is tilted through an angle $\theta$ from the normal beam direction, electron beam path inside the sample increases by $1/\cos \theta$.

$$\text{Contrast-C}=\tan \theta \cdot \theta$$ \hspace{1cm} (2.29)

Sample stage is an important parameter. It should allow sufficient tilt and rotation for the sample to be viewed in all directions. In SEM, the detector collects even those electrons moving away from it, unlike an optical microscope.

The electron gun emits electrons. It should have low electron dispersion. Usually tungsten filament is used which produces electron dispersion in the range 2eV. Lithium hexaborate and field emission sources have lower energy dispersion, longer life and higher brightness. The electron beam passes through scanning coils and lens system to the sample. Auger electrons, characteristic and continuous X-rays, photons, back scattered electrons and secondary electrons are produced. Secondary electrons are detected by a detector which is usually a scintillation material which produces light when highly accelerated electrons (10-12KV) fall on it. To accelerate electrons, scintillator is placed in a faraday cage of high electric field. The electrons from the detector are connected to a photomultiplier tube which multiplies the number of electrons several folds. It is finally connected to Cathode
Ray Tube (C.R.T). C.R.T image is a mapping of the scanned signal image. The beam diameter used in SEM is 10nm. Still resolution is not good [38]. The major reasons are,

a) Large number of electrons is elastically and inelastically scattered. Elastic scattering occurs due to scattering of electrons by positive nuclei and inelastic scattering is due to valence and core electrons.

b) The shape of electron distribution cloud depends on the ion beam energies and the atomic number of the target. For $Z \leq 15$, the distribution is tear drop shaped. For $15 < Z < 40$, it becomes more spherical. In the case of elements with $Z \geq 40$, the distribution is hemi spherical.

c) For low atomic numbers, electrons are absorbed and for high atomic numbers, back scattered electrons are large.

2.4.7 Thermo gravimetric Analysis (TGA)

Sample and reference are heated by a single source and the temperatures are measured by thermo couples embedded in the sample and reference, and attached to their pans. Weight loss corresponding to various temperatures is noted [1].

2.4.8 UV/Vis/NIR Absorption Spectroscopy

In this technique, the absorption of light in the ultraviolet (10–420 nm), visible (420–700 nm) and near-infrared (700–2500 nm) regions by a sample is measured. The absorption of light in the
UV/Vis/NIR region depends on the nature of chemical groups present in the structure.

A polymer molecule, in its ground state contains two electrons of equal and opposite spin in each filled molecular orbital. One of the electrons in the highest filled $\Pi$ molecular orbital absorbs light and is raised to the lowest unfilled $\Pi$ molecular orbital. If the spins are antiparallel, we get an excited singlet state and if they are antiparallel, an excited triplet state results. The different possible transitions are,

1. $\sigma-\sigma^*$ transition

Here the transition of electron is from a bonding sigma orbital to a higher energy antibonding sigma orbital. Since sigma bonds are very strong, this transition is a high energy process.

2. $n-\sigma^*$ transition

This transition is observed in saturated compounds having one heteroatom with unshared pair of electrons. These transitions require less energy than $\sigma-\sigma^*$ transitions.

$n-\sigma^*$ transitions are sensitive to hydrogen bonding.

3. $\Pi-\Pi^*$ transition

Such transitions occur in compounds with unsaturated centers and requires less energy than $n-\sigma^*$ transitions.
4. n- $\Pi^*$ transition

Here an electron of unshared electron pair on a heteroatom is excited to a $\Pi^*$ antibonding orbital. n- $\Pi^*$ transition requires the least amount of energy than all the above transitions and consequently this transition gives rise to an absorption band at longer wavelengths.

The absorption co-efficient $\alpha$ is measured, by dividing the absorption values by the film thickness.

The photon absorption in many amorphous materials is found to obey the Tauc relation given by, 

$$\frac{(\alpha \nu \nu)}{B} = (\nu \nu - E)^n$$

Here $\alpha$ is the absorption coefficient in eVcm$^{-1}$, $\nu \nu$ the photon energy, $B$ a constant and the index $n$ is connected with the distribution of the density of states. For direct allowed transition energy gap, $n=1/2$ and for indirect allowed transition energy gap, $n=2$. $(\alpha \nu \nu)^2$ as a function of photon energy $\nu \nu$ gives direct allowed transition energy gap. $(\alpha \nu \nu)^{1/2}$ as a function of photon energy $\nu \nu$ gives indirect allowed transition energy gap [59-60].

![Block diagram of UV/VIS/NIR Spectrometer](image)

**Fig. 2.9** Block diagram of UV/VIS/NIR Spectrometer
In the present work we have used Jasco V 570 UV/VIS/NIR spectrometer employing a Deuterium lamp (190-350nm) and a halogen lamp (330-2500nm). The optical system used is a single monochromator. The spectrometer has two detectors-1. PhotoMultiplier Tube (PMT) 2. Lead sulphide (PbS) Photoconduction cell. The instrument has a resolution of 0.1nm in the UV/VIS region and 0.5nm in the NIR region.

2.4.9 Photo acoustics measurements

The Thermal Diffusivities are calculated using thermo elastic bending formula applied to open photo acoustic technique in transmission configuration. The detailed theory regarding this technique is given in chapter 7.

2.4.10 Raman measurements

Raman Spectroscopic measurements of the samples are carried out in the range 200cm⁻¹-1800cm⁻¹, using a Jobin Yvon Horiba micro Raman system employing a 488nm Argon laser as source.

Raman spectroscopy is based on the Raman effect, first reported by C.V. Raman in 1928[61]. If the incident photon imparts part of its energy to the lattice in the form of a phonon, it emerges as a lower energy photon. This is called Stokes shift. When the photon absorbs a phonon and emerges with higher energy, it is termed Anti-Stokes shift. The Anti-Stokes mode is much weaker than the Stokes mode. So Stokes mode scattering is usually monitored. In Raman scattering, incident light interacts with optical phonons, while in Brillouin
scattering, the incident light interacts with acoustic phonons. Since optical phonons have higher energies than acoustic phonons, giving larger photon energy shifts, Raman scattering is easier to detect than Brillouin scattering.

In Raman spectroscopy, a low power laser beam is pumped onto the sample [62]. The weakly scattered light is passed through a double monochromator, which rejects the Rayleigh scattered light. The Raman shifted wavelengths are detected by a photodetector. The fluorescent background problem is eliminated by combining Raman spectroscopy with FTIR [63]. By using lasers of different wavelengths and hence different absorption depths, it is possible to profile the sample to some depth. The wavelengths of the scattered light are analyzed and matched to known wavelengths for identification.

Raman spectroscopy can be used to detect both organic and inorganic species. It is free from charging effects, which is a disadvantage for electron and ion beam techniques. It is sensitive to strain, allowing it to be used for detecting stress in a semiconductor material or device. The major semiconductor applications of Raman spectroscopy include structural defects, ion damage, laser annealing, alloy fluctuations, interfaces and heterojunctions [64].

2.4.11 Mechanical strength measurements

Mechanical strength measurements are carried out using a *AG I Shimadzu Universal Testing Machine (UTM)* (figure 2.10). The machine can measure a load up to 10kN. The pellets samples are standardized by
applying a uniform pressure. The diameter of the probe employed is 5mm.

Fig. 2.10 Universal testing Machine

For quantitative description of mechanical behaviour, it is necessary to derive stress-strain relationships. An ideal elastic solid obeys Hooke's law.

There are 5 important ways in which the mechanical behaviour of a polymer may deviate from this ideal case. The polymer may exhibit

a. Time dependence of response
b. Non-recovery of strain on removal of stress
c. Non-linearity of response (It does not imply non-recovery).
d. Anisotropy of response

These are essentially independent effects. A polymer may exhibit all or any of them [1].
2.4.12 Thermo power measurements

Thermo power measurements are conducted using a home made Thermo Electric Power (TEP) set up in dc differential technique using copper electrodes. Copper contribution is properly deducted.

The thermo power, or thermoelectric power (also called the Seebeck coefficient) of a material is a measure of the magnitude of an induced thermoelectric voltage in response to a temperature difference across that material. The thermo power has units of (V / K). The term thermo power is a misnomer, since it measures the voltage or electric field (not the electric power) induced in response to a temperature difference.

Classically, an applied temperature difference causes charged carriers in the material, whether they be electrons or holes, to diffuse from the hot side to the cold side, similar to a gas that expands when heated. Mobile charged carriers migrating to the cold side leave behind their oppositely charged and immobile nuclei at the hot side thus giving rise to a thermoelectric voltage (thermoelectric refers to the fact that the voltage is created by a temperature difference). Since a separation of charges also creates an electric field, the buildup of charged carriers onto the cold side eventually ceases at some maximum value since there exists an equal amount of charged carriers drifting back to the hot side as a result of the electric field at equilibrium. Only an increase in the temperature difference can resume a buildup of more charge carriers on the cold side and thus lead to an increase in the thermoelectric voltage. Incidentally the thermo power also measures the entropy per charge
carrier in the material. The thermo power of a material, represented as $S$, depends on the material’s temperature, and crystal structure.

If the temperature difference $\Delta T$ between the two ends of a material is small, then the thermo power of a material is conventionally (though only approximately, see below) defined as:

$$S = -\frac{\Delta V}{\Delta T} \tag{2.31}$$

Where $\Delta V$ is the thermoelectric voltage seen at the terminals.

This can also be written in relation to the electric field $E$ and the temperature gradient $\nabla T$, by the equation:

$$S = -\frac{E}{\Delta T} \tag{2.32}$$

Strictly speaking, these two expressions are only approximate: The numerator of the first equation should be the difference in (electrochemical potential divided by $e$), not electric potential. Likewise, the second equation should have the gradient of electrochemical potential divided by $e$ rather than the electric field. However, the chemical potential is often relatively constant as a function of temperature, so using electric potential alone is, in these cases, a very good approximation.[65]. Taking the sign into consideration, the equations 2.31 and 2.32 may be rewritten as,

$$S = -\frac{V_{\text{left}} - V_{\text{right}}}{T_{\text{left}} - T_{\text{right}}} \tag{2.33}$$
\[ E = SVT \]  \hspace{1cm} (2.34)

where "left" and "right" denote two ends of the material. Thus, if \( S \) is positive, the end with the higher temperature has the lower voltage, and vice-versa. The electric field will point in the same direction as the temperature gradient.

Note that there is a minus sign in the first equation, but not in the second. This is because the electric field points from the higher voltage towards the lower voltages, whereas the temperature gradient points from the lower temperature towards the higher temperature [66].

2.4.13 Film thickness measurements

Film thickness is recorded using a DEKTAK 6M STYLUS PROFILER working in the range 0.005 \( \mu \text{m} \) to 262 \( \mu \text{m} \).

The thickness of the film can be calculated using a modern technique called stylus profiler. It is an advanced thin and thick film step height measurement tool capable of measuring step even below 100 \( \text{A}^0 \). One can use this to profile surface topography and waviness as well as measuring surface roughness in a sub nanometer range. The stylus is mechanically coupled to the core of an LVDT (Linear Variable Differential Transformer). As the stage moves the sample, the stylus rides over the sample surface. Surface variations cause the stylus to be translated vertically. Electrical signal corresponding to the stylus movement is produced, as the core position of the LVDT changes. The LVDT scales an ac reference signal proportional to the position change, which in turn is conditioned and converted to digital format, through a
high precision integrating analog to digital converter. This signal is stored in computer memory for display [67-69].

![Block diagram of stylus profiler thickness monitor](image)

**Fig. 2.11** Block diagram of stylus profiler thickness monitor

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