As pointed out in the previous chapter that the glass transition phenomena is relaxational in nature, and hence, can be investigated using various experimental techniques\textsuperscript{1-9} such as Dielectric Spectroscopy, Nuclear Magnetic Resonance Spectroscopy, Photon Correlation Spectroscopy, Neutron Scattering, Dilatometry, and Differential Scanning Calorimetry (DSC). Among the above mentioned techniques, Dielectric spectroscopy is the most widely used technique to study the rotational motion of individual molecules near and below the glass transition temperature ($T_g$). Hence our main interest is the dielectric measurements with DSC and x-ray as the supporting techniques. The dielectric relaxation technique is very well developed commercially for the frequency domain measurements in the form of extensive range of a. c. bridges with the advantage that signal-to-noise ratio is very high. The dielectric measurements that we are interested here correspond to sub-microwave range of frequencies, where quantum and phonon phenomena do not enter in any significant way, and measurements will extend down to the very low frequencies in the mille hertz range and below, made accessible by recent developments in Instrumentation using time domain step response technique. In the range above 10 Hz excellent bridge techniques are available, giving high accuracy in the measurements of even nearly non-polar (very low loss) materials. The general draw back of these bridge techniques is the limited range of frequencies which are attainable on any one instrument. However, with the invention of Personal computers
(PCs) it is no more a problem as different bridges can be controlled by a single PC. Moreover, time domain techniques have become available commercially even very high frequencies up to 30-40 GHz. and hence, the range of frequencies from 10 Hz-40 GHz can be covered in a short time. The time domain technique has been developed in our laboratory to facilitate the dielectric measurements in the ultra low frequency region. A combination of the two techniques namely, dielectric spectroscopy and DSC will provide an excellent information about the relaxation processes in the supercooled liquids as well as supercooled plastic crystals. The DSC explores various phase transitions and the structural relaxation in glassy materials. For the dielectric measurements, an HP 4284A precision LCR meter in the frequency range of 20 Hz-1 MHz is used as before. For frequencies below 20 Hz to 10^{-3} Hz, we have sampled the dielectric absorption currents in the time window of 0.01-1000 secs., using a digital storage oscilloscope (DSO) card DSO-2200 (Link Instruments Inc. USA), in combination with a Keithley Model No. 617 Programmable Electrometer. The complex permittivity was calculated by taking Discrete Fourier Transform (DFT) of the discharging current. However, there is a limitation in this kind of measurements, set by the resolution of the DSO card. Because of this, we are not able to determine the actual dielectric strength as well as complete spectral characteristic at these low frequencies. However, the $f_m$ values measured with the help of this technique are as good as that measured by the LCR bridge.

2.1 Differential Scanning Calorimetry Measurements

In a DSC, there are two pans. In one pan called the sample pan, we put our sample. The other one is the reference pan, that leave empty. Each pan sits on top of a heater. (see Figure 2.1) Then we tell the interfaced computer to turn on the heaters. So the computer turns on the heaters, and tells it to heat the two pans at a specific rate, usually something like 10° C per minute. The computer makes absolutely sure that the heating the rate stays
exactly the same throughout the experiment. But more importantly, it makes sure that the two separate pans, with their two separate heaters, heat at the same rate as each other. Why wouldn’t they heat at the same rate? The simple reason is that the two pans are different. One has sample in it, and one doesn’t. The sample means there is extra material in the sample pan i.e. it will take more heat to keep the temperature of the sample pan increasing at the same rate as the reference pan. So the heater containing sample in the sample pan has to work harder than the heater containing the reference pan. It has to put out more heat. By measuring just how much more heat it has to put out is what we measure in a DSC experiment.

Hence DSC\textsuperscript{10–15} is a technique that records the energy necessary to establish a zero temperature difference between a substance and a reference material against either time or temperature. The reference material usually chosen on the merit that it should not undergo any transition in the desirable temperature range. Should an endothermic thermal event (\(\Delta H\) positive, such as melting) occur in the sample, the temperature of the sample, \(T_s\), will
Figure 2.2: A typical DSC output showing various transitions. Where q is the amount of heat at a given time 't'.

lag behind the temperature of reference, \( T_r \). In DSC, the sample and the reference material are maintained at the same temperature (\( \Delta T = T_s - T_r = 0 \)) by supplying the energy difference to the sample by an independent supply and the energy difference is then recorded against the program temperature. Thermal events in the sample appear as deviations from baseline, in either an endothermic or exothermic direction, depending upon whether more or less energy has to be supplied to the sample relative to the reference material as shown in Figure 2.2. A glass transition event appears as a step-like change in DSC scans (Figure 2.2).

If 'q' is the amount of heat supplied to the sample at a given time 't', then

\[
\frac{q}{t} = \text{Heat flow} \tag{2.1}
\]

If \( \Delta T \) is the temperature increase with time 't', then

\[
\frac{\Delta T}{t} = \text{Heating rate} \tag{2.2}
\]

from eq. 2.1 and eq. 2.2,
\[ \frac{q}{\Delta T} = C_p = \text{Heat Capacity} \]  \hspace{1cm} (2.3)

### 2.1.1 Description of DSC Set-up

The DSC measurements reported in this thesis are performed using Perkin-Elmer Sapphire DSC at a heating rate of 2 deg./min. For the measurement of glass transition \((T_g)\), a different heating rate 10 deg./min was employed. The system measures the temperature and differential heat flow associated with material transitions and provides quantitative and qualitative data on endothermic and exothermic processes. The Sapphire DSC consists of a cell base module, which supports the standard DSC cell. The cell base is an operating base for the DSC cell. It transmits heater voltage and thermocouple signals between the thermal analyzer and DSC cell. Output from thermocouple is controlled and amplified by circuitry in the cell base. Input ports for vacuum, cooling and purge gases, connector and calibration controls are located at the rear of cell.

The cross sectional view\(^{14}\) of the DSC cell can be seen in Figure 2.3. In the cell, the sample and reference pan sit on raised platforms on a constantan disc. Heat is transferred through the disc to the sample and reference. Differential heat flow is monitored by thermocouples located beneath the disc. The DSC cell has two separate thermocouples for sample and controlling purpose. The sample thermocouple monitors the sample temperature which is the temperature displayed on the thermal analyzer and recorded as sample temperature. The control thermocouple, is embedded in the furnace and permits precise monitoring and controlling of the heater. For cooling the sample, a quench cooling accessory is used which consists of a metal can that fits over the cell. A reservoir in the top of this can is filled with liquid nitrogen to cool the sample. For liquid and solid samples, aluminium pans have been used. The operating temperature range using aluminium pans is from 100 K to 823K. The samples for calorimetric measurements are sealed in the pans using a sample encapsulating.
press.

### 2.1.2 Calibration of DSC

The system is first calibrated so that both sample thermocouple and control thermocouple read temperature correctly. There are three calibration routines for a Perkin Elmer Sapphire DSC:

a. Temperature calibration

b. Heat Flow calibration

c. Furnace calibration

The temperature calibration as well as furnace calibration has been done using Perkin Elmer Sapphire standard calibration programme with indium and n-pentane as the standards. (more details on this front has been given in user Perkin Elmer manual\textsuperscript{14}).

For heat flow calibration, the cell is calibrated using various standards having different
melting temperatures and whose heat of fusions are known very accurately. The calibration coefficient is determined from the following formula:

\[ E = \frac{\Delta H_m}{A} \]  

(2.4)

where \( \Delta H \), \( m \) and \( A \) are heat of fusion, sample mass in and peak area, respectively. This procedure is repeated with various standards covering the entire temperature range of relevance and corresponding \( E \) values are measured. The standards used for this purpose are: indium \((T_m = 429.8 \, \text{K}, \, \Delta H_m = 3.27 \, \text{kJ/mol})\); water \((T_m = 273.0 \, \text{K} \quad \text{and} \quad \Delta H_m = 6.01 \, \text{kJ/mol})\) and cyclohexane for solid-solid transition \((186.09 \, \text{K})\). The plot of \( E(T) \) vs \( T \) is used for the exact calculation of \( \Delta H \) of transition under consideration. The accuracy of \( \Delta H \) is limited by the accuracy of weighing measurements of the sample which is \( \pm 0.1 \, \text{mg} \).

2.1.3 Procedure For the Determination of Transition Temperatures

A sample weighing 8-12 mg is taken in the aluminium pan and is cooled using quench cooling accessory. The time required to cool the DSC cell from room temperature down to 100 K is approximately 25 minutes, with an average cooling rate of \( 8^\circ/\text{min} \). The sample is equilibrated for some time (\( \approx 2-10 \, \text{min} \)) at the lowest set temperature. Data is then taken while heating of the sample at a fixed rate starts. Since the quench cooling accessory does not provide high enough cooling rates required to form glass in some of the systems, the following cooling technique has been used with such samples: First the DSC cell (without sample pan) is cooled to the lowest temperature. The sample pan is dipped directly into liquid nitrogen and then it is quickly introduced in to the DSC cell at a temperature of 100K. With this technique, the sample is cooled down to liquid nitrogen temperature in 10-15 secs, thus yielding an average cooling rate of \( 800^\circ/\text{min} \). This method is used in those cases where glass formation is not possible otherwise. Though this technique causes some distortion in base line due to moisture condensation, the base line is usually good enough to measure the
transition temperatures within experimental accuracy. The transition temperatures, at the specified heating rates are determined from the DSC curves using the software provided by the manufacturer of the instrument.

2.2 Dielectric Relaxation Measurements

Dielectric measurements are made in two steps. In the frequency range from $1 MHz$ to $20 Hz$, measurements are made with the help of a precision Hewlett Packard HP4284A precision LCR meter bridge. In the ultra low frequency range ($10^{-0.5} - 10^{-3} Hz$), a dc step response technique incorporating Keithley 617 Programmable Electrometer is used. The problem of slow switching has been eliminated in some experiments using fast electronic switches (imported from Supertex, Inc.) and the transient current data has been sampled at a very high rate using DSO-2200 oscilloscope, consequently, filling the frequency gap of $20 Hz - 10^{-0.5} Hz$.

2.2.1 Bridge Technique

For the measurements of real and imaginary parts of complex dielectric constant ($\varepsilon^* = \varepsilon' - i\varepsilon''$), the measurements are performed in $C_p - D$ mode of the LCR meter. In $C_p - D$ mode of LCR meter, the sample is represented as a parallel combination of capacitor $C_p$ and resistance $R_p$. A sinusoidal voltage of angular frequency $2\pi f$ ($f$ is frequency in $Hz$) is applied between the electrodes of sample and the net current passing through the sample is measured. The root mean square components of current in phase $I_{ph}$ and the one $90^0$ out of phase $I_{ou}$ with the applied voltage are measured by a phase sensitive detection technique. The component in phase is proportional to the conductance of the sample under test and the other one to $2\pi f C$ value. The ratio of these two currents gives $\tan \delta$ value which is called dissipation factor $D$ of the capacitor.

$$D = \frac{I_{ph}}{I_{ou}} = \frac{1}{2\pi f R_p C_p}$$
and

\[ 2\pi f C_p = I_{ou}/V \]  \hspace{1cm} (2.6)

where, \( V \) is the a.c. voltage. Capacitance \( C_p \) and dissipation factor \( D \) are computed from the measured \( I_{ph} \) and \( I_{ou} \) components using applied voltage \( V \) and frequency \( f \). The values displayed on screen and are simultaneously stored on computer using a GPIB card with the help of a program written in HP VEE language.

### 2.2.2 D.C. step - response Technique

The schematic diagram of this technique has been given in Figure 2.4. In this method\(^{15}\), sample capacitor is charged by applying a d.c. step voltage \( (V_0) \), which, on fully charging is discharged by short-circuiting the capacitor. The charging and discharging currents are sampled with the help of a Keithley Programmable Electrometer (Model 617). The calculation of complex permittivity constant \( \epsilon^* \) from discharging current can be done as follows\(^{16}\): For a sample with geometrical capacitance \( C_0 \), subjected to a time dependent voltage \( V(t) \), the corresponding charge \( Q(t) \) for a linear dielectric is given by,

\[ Q(t) = C_0 \left[ \epsilon_\infty V(t) + \int_{-\infty}^{t} dt' \Phi(t - t')V(t') \right] \]  \hspace{1cm} (2.7)

where \( \epsilon_\infty \) is the limiting permittivity and \( \Phi \) is a response function. When a step voltage \( V(t) = 0 \) \( (t < 0) \), \( V(t) = V_0 \) \( (t > 0) \) is applied to the sample, the transient current \( I(t) \) is given by,

\[ I(t) = dQ/dt = C_0 V_0 \left[ \epsilon_\infty \delta(t) + \Phi(t) \right] \]  \hspace{1cm} (2.8)

The response function \( \Phi(t) \) is related to complex permittivity \( \epsilon^* \) by,

\[ \epsilon^* = \epsilon_\infty + L\Phi(t) \]  \hspace{1cm} (2.9)

where,

\[ L\Phi(t) = \int_0^\infty \exp(-j\omega t)\Phi(t)dt \]  \hspace{1cm} (2.10)
From eqs. 2.7-2.9, we get

\[ \varepsilon^* = \left( \frac{1}{C_0 V_0} \right) L(I(t)) \]  

(2.11)

Thus, complex permittivity can be obtained by taking Fourier Transformation of the transient current. Discrete Fourier Transformation of transient current is done by a program developed by us. The accuracy of this program has been checked with several known functions before using it for transient current.
2.2.3 Description of Dielectric Set-Up

For the low temperature measurements a stainless steel cryostat has been used (Figure 2.5). The lower part and upper part of this cryostat has been separated by a Teflon connector to avoid water condensation on the upper part of the cryostat. The lower portion of the cryostat is dipped into liquid nitrogen kept in a dewar flask.

The upper part contains two ports (input and output) which are used for gas purging. Shielded co-axial cables have been used for various connections from the dielectric cell to the measuring units to reduce the noise. The complete set-up for low temperature dielectric measurements is shown in Figure 2.5. Two types of dielectric cells have been used mainly for our samples which are described below:
(i) For the liquid samples a two terminal co-axial cell with guarded arrangement has been used. Teflon spacers have been used to separate inner electrodes (Figure 2.6). The empty cell capacitance achieved is usually around $100 \ pF$. The Copper-Constantan thermocouple is placed deep inside liquid to measure the sample temperature through Digital Panel Meter (DPM). The sample thermocouple is calibrated at five different temperatures using slash bath method. The accuracy of temperature has been found to be ± 0.5K. This cell has

Figure 2.6: Schematic diagram of Liquid cell used for Dielectric measurements
been heated with the help of a heater around it. The control thermocouple kept near the heater winding monitors the heater temperature and the heater temperature is controlled with the help of a Indotherm-401 temperature controller.

ii) A different cell assembly has been used for powdered samples as shown in Figure 2.7. A disc of about 2.5 cm. in diameter and of about 0.2 cm. in thickness is made out of the sample by pressing it in a pressure dye at a pressure of 10 K bar. The two electrodes are made from silver powder pressed at the same pressure. The sample disc is then pressed between the

---

Figure 2.7: Dielectric measurement setup for powdered samples in the form of pellets.
silver pellets at the same pressure to make the capacitor. This capacitor is held between two brass electrodes with the aid of a light weight spring. The empty cell capacitance of this cell arrangement is usually around 2-4 pF. The sample temperature is measured with the help of Copper-Constantan thermocouple kept deep inside the bottom electrode. The temperature is controlled in the same way as discussed in the case of liquid cell.

2.2.4 Procedure for the Calculation of $\epsilon'$ and $\epsilon''$

Before taking the dielectric measurements, the cell is calibrated with standard nonpolar liquid namely, Benzene. Lead capacitance has been calculated by measuring total empty cell capacitance ($C_e = C_0 + C_l$) (Figure 2.6) and the total capacitance with the standard liquid ($C_s = C_p + C_l$). The empty cell capacitance $C_0$ and lead capacitance $C_l$ are calculated from the following formulae:

$$
C_0 = (C_s - C_e)/(\epsilon' - 1)C_l = C_p - C_0 = C_s - (C_s - C_e)/(\epsilon' - 1) \tag{2.12}
$$

where $\epsilon'$ is dielectric constant of benzene at a given frequency. For measurements on sample, the cell is filled with the liquid and kept inside the cryostat for measurements. $C_p$ and $D$ have been measured at different temperatures as a function of frequency and stored on the computer. The real and imaginary parts of complex permittivity have been measured with the help of following:

$$
\epsilon' = (C_p - C_l)/C_0; \quad \epsilon'' = D\epsilon' \tag{2.13}
$$

Analysis for the determination of the various dielectric constants using appropriate empirical law is done by fitting of $\epsilon'$ and $\epsilon''$ to the corresponding law. For this purpose various non-linear fitting programmes have been developed which make use of Marquardt-Levenberg least square method. The separate fitting of $\epsilon'$ and $\epsilon''$ yield the same result because of the validity of Kramer-Kronig relationship. Accuracy of $\epsilon'$ is limited by the error in $C_0$ value and estimated to be up to 3%. The peak loss frequency $f_m$ values are calculated from the
parameters using the following eq21:

\[
f_m = f_0 \left\{ k' / \left[ \cos(\alpha \pi / 2) - \sin(\alpha \pi / 2) k' \right] \right\}^{1/(1-\alpha)}
\]  (2.14)

where \( k' = \tan((1 - \alpha)\pi / 2(1 + \beta)) \). The parameters thus evaluated are used for the further analysis as given in the later chapters.

For the ultra low frequency measurements, the cell filled with the sample is charged with a d.c. source (\( V_0 = 100 \) V). The discharging current \( I(t) \) is digitized at pre-set time intervals. The imaginary part of the dielectric constant is then calculated using Hamon's approximation\textsuperscript{22} or as FFT as the case is.

For the approximate calculation of high frequency limiting dielectric constant \( \varepsilon_{\infty} \) using eq. 1.23, we measure the refractive index \( n_D \) of the samples using Abbe's refractometer for sodium \( D \)-lines. The Abbe's refractometer can measure refractive indices over the range of 1.3 to 1.7 and is provided with a linear scale which can be read to 0.001 and is accurate to 0.0002. The measurements are based on the observation of the refracted beams passing through the sample and entering a prism of high refracting index at grazing angle, hence, measuring the critical angle \( r_c \) which is related with refractive index as:

\[
n_D = 1 / \sin(r_c)
\]  (2.15)

A drop of the liquid whose index is desired is placed upon the hypotenuse of one of the two prisms, and the hypotenuse of the other prism is placed upon that of first one so that the two prisms together form a cubical block of glass. A telescope focused for parallel light shows the characteristic divided field. The index of the liquid is then read directly from the calibrated scale. The actual \( \varepsilon_{\infty} \) can be approximated as 1.05 \( n_D^3 \) taking into account the contribution from atomic polarization.
2.3 X-Ray diffraction

The X-ray diffraction\textsuperscript{23} (XRD) pattern was taken for the samples at room temperature using Philips Xpert diffractometer using CPS 120 Detector. The X-ray unit was monochromatized using Cu $K_{\alpha 1}$ ($\lambda = 1.54056$ A\textdegree) with silicon ($a = 0.543088$ nm) for internal standard. The diffractograms are analyzed for indexing and crystal structure determination using standard software supplied by the manufacturer of the X-ray unit.

2.4 References


