CHAPTER III

THEORETICAL BACKGROUND

OF

STUDIES
In this chapter we discuss the theoretical background of the various studies proposed for the present investigation.

3.1 THERMALLY STIMULATED DISCHARGE CURRENT

The basic principle of TSD is to study the process of charge decay by heating the electret at a constant rate. The decay processes are investigated as a function of temperature instead of time. During its short history, TSD has evolved into a basic tool for the identification and evaluation of dipole orientation processes and of trapping and recombination levels. Its rapid growth has been spurred on by the fact that charge trapping and charge transport phenomena are not only of vital importance for electrets but also for materials used in thin films.

In TSD measurements, a charged/polarised sample is heated up from some low temperature $T_0$ (usually in the absence of an external field), while its electrodes are short circuited through a sensitive current detector. The current which appears in the external circuit due to depolarisation processes is recorded as a function of temperature. Each depolarisation process becomes detectable when its relaxation time is short enough, by producing a depolarisation current which increases at first with the temperature, then reaches a maximum and drops to zero as the equilibrium distribution is accomplished [1].

In an ideal case, a separate peak is produced for each relaxation process. If partial overlapping between two peaks occurs, separation of
high temperature peaks can be perused by the usual thermal cleaning. Let the maximum temperature of the two peaks be $T_1$ and $T_2$ and $T_1 < T_2$. Heating the crystal to an intermediate temperature $T'$ (where $T_1 < T' < T_2$) and subsequently cooling it, erases the low temperature peak. Then the sample is heated again to exhibit the second peak which is now nearly clear.

Early experiments of TSD were carried out without programmed heating since their main purpose was to measure the total related charge. Since mid-sixties, however, investigators have applied linear increase in temperature.

3.2 FACTORS GOVERNING THE TSD SPECTRA

There are a number of observations to the fact that poling conditions used for the formation of an electret and deliberately added impurities prior to the formation of an electret, play an essential role on the shape and size of the TSD spectra. Essentially, there are three poling parameters which affect the TSD spectra, they are: poling temperature, poling field and poling time.

3.2-i EFFECT OF POLING TEMPERATURE

Of the three poling parameters, poling temperature ($T_P$) has a special significance on the position and intensity of the TSD spectra. An electret may have a non-distributed (single relaxation) or distributed polarization and this can be detected from the shift in position of TSD
spectra with variation of $T_P$. The position of the current maxima in the TSD spectra remains unaltered. While the magnitude of current increases with increase in $T_P$, in the case of non-distributed polarization, the position of current maxima shifts to higher temperature and magnitude of current maxima increases for the distributed polarization [2,3]. At lower value of $T_P$, only the fast activated carriers contribute to the magnitude of current but as $T_P$ increases more and more carriers, even those with higher relaxation times will be activated and current maxima will increase.

3.2-ii  EFFECT OF POLING FIELD

The distinction between uniform and non-uniform polarizations can be made with variation of poling field ($E_P$). For uniform polarizations, charge increases linearly [4] while for non-uniform polarizations charge increases non-linearly [5] with $E_P$. Generally, the peak position is not affected by a change in field. However, there are reports regarding the shift in the position of current maxima towards lower temperature with $E_P$. This has been explained on the basis of field-assisted detrapping due to Poole-Frenkel effect [6] and on the mobility induced TSD where recombination factor is neglected. Lowering of activation energy with increase in $E_P$ but without a shift in the current maxima has been observed [7]. This has been attributed to the lowering of barrier height of the charge traps with the increase in $E_P$. Shrivastava et al. [8] have observed a linear relation
between peak current and square root of the polarizing field and they have explained this on the basis of charge injection from the electrodes.

3.2-iii  EFFECT OF POLING TIME

Effect of poling time ($t_p$) on the TSD spectra is similar to that of poling temperature. However, poling time should be changed logarithmically in order to obtain the changes of the same magnitude as that of poling temperature [9].

3.2-iv  EFFECT OF DELIBERATELY ADDED IMPURITIES

Magnitude of peak current in the TSD spectra increases many fold and peak position shifts to lower temperature side on introducing impurities into the specimen [10-14]. Both inorganic and organic doping agents have been used for this purpose. According to some authors [15], life and charge stability of polymer electrets increases with doping. This has been attributed to the modification of trap levels in the presence of impurity. the decrease in activation energy of the discharge process with doping has been observed by Gupta et al. [10]. It is surprising to find that sometimes the electret can be formed just by the incorporation of impurity and without the application of the field [16] which has been attributed to the formation of charge transfer complexes between dopant and the main molecular chain of polymer.
3.2-v EFFECT OF HEATING RATE

The TSDC peak shifts to higher temperature and their magnitudes increase with increasing heating rate. By varying the heating rate, activation energy of the dielectric relaxation process can be obtained [17].

Humidity can also affect the polarization. Effects of pressure and high energy radiations [18] on the charge storage have also been studied.

3.3 THEORY OF TSD

The disorientation of dipoles, on thermal stimulation can take place in the following two ways which are discussed in subsections.

(a) TSD of dipoles with one relaxation time, and
(b) TSD for a distribution of relaxation time.

(a) TSD OF DIPOLES WITH ONE RELAXATION TIME

In this discharge, the TSD peak appears in a narrow temperature interval and that its shape and position are unaffected by changes in polarisation conditions. The discharge of frozen in dipole polarisation, $P(t)$ in a short circuited polar electret under a linear heating rate, $r$, is considered here. Assuming that the polarisation $P(t)$ decays with a single temperature dependent relaxation frequency on reciprocal relaxation time $\alpha(T)$, according to the Debye rate equations, we have

$$\frac{dP(t)}{dt} + \alpha(T) \cdot P(t) = 0 \quad \ldots (3.1)$$

Integrating above yields

$$P(t) = P_d \exp\left[-\int_{t_d}^{t} \alpha(T) \, dt\right] \quad \ldots (3.2)$$

where, $t_d$ is the time of commencement of TSD.
$P_d$ is the attained equilibrium polarisation before the start of the TSD and could be expressed by

$$P_d = N_p \cos \theta$$  \hspace{1cm} \text{...(3.3)}

where $N$ is the density of dipoles, $p$ is the electric dipole moment and $\theta$ is the angle the dipoles subtend with the applied field. For a low concentration of dipoles, the average orientation can be expressed as

$$\cos \theta = \frac{pE_p}{3kT_p}$$  \hspace{1cm} \text{...(3.4)}

where $E_p$ is applied field, $k$ is the Boltzmann's constant and $T_p$ is polarisation temperature.

The current density, $j(t)$ due to the decay of the polarisation is

$$j(t) = \frac{dP(t)}{dt}$$

$$= \alpha(T).P(t)$$  \hspace{1cm} \text{...(3.5)}

Substituting $P(t)$ in eqn. (3.5), we get

$$j(t) = \alpha(T) P_d \exp\left[-\int_{t_d}^{t} \alpha(T) \, dt\right]$$  \hspace{1cm} \text{...(3.6)}

In a TSD run, the temperature $T$ is raised at a rate $r = dT/dt$, and the released current is expressed as

$$j(T) = \alpha(T) P_d \exp\left[-\frac{1}{r} \int_{T_d}^{T} \alpha(T) \, dT\right]$$  \hspace{1cm} \text{...(3.7)}

using the condition that at the start of the TSD run, i.e. at $t = t_d$, we have $T = T_d$. 

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The relaxation frequency for the dipole disorientation, $\alpha(T)$ is often envisaged to follow an Arrhenius shift, therefore

$$\alpha(T) = \alpha_0 \exp(-A/kT) \quad \cdots (3.8)$$

where $\alpha_0$ is the characteristic relaxation frequency ($T \to \infty$) and $A$ is the activation energy for dipole disorientation. Eqn. (3.8) can be applied to describe the temperature shift of the relaxation frequency of well characterised dipole groups nromally associated with the $\beta$-type of relaxations. For dipole groups, where disorientation are brought about by the segmental and cooperative movements of segments of the main chains, the frequency shift can be better described by the Williams Landel Ferry (WLF) shift (applicable for $T > T_g$).

$$\alpha(T) = \alpha_s \exp[2.303 \, C_1 (T - T_s) \cdot (C_2 + T - T_s)^{-1}] \quad \cdots (3.9)$$

where for most of the amorphous polymers $\alpha_s = 7 \times 10^{-3}$ sec$^{-1}$, $C_1 = 17.44$ and $C_2 = 51.6$ K.

Combining eqns. (3.7) and (3.8), we get the following expression for current density:

$$j(T) = \alpha_0 \exp[-A/kT] P_d - \exp \left[ -\frac{1}{r} \int_{T_d}^T \alpha(T) \, dT \right] \quad \cdots (3.10)$$

expressed as

$$\cos \theta = \frac{p E_p}{3 \, k \, T_p} \quad \cdots (3.11)$$

where $E_p$ and $T_p$ are the applied field and temperature respectively. Using eqns. (3.3) and (3.11)
\[ j(T) = \frac{\alpha_0 N_P^2 \varepsilon_0 E_p}{3kT_p} \left\{ -\frac{A}{kT} \cdot \exp \left( -\frac{\alpha_0 t}{r} \cdot \exp \left( -\frac{A}{kT} \cdot dt \right) \right) \right\} \] ... (3.12)

here \( \varepsilon_0 \) is the permittivity of free space.

Equation (3.12) describes the depolarisation current density released due to dipolar depolarisation in a shorted electret. The first exponential, which dominates the expression at low temperatures, describes the initial increase of the depolarisation current as the frozen in dipoles gradually become disoriented. The second exponential which dominates at high temperatures will gradually depress the current released until a maximum output current is reached, after which the current rapidly falls as the induced polarisation is exhausted. The current peak is thus asymmetric, having a steep slope on its high temperature side. The theory of TSD due to dipolar disorientation as described above, can be extended to include systems with a distribution in relaxation times.

The peak temperature, \( T_m \), for the current peak can be found by differentiating eqn. (3.10) and substituting for \( \alpha(T) \) from eqn. (3.8), we get

\[ T_m = \left[ \frac{r A}{k \alpha_0} \exp \left( \frac{A}{kT_m} \right) \right]^{1/2} \] ... (3.13)

From the above equation it can be seen that \( T_m \) will shift towards a higher temperature if a higher heating rate, \( r \), is employed. Also, for a fixed heating rate, the position of the peak (i.e. along the temperature axis) will be an increasing function of \( A \), the activation energy for disorientation as well as the natural relaxation time, \( 1/\alpha_0 \), for the process. It may also be
noted that $T_m$ is independent of the forming conditions, $E_p$ and $I_p$, provided the equilibrium polarisation has been attained.

(b) TSD FOR A DISTRIBUTION OF RELAXATION TIME

In the essentially non-crystalline polymeric solid, different conformations that the macromolecules may adopt, will result in an environment that can offer, differing resistance to the disorientating or rotating dipoles in different areas of the bulk. The dipoles will then have to surmount different activation energies resulting in different relaxation frequencies, $\alpha_i(T)$. Assuming that they still obey an Arrhenius shift, this can be written as

$$\alpha_i(T) = \alpha_o \exp(A_i/kT) \quad \cdots (3.14)$$

Different relaxation frequencies may also arise from different values of $\alpha_o$, for which we have

$$\alpha_i(T) = \alpha_{oi} \exp(A_i/kT) \quad \cdots (3.15)$$

A distribution of the type described by eqn. (3.14) is usually encountered in $\beta$-type relaxation. The type described by eqn. (3.15) is more likely to arise from relaxation associated with movements of the dipolar groups that move in unison with the micro-Brownian motions of the main chain segment, like the $\alpha$-relaxation near $T_g$. Here, different masses for the relaxing segments are most likely to be involved.
Assuming that distributions in $\alpha_0$ and $A$ are continuous, their contributions towards the polarisation, $P(t)$, could be expressed as

$$P(t) = P_d \int_{0}^{\infty} f(\alpha_0) \cdot \exp \left[ -\alpha_0 \int_{0}^{t} \exp(-A/kT) \, dt \right] \, d\alpha_0 \quad \cdots (3.16)$$

for a distribution in $\alpha_0$. For a distribution in $A$, this can be given as

$$P(t) = P_d \int_{0}^{\infty} g(A) \cdot \exp \left[ -\alpha_0 \int_{0}^{t} \exp(-A/kT) \, dt \right] \, d\alpha_0 \quad \cdots (3.17)$$

The distributions are also normalised such that

$$\int_{0}^{\infty} f(\alpha_0) \, d\alpha_0 = \int_{0}^{\infty} g(A) \, dA = 1 \quad \cdots (3.18)$$

The corresponding expressions for the current can be found by differentiating eqns. (3.16) and (3.17) which yields

$$j(t) = P_d \exp(-A/kT) \int_{0}^{\infty} f(\alpha_0) \cdot \exp \left[ -\alpha_0 \int_{0}^{t} \exp(-A/kT) \, dt \right] \, d\alpha_0 \quad \cdots (3.19)$$

and

$$j(t) = P_d \exp(-A/kT) \int_{0}^{\infty} f(\alpha_0) \cdot \exp \left[ -\alpha_0 \int_{0}^{t} \exp(-A/kT) \, dt \right] \, d\alpha_0 \quad \cdots (3.20)$$

Above equations also show that the TSD currents are independent of the forming conditions provided that the fullest possible polarisation has been reached. If this condition is not achieved, say due to too short a polarisation time $t_p$, or too low a temperature, $T_p$, then an effective distribution can be defined by

$$f^*(\alpha_0) = f(\alpha_0) \cdot FS(\alpha_0) \quad \cdots (3.21)$$

$$g^*(\alpha_0) = g(A) \cdot FS(A) \quad \cdots (3.22)$$

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where $FS(\alpha_0)$ or $FS(A)$ refers to the filling state of the polarisation. For a completely filled state, i.e. one where the electret has been polarized to its equilibrium polarisation value, $P_d$, the parameter $FS$ equals unity.

### 3.4 MECHANISM OF TSD

TSD is actually the mirror image of the charging process contributing to the discharge of electrets but the driving force of all of these is the restoration of charge neutrality. In electrets, prepared from polar materials, disorientation of dipoles play an important role. This disorientation tends to destroy the persistent dipole polarisation by distributing all dipoles at random.

The disorientation of dipoles involves the rotation of coupled pair of positive and negative charges and requires a certain energy. It is for this reason that the discharge by dipole disorientation is thermally activated and, therefore, can be speeded up by heating. Often disorientation energy is not the same for all dipoles. The current-temperature plot, therefore, consists of several peaks because the dipoles with low activation energy will disorient at low temperatures, while those with a high activation energy will respond at higher temperatures. If the difference in the various activation energies is not large, it is appropriate to assume a continuous distribution of activation energies, for which all the individual peaks overlap and average into a single peak. Such broad peaks often result as a disorientation of polar side groups in a polymer at low temperature. Another
possible cause for the appearance of broad peaks is a difference in the rotational mass of the dipoles. These differences occur in a polymer when heated to its softening temperature, where the dipoles are disoriented by the motion of main chain segments. This disorientation is responsible for the peaks which are located near glass transition.

In addition to dipoles, the electret usually contains immobile space charges which are distributed randomly, often near the electrodes. During the heating process, these get mobilised and neutralised either at the electrodes, or in the sample by recombination with charges of opposite sign. The forces driving the charges are their 'drift' in the local electric 'field' and 'diffusion', which tends to remove concentration gradient. The space charge peak appears at a higher temperature than the dipolar peak. This is because the disorientation of dipoles merely requires local rotation, whereas the neutralisation of space-charge requires them to move over many atomic distances.

If the space charges are ions, these are generally considered to be free to move with a thermally activated mobility. One can visualise them as trapping from one vacancy to another across a potential barrier equal to the activation energy. If, however, the charges are electrons or holes, it is more appropriate to visualise them as being immobilised in local traps, from which the heating releases them into a band of energies in which these are freely diffused to the electrodes.
At a higher temperature, the motion of space charge is accompanied by a second neutralisation mechanism, namely, recombination with thermally generated carriers. These carriers are generated uniformly in the entire bulk of the specimen by dissociation of neutral entities. These are responsible for conductivity of the specimen which can be either electronic or ionic. In polymers, it seems to be the impurity ions which contribute to the ohmic conduction because polymers show appreciable conduction only above \( T_g \) where enough free volume is available for the ions to move.

Usually, the detrapping of electronic carriers is analysed with the band gap model developed for crystalline solids. However, most electret materials are amorphous or at most partially crystalline. The high degree of positional (and compositional) disorder in these materials results in many localised states in the forbidden energy gap [19]. These trapping states differ in number and depth, the higher the order, the fewer these are and the deeper they tail off into the energy gap. The energy gap is thus replaced by a pseudo-gap, in which the density of states remains finite. As a result, the band edges are blurred, so that it is difficult to mark the energy at which a carrier is completely nonlocalised.

Mott et al. [1] have, therefore, proposed to base the definition of the transport bands in amorphous materials on the mobility of the carriers. This is illustrated in Fig. 3.1, the critical energy \( E_C \), at the mobility edge (where the mobility drops by three orders of magnitude) separates localised from
**Fig. 3.1**: Field - Temperature scheme for thermo electret formation.
delocalised states. Clearly, it is only above $E_c$ that electrons can move through the solid without the help of thermal energy. In addition to the disorder-induced band-tail states (which stretch out monotonically from the band edges), clearly recognisable gap states may be formed by intrinsic structural defects. In polymers, intrinsic defects are branching, chain entanglements, chain ends, pendant groups, etc.

However, the actual situation being unknown for most amorphous materials, the conventional band gap model is still used as a first approximation. With this model, it is easy to visualise the other two processes that a carrier may undergo after its thermal release from a trap. It is a retrapping, when on its way to the electrodes it meets another trapping centre, and recombines with an opposite charge when it is caught by a recombination centre. At low temperatures, the multitude of trapping sites in disordered materials allows the electronic carriers to move in the direction of the field by hopping across the localised gap state instead of moving freely along extended band states.

### 3.5 TSD PARAMETERS

#### 3.5-i ACTIVATION ENERGY

Theoretically the activation energy of non-distributed relaxation process can be calculated from a single TSD curve by means of some characteristic elements of the peak such as its half width, inflection point or initial part of the current rise. Other methods based on utilizing the whole
current-temperature curve or that which use several heating rates are also available. Most of these methods, except for one using the whole TSD plot are derived from methods based on the early works on thermoluminescence or thermally stimulated conductivity [19].

Methods for calculation of activation energies are explained in succeeding subsections.

(a) **INITIAL RISE METHOD**

This method is accredited to Garlick and Gibson [20] and is based on the fact that the second integral term in the \( j(T) \) expression is negligible at temperatures \( T < T_m \). Thus, differentiating with respect to \( 1/T \), the following expression for the initial portion of the current rise is obtained

\[
\frac{d}{d(1/T)} \log j(T) = -\frac{A}{k} \quad \text{... (3.23)}
\]

By plotting \( \log j(T) \) versus \( 1/T \), activation energy \( A \) can be determined. This procedure is generally advocated to be satisfactory and is widely used. It does not necessitate a linear heating rate nor a precise knowledge of the absolute temperature.

The approximation that at \( T < T_m \), the TSD current can be simplified into \( j(T) = \text{constant exp}(-A/kT) \) may not be true if the magnitude of the TSD current in the rising portion of the plot is large when compared to the peak height. When this happens, the plot of \( \log j(T) \) versus \( 1/T \) ceases to be linear and the value of \( A \) (obtained from the slope) has to be corrected as...
\[ A_{\text{corrected}} = (1 + 0.74d_1 + 0.092d_2)A - (2d_1 + 0.22d_2)kT_m \quad \ldots (3.24) \]

where \( A \) is the value obtained from the least squares fitted plot of \( \log j(T) \) versus \( 1/T \) with experimental values of \( j(T) \) that had been called between two values of the current \( j(T_2) \) and \( j(T_1) \), where \( T_1 < T_2 < T_m \). The parameters \( d_1 \) and \( d_2 \) are defined as

\[
d_1 = \frac{j(T_1)}{j(T_m)} \quad \ldots (3.25a)
\]

\[
d_2 = \frac{j(T_2)}{j(T_m)} \quad \ldots (3.25b)
\]

The ranges of applicability of eqn. (3.23) are \( d_2 \leq 0.5, \ d_2/d_1 \geq 5 \).

\[
10 \leq \frac{A_{\text{corrected}}}{kT_m} \leq 100 \quad \ldots (3.26)
\]

(b) **GRAPHICAL INTEGRATION METHOD**

The relaxation time can be written as [21]

\[
\tau(T) = \frac{P(T)}{j(T)} = \frac{1}{r} \left[ \int_{T}^{\infty} J(T') \,dT' \right] \frac{1}{J(T)} \quad \ldots (3.27)
\]

\[
\log \tau(T) = \log \left[ \frac{1}{r} \int_{T}^{\infty} J(T') \,dT' \right] - \log J(T) \quad \ldots (3.28)
\]

Assuming an Arrhenius shift for \( \tau(T) \), we have

\[
\log \tau(T) = \log \tau_0 + A/kT \quad \ldots (3.29)
\]

The quantity \( \tau(T) \) can be calculated by using eqn. (3.28) where we have taken the integral term to be easily evaluated by graphical integration of the area of the TSD peak from \( T \to \infty \). Knowing \( \log \tau(T) \) and plotting it
against $1/T$, a straight line may be obtained, yielding the activation energy $A$. The straight line is usually called the BFG plot after Bucci et al. [22]. Like the initial rise method, this procedure does not presume a linear heating rate, but unlike the former, it utilises data from the whole of the TSD peak. The BFG plot is to be preferred if the TSD plot exhibit larger parasitic background currents which may be difficult to eliminate from the small current signal portion of the initial rise.

(c) METHODS BASED ON THE VARIATION OF HEATING RATES

These methods are based on the shifts of the TSD current maximum with the heating rates employed. Several ways of plotting the results have been proposed [23,24]. It can be seen that

$$A = \frac{k T_{m_1} T_{m_2}}{T_{m_1} - T_{m_2}} \log \left( \frac{r_1 T_{m_1}^2}{r_2 T_{m_1}^2} \right) \quad \ldots \quad (3.30)$$

i.e. if the heating rate is changed from $r_1$ to $r_2$, the activation energy for the relaxation can be calculated from the corresponding shift of the peak temperature $T_{m_1}$ to $T_{m_2}$.

A better procedure utilising a series of heating rates, $r$ (resulting in corresponding $T_m$s), was also suggested by Hoogenstraaten whereby the plot of $\log(T_m^2/r)$ against $1/T_m$ should yield a straight line, from the slope of which the activation energy can be found [25]. The accuracy of these methods will depend on the accurate control of the heating rates employed and also on the magnitude of the actual shifts of the $T_m$s. Therefore, that
the method is less suitable for relaxations with large activation energies, \( A \), because the shifts of the current maxima will be smaller and experimentally more difficult to measure.

Several other methods to calculate the activation energy based on utilising the shape or symmetry of the TSD peak can also be found [26-28]. More recently, a new procedure has been proposed for a more accurate determination of activation energy [29].

(d) **ACTIVATION ENERGY FOR DISTRIBUTED PROCESSES**

The methods described hitherto to calculate the activation energy only holds good strictly for relaxations of a single, well-defined frequency. For a distributed relaxation, the initial rise method for calculation of activation energy would theoretically yield too low a value by over emphasising the role of the components with the slowest relaxation times. The graphical integration method will also have the same systematic error as a result of taking into account too high a number of components.

It has been shown that the initial rise method can still be applied to the case where there is a symmetrical distribution in \( 1/\alpha_0 \) [30]. Up to the lower half width temperature, the TSD current was shown to obey, approximately

\[
\log J(T) \sim \text{constant} - \frac{WA}{kT} \quad \ldots(3.31)
\]

where \( W \) is a constant whose value will depend on the type of the distribution describing \( 1/\alpha_0 \). Above equation will also show that \( A \) can still be calculated by the initial rise plot.
The methods based on the variations of the heating rates are still theoretically applicable without modification, for the distributed process. This is so because the peak of the TSD current plot is determined essentially by the components with the average value of the activation energy. However, a problem would exist in the exact determination of \( T_m \) and their shifts due to the broader nature of the TSD plots of the distributed systems.

The determination of other relaxation parameters, such as characteristics frequency, equilibrium polarisation and relaxation strength is little affected by the existence of a distribution in relaxation times [31]. The quantities can still be approximated by equation given in the graphical integration method [32].

3.5-ii RELAXATION TIME \((\tau_0)\)

The low temperature tail equation is given by

\[
\log i(T) = \text{Const} \left( -\frac{A}{kT} \right)
\]  \(\ldots(3.32)\)

Thus, from equation (3.20) the activation energy \( A \) of the discharge process responsible for the peak can be obtained from a plot of \( \log I \) versus \( 1/T \).

On differentiating of low temperature tail equation with respect to temperature and equating it to zero \((\text{di}/\text{dt} = 0)\), one obtains the temperature \((T_m)\) where maximum current occurs. \( T_m \) is given by
\[ \tau_0 = \frac{k T_m^2}{\beta A \exp\left(\frac{A}{kT_m}\right)} \quad \ldots \text{(3.33)} \]

Finding \( T_m \) from current versus temperature plots, one can calculate \( \tau_0 \). Knowing \( \tau_0 \) we can easily calculate the relaxation time at \( T_m \) and at any temperature, i.e.

\[ \tau(\tau_m) = \tau_0 \exp\left(\frac{A}{kT_m}\right) \quad \ldots \text{(3.34)} \]

Calculations of \( \tau(\tau_m) \) from equation (3.22) requires the value of \( \tau_0 \) one can, however, calculate \( \tau(\tau_m) \) without knowing \( \tau_0 \). From equation (3.33), we have

\[ k T_m^2 = \beta A \tau_0 \exp(A/kT_m) \]

\[ = \beta A \tau(\tau_m) \]

or

\[ \tau(\tau_m) = \frac{k T_m^2}{\beta A} \quad \ldots \text{(3.35)} \]

Knowing \( T_m \) from experimental plots \( \tau(\tau_m) \) can be obtained directly from 3.35.

3.5-iii CHARGE RELEASED (Q)

Charge released (Q) during the discharge was calculated by integrating the current versus temperature/time curves using Simson's rule.

Polymers are generally good dielectrics which are capable of storing the charge in them permanently when subjected to field temperature treatment. Such dielectric materials bearing persistent charge are called thermoelectrets. When thermoelectrets are subjected to a programmed
heat treatment, they give rise to a current in the external circuit and this is called thermally stimulated discharge current (TSDC). Thermally stimulated discharge current technique is a convenient and sensitive method for studying the charging and discharging process in dielectrics. These currents are due to dielectric relaxation behaviour and motion of free charges in the polymer. Hence, the TSDC technique can be used to understand the low frequency dielectric relaxation in solids and the relaxation between dielectric behaviour and process on the atomic scale. Because of the high sensitivity of this technique, it is also used to investigate the low concentration of dipolar impurities.

3.6 TRANSIENT CURRENTS IN CHARGING AND DISCHARGING MODES

The charge of electrets may be generated by various mechanisms: orientation of permanent dipoles (in polar materials), trapping of charges by structural defects and impurity centres, and build up of charge near heterogeneity such as the amorphous-crystalline interfaces in semi-crystalline polymers and the grain boundaries in polycrystalline materials.

At room temperature, charge decay measurements are rather time consuming, because at such temperatures, the dipoles and charges remain virtually immobile. However, when an electret is heated, the dipoles and charges quickly regain their freedom of motion. Thermal stimulation of the discharge, therefore, shortens the measurement considerably. During such a heat stimulated discharge, an electret connected to two electrodes
generates a weak current that shows a number of peaks when recorded as a function of temperature. The shape and location of these peaks are characteristics of the mechanisms by which electrets store their charges. Analysis of the curves yield detailed information on the dipoles (density, relaxation and activation energy) [33,34] and trapping parameters (energies, concentration and capture cross section of traps). Inspite of the fact that the charge of the electret is destroyed, the method has come into extensive use for the analysis of electrets as well as the development of electrets having a longer lifetime. Schematic diagram of measuring system for the DC transient current experiment and typical charging-discharging cycle are shown in Figure (X).

3.7 THEORY OF TRANSIENT CHARGING AND DISCHARGING CURRENTS IN POLYMERS

On applying an electric field to a polymer sample, a charging current flows in the external circuit. This current is composed of two components, namely, the polarization current component and the conduction current component. On assuming that the polarization current is due to the dipole of a single relaxation frequency $\alpha(T)$, it can be expressed as

$$\frac{dP_s(t)}{dt} + \alpha(T) P_s(t) = \varepsilon_0(\varepsilon_s - \varepsilon_\infty) \cdot \alpha(T) \cdot E \quad \ldots \quad (3.36)$$

where $T$ is the absolute temperature, $t$ is the time, $\varepsilon_0$ the permittivity of free space, $E$ the steady charging field, $\varepsilon_s$ and $\varepsilon_\infty$ are the static and high.
Schematic diagram of the measurement system for the DC transient current experiment.

Fig. (X): Typical charging - discharging cycle.
frequency dielectric constants respectively. The current density generated by decay in polarisation is given by

\[ i_p(t) = \frac{dP(t)}{dt} \]

\[ = -\alpha(T)P_s(t) + \varepsilon_o (\varepsilon_s - \varepsilon_\infty) \cdot \alpha(T) \cdot E \] \hspace{1cm} \ldots (3.37)

the conduction current \( i_c \) at a fixed temperature \( T \) and the field \( E \) is defined as

\[ i_c = \sigma(T) \cdot E \] \hspace{1cm} \ldots (3.38)

where \( \sigma(T) \) is the conductivity of the material at a fixed temperature \( T \). Thus, the total absorption current will be the sum of both the components, i.e.,

\[ i_{ab} = i_c + i_p(t) \]

\[ = \left[ \varepsilon_o (\varepsilon_s - \varepsilon_\infty) \cdot \alpha(T) + \sigma(T) \right] E - \alpha(T) \cdot P_s(T) \] \hspace{1cm} \ldots (3.39)

The discharging current is obtained when the sample is short circuited and the field is made zero. Thus, from eqn. (3.37), we have

\[ \frac{dP_s(t)}{dt} + P(t) \cdot \sigma(T) = 0 \] \hspace{1cm} \ldots (3.40)

The above is a differential equation with constant coefficients. Its isothermal solution can be written as

\[ P_s(t) = P_0 \exp \left[ -\int \alpha(T) \, dt \right] \] \hspace{1cm} \ldots (3.41)

The current generated during disorientation of dipoles is only due to polarisation. There is no conduction current present since the external field is zero. The discharge current is thus given by
\[ i_d(t) = -dP_s(t)/dt \]
\[ = \varepsilon_0 \cdot E \cdot f(t) \]
\[ = \alpha(T) \cdot P_0 \cdot \exp[-\alpha(T) t_0] \]

... (3.42)

where \( f(t) \) is the dielectric response function, \( P_0 \) is the initial polarization and \( \alpha(T) \) the dielectric response loss peak in frequency domain.

Alternatively, this can also be expressed in terms of the frequency response of the complex dielectric constant, \( \varepsilon(\omega) \)

\[ \varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \cdot (1+i\omega t)^{-1} \]

... (3.43)

where \( \varepsilon'(\omega) \) and \( \varepsilon''(\omega) \) are the real and imaginary part of the dielectric constant, \( \omega \) the angular frequency and \( t \) the relaxation time.

Thus, the isothermal discharge current measurements offer an alternative technique for dielectric constant and dielectric loss measurements as a function of temperature and frequency.

Frequency dependence of dielectric loss factor can also be obtained using Hamon's approximation,

\[ \varepsilon^H(t) = \frac{i(t)}{2\pi f \cdot c \cdot V} \]

... (3.44)

where \( i(t) \) is the magnitude of the transient current at time \( t \), \( c \) is the geometrical capacitance of the electrode assembly without the sample, \( V \) the applied voltage and \( f \) is the Hamon's frequency \( (= 0.1/t) \). This
approximation gives adequately good accuracy in calculation of the
dielectric loss provided there is a broad distribution of relaxation times.

The time dependence of transient currents can be expressed
according to the Curie von Schweidler law [35] expressed as

\[ i(t) = k \cdot t^{-n} \]  \hspace{1cm} (3.45)

In the optimum time range if the charging phenomenon persists for a
time \( t_p \), then according to the principle of superposition, time dependence
of the transient currents can be expressed by the following equation.

\[ i_d(t) \alpha(T) (t) = i_p(t) - i_p[\alpha(t) + t] \]  \hspace{1cm} (3.46)

Using eqn. (3.46), we have

\[ -i_d(t) \alpha(T) (t) = -k t^{-n} \left[ 1 - \left\{ \alpha(t)/(t+1) \right\}^{-n} \right] \]  \hspace{1cm} (3.47)

For \( t << 1/\alpha(T) \), eqn. (3.47) gives

\[ i_d \alpha(T) (t) = -k t^{-n} \]  \hspace{1cm} (3.48)

and for \( t >> 1/\alpha(T) \),

\[ i_d \alpha(T) (t) = -n \alpha(T) k t^{-n-1} \]  \hspace{1cm} (3.49)

where \( 0 < n < 1 \).

3.8 THEORY OF ELECTRICAL CONDUCTION MECHANISM
IN POLYMER FILMS

To explain the transport of charge carrier in a thin polymeric films
sandwiched between metal electrodes, there appears to be six separate
conduction mechanisms used. They are (i) Ionic conduction, (ii) Tunnelling mechanism, (iii) Hopping mechanism, (iv) Richardson-Schottky emission, (v) Poole-Frenkel effect, and (vi) Space charge limited current. Brief theoretical details of each mechanisms is discussed below:

(i) IONIC CONDUCTION

The concept of ionic conduction due to lattice defects has been understood for some time [36-38] and it depends principally on the rate of drift of the defects in an applied electric field. The actual conduction mechanism of this drift is jump of ions (or vacancies) over a potential barrier from one site to the next. If $F$ is the electric field and $l$ the distance between successive defect sites, then the current density $J$ at high fields for ionic conduction is given by [39]

$$J = J_0 \exp[-(\Phi/kT - Fel/2kT)]$$ ...

(3.50)

where $\Phi$ is the potential barrier height. Eqn. (3.50) explains satisfactorily the observed results in thin insulating films [40,41].

(ii) TUNNELLING MECHANISM

Consider a thin insulating film sandwiched between two metal electrodes. If the potential barrier is thin enough, electrons can flow through the barrier between the electrodes by quantum mechanical tunneling [42]. The energy level diagram of an insulator having an arbitrary potential barrier is shown in Fig. 3.2. The relationship connecting the current density
Fig. 3.2: Tunneling process in an insulator.
due to electrons tunneling through an arbitrary potential barrier with applied voltage \( V \), is given by [43]

\[
J = J_0 \left[ \Phi \exp(-A\Phi^{1/2}) - (\Phi + eV) \exp(-A(\Phi + eV)^{1/2}) \right] \tag{3.51}
\]

In eqn. (3.38), \( J_0 = e/2\pi h (\beta\Delta s)^2 \) and \( A = 4\pi\beta\Delta s (2m)^{1/2}/h \), where \( \Delta s \) is the width of the barrier at the Fermi level, \( \Phi \) is the mean barrier height, \( h \) is the Planck's constant, \( \beta \) is a function of barrier shape, \( m \) and \( e \) are mass and charge of electron, respectively.

The above equation (3.51) is readily applicable to potential barriers of arbitrary shape and to all practical voltage ranges.

(iii) HOPPING MECHANISM

In solids with broad intermolecular barriers, electron can migrate from one molecule to the other by moving over the barrier via an activated rate and this process is called hopping [44]. An electron is an occupied state with energy below Fermi level receives energy and hops to the nearby state above Fermi level. A generalized relation between hopping conductivity and temperature is given by [45].

\[
\sigma = a_0 \exp(-E'/kT) \tag{3.52}
\]

where \( a_0 \) is a constant and \( E' \) is the hopping activation energy.

Equation (3.52) suggests that conductivity varies exponentially as a function of \( T^{-1} \) and \( E' \) decreases with temperature. This expression is valid generally at higher temperatures. Mott [46] pointed out that at low
temperatures the most hopping would not be to the nearest neighbour. His analysis resulted an expression for the conductivity (Fig. 3.3).

\[ \sigma = A \exp(-B/T^{1/4}) \]  

... (3.53)

where A and B are constants.

(iv) RICHARDSON-SCHOTTKY EMISSION

This type of electron emission from the metal at negative potential is analogous to thermionic emission except that the applied field lowers the barrier height, essentially by reducing the metal-insulator work function as shown in Fig. 3.4.

When an electric field exists at a metal-insulator interface, it interacts with the image force and lowers the potential barrier. The line CD in Fig. 3.4 represents the potential due to a uniform field F, which when added to the barrier \( \Phi(x) \) produces the potential step shown by the dotted line, which is seen to be \( \Delta\Phi_s \) lower than that without the electric field. The change in the barrier height due to this interaction of the applied field with the image potential is given by

\[ \Delta\Phi_s = \left( \frac{e^3}{4\pi \varepsilon \varepsilon_0} \right)^{1/2} F^{1/2} = \beta_{RS} F^{1/2} \]  

... (3.54)

where \[ \beta_{RS} = \left( \frac{e^3}{4\pi \varepsilon \varepsilon_0} \right)^{1/2} \]  

... (3.55)

Equation (3.43), \( e \) is the electronic charge, \( \varepsilon_0 \) the permittivity of the free space and \( \varepsilon \) is the dielectric constant of the material. Because of image
**Fig. 3.3**: Schematic diagrams illustrating the electron hopping across and the electron tunnelling through a square and a triangular potential barrier. The electron hopping or tunnelling in one direction is equivalent to the hole hopping or tunnelling in the opposite direction.
**Fig. 3.4:** The Schottky effect. Reduction in barrier height ($\Delta\phi$) on application of the applied field ($F$) due to the image charges operative in the distance $X_0$. 
force lowering of the barrier, the electrode limited current does not saturate even at high fields and obeys the Richardson-Schottky law \[37\]

\[ J = \frac{A T^2}{\exp(-\frac{\phi_0}{kT})} \exp\left(\frac{\beta_{RS} F^{1/2}}{kT}\right) \]  \hspace{1cm} (3.56)

where,

\[ A = 4\pi m e k^2/h^3 = 120 \, \text{A cm}^{-2} \text{deg}^{-1} \]

(v) **POOLE-FRENKEL EFFECT**

The Poole-Frenkel \[47,48\] effect (field assisted thermal ionization) is lowering of a Coulombic potential barrier when it interacts with an electric field as shown in Fig. 3.5. This process is analogous to Schottky effect at an interfacial barrier.

The Poole-Frenkel attenuation of a Coulombic barrier \(\Phi_{\Delta PF}\) in a uniform electric field is twice that due to the Schottky effect at a neutral barrier.

\[ \Delta \phi_{PF} = \left(\frac{e^3}{\pi \varepsilon \varepsilon_0}\right)^{1/2} F^{1/2} = \beta_{PF} F^{1/2} \]  \hspace{1cm} (3.57)

where \(\beta_{PF} = \left(\frac{e^3}{\pi \varepsilon \varepsilon_0}\right)^{1/2}\)  \hspace{1cm} (3.58)

It is interesting to note from eqns. (3.55) and (3.57) that

\[ \beta_{PF} = 2 \beta_{RS} \]  \hspace{1cm} (3.59)

The current density in the case of Poole-Frenkel effect is given by \[48\]

\[ J = J_0 \exp\left(\frac{\beta_{PF} F^{1/2}}{kT}\right) \]  \hspace{1cm} (3.60)
Fig. 3.5: The Poole Frankel effect. Reduction in coulombic potential ($\Delta \phi_{\text{eff}}$) on application of the applied field (F). Here $E_d$ is the trap depth below the conduction band.
where \( J_0 = \sigma_0 F \) is the low field current density and \( \sigma_0 \) is the low field conductivity. Mead [49] was the first to report the field dependent conductivity apparently of the form given by eqn. (3.60) in thin insulating films.

**(vi) SPACE CHARGE LIMITED CURRENT**

In the case of polymers, the mobility of charge carriers is usually very low and hence their drift velocity under the applied electric field is also quite small. Thus, when charges are injected from the electrode into the insulator they tend to accumulate and tend to form space charge at the inter-electrode region. The formation of space charge also takes place due to the presence of large number of traps in the bulk of the material [39].

For simplicity, let us consider a perfect trap free insulator, with no intrinsic carriers, of thickness \( d \). Assuming the current density is only due to the charges injected from the electrode, then the current density is given by [39].

\[
J = \frac{9}{8} \mu \varepsilon V^2/d^3
\]  \hspace{1cm} \ldots (3.61)

where \( \mu \) is the mobility of the charge carriers, \( V \) the applied voltage, and \( \varepsilon \) the high frequency dielectric constant. The interesting feature of eqn. (3.52) is that it predicts that SCL currents is directly proportional to \( V^2 \) and inversely to \( d^3 \).
If now thermally generated free carriers with density, \( n_0 \) are included, then at low voltages where the injected carrier density is less than \( n_0 \) Ohm's law will be obeyed, i.e.

\[
J = e \, n_0 \, \mu \, V/d \quad \quad \quad \quad \text{(3.62)}
\]

The transition from Ohm's law, [eqn. 3.62] to Mott and Gurney law [50], [eqn. 3.38] takes place at the so called transition voltage, \( V_{\text{tran}} \) which is given by

\[
e \, n_0 \, \mu \, V_{\text{tran}}/d = \frac{9}{8} \, \mu \, \varepsilon \, V_{\text{tran}}/d^3
\]

\[
V_{\text{tran}} = \frac{8}{9} \, e \, n_0 \, d^2/\varepsilon
\quad \quad \quad \quad \text{(3.63)}
\]

This suggests that transition voltage \( V_{\text{tran}} \) is directly proportional to \( d^2 \).

Equations (3.61) and (3.63) are applicable to trap-free insulators. However, when a more realistic insulator, that is, which contains traps, is considered, the above equations get modified. The modified equations for current density, \( J \) and \( V_{\text{tran}} \) for shallow traps are [51]

\[
J = \frac{9}{8} \, \mu \, \varepsilon \, \theta \, V^2/d^3 \quad \quad \quad \quad \text{(3.64)}
\]

and

\[
V_{\text{tran}} = \frac{8}{9} \, e \, n_0 \, d^2/\varepsilon \, \theta
\quad \quad \quad \quad \text{(3.65)}
\]

where \( \theta \) is a constant and for shallow traps, it is the ratio of the free carrier density to the trapped carrier density, i.e.

\[
q = n/n_t
\quad \quad \quad \quad \text{(3.66)}
\]

Equation (3.65) clearly shows that the smaller the value of \( \theta \), the more effective are the traps in immobilizing the injected carriers. \( \theta \) can be as slow
as $10^{-7}$. Thus, the very large effect of shallow traps on SCL current is obvious.

### 3.9 CONDUCTION PARAMETERS

(i) **POWER 'm'**

The variation of current with applied DC voltage is important because power law given below is obeyed.

$$I = KV^m \quad \ldots (3.67)$$

$m$ determines the degree of linear relationship between log $I$ and log $V$.

Taking logarithm of above eqn.

$$\log I = \log K + m \log V \quad \ldots (3.68)$$

Putting $\log I = y; \log V = x$ and $\log K = c$,

We have $y = mx + c \quad \ldots (3.69)$

It is an equation of straight line. The problem has now reduced to the problem of fitting a straight line to a set of points on the $XY$ plane and thus to a simple problem of least squares as follows.

$$m = \frac{\Sigma XY - n \Sigma (XY)}{(\Sigma X)^2 - n \Sigma X^2} \quad \ldots (3.70)$$

The values obtained from above equation are some what different from those obtained by solving original least square equation, but these differences are small.
(ii) **CONDUCTIVITY**

The conductivity was calculated by using the equation

\[ \sigma = \left[ \frac{d}{A \times V} \right] \times I \quad \text{...(3.71)} \]

where \( d \) is the thickness of the sample (cm), \( A \) is the area (cm\(^2\)), \( V \) is the voltage applied across the material and \( I \) is the conduction current.

(iii) **ACTIVATION ENERGY**

Relation between conductivity and temperature governed by the eqn. (3.71). On the basis of this eqn., activation energy can be calculated as

\[ E = \frac{K (\log_e \sigma_1 - \log_e \sigma_2)}{ \frac{1}{T_2} - \frac{1}{T_1} } \quad \text{...(3.72)} \]

where \( K \) is the Boltzmann constant = 8.617 \times 10^{-5} \text{ eV}. \( \sigma_1 \) and \( \sigma_2 \) are the values of conductivity at two points corresponding to temperature \( 1/T_1 \) and \( 1/T_2 \).

### 3.10 EFFECT OF ENVIRONMENT AND OTHER FACTORS ON ELECTRICAL CONDUCTION OF POLYMERS

Electrical properties of polymers are highly sensitive to the environmental conditions such as temperature, pressure, humidity, ambient gases, high energy radiations, etc. and also to number of material parameters such as structure, crystallinity, mol. wt., orientation, deliberately added impurities. The variation of conductivity with temperature is of great importance and can be made as a basis of differentiating between metals...
and semiconductors. Electrical conductivity of all polymers increases exponentially with temperature and follows the Arrhenius relation [52]

$$\sigma = \sigma_0 \exp(-E/kT)$$  \hspace{1cm} (3.73)

where $\sigma$ is the conductivity measured, $E$ the activation energy for conduction, $\sigma_0$ a pre-exponential factor, $k$ the Boltzmann constant and $T$ the absolute temperature.

A linear relation between logarithm of pre-exponential factor ($\log \sigma_0$) and activation energy in eqn. (3.61) has been observed for a class of substances and has been termed the "compensation effect" [53,54]. The linear relation is of the form

$$\log \sigma_0 = aE + b$$  \hspace{1cm} (3.74)

where $a$ and $b$ are constants for a class of substances. A more detailed study of compensation effect for polymeric semiconductors has been carried out by Gelfman and Larzan [55]. It is interesting to note that impurities introduced into a polymer after both $\log \sigma_0$ and $E$ values but the linear relation between them remains valid [56].

The pressure dependence of electrical conductivity has been the subject of several papers [57-59]. The conductivity of polymeric films increases with increase in pressure. This has been attributed to the orbital overlaps between adjacent molecules during compression. According to some workers [59,60] logarithm of conductivity of polymers is proportional to the square root of the pressure. However, there is a certain amount of
evidence [58] that the conductivity tends to level off and become pressure independent after certain value.

If the polymer is exposed to humid atmosphere its conductivity increases considerably [61-63]. The effect of water on the conduction process is by no means clear. Water may act as an electron donor and source of charge carriers. Rosenberg [64] observed a change in conduction from electron to ionic in hydrated proteins as the water content increases.

Adsorbed and absorbed gases exert a profound influence on the conductivity. The effect of ambient gases on the electrical properties of polymers has been studied by many workers [65-67]. Hydrogen, oxygen, and nitrogen were found to be active. It is known that polyacrylonitrile which is a hole semiconductor in the air, changes not only in magnitude but also the type of conduction when its surface is degassed [67]. Adsorbed oxygen on polyphenylacetylene suppresses the electrical conductivity [68]. The influence of various gases on electrical conductivity has been used to establish whether the semiconductor is n-type or p-type [52].

When a polymer is exposed to high energy radiation (Gamma rays, X-rays, electron beams) changes often occur which significantly after the physical, chemical and mechanical properties of the polymer [69-71]. The type and degree of change may vary over a wide range and can be easily controlled by the type of radiation, exposure time, temperature, environment and the composition of the material [69]. The large effect of
radiation on polymers is due to the sensitivity of the material properties to molecular weight [72]. Only a few scissions or cross links per polymer molecule are sufficient to change markedly the tensile strength, solubility, melting point, glass transition temperature and so on. The decrease or increase in conductivity of a polymer depends on whether it is degrading or crosslinking on irradiation [73].

It is shown that conduction is strongly structure sensitive and it may differ between samples of the same material prepared by different methods as between samples of different materials [74]. In spite of extensive experimentation, the knowledge of relationship between conductivity and structure is still fragmentary. According to Seanor [75] polymer structure may be considered in three levels. The first level is the basic chemical composition of the monomer unit, the second level is the special arrangement of the basic polymer units within the individual polymer molecules and the third level is the special arrangement of polymer chains in the solid state. Eley and Parfitt [76] observed in a series of polycyclic aromatics differing in the number of condensed rings, that electrical conductivity increases with the number of condensed aromatic rings.

Wilk [77] argued that current flows mainly along the longitudinal axis of the molecule and that angular joints represent a disturbance which reduces the conductivity. He also found an empirical relation between activation energy \( E \) and number of linearly joined rings \( n \), as
\[ E = \frac{(17 - n)^2}{100} \quad \ldots (3.75) \]

which holds quite well up to 5 rings. In the study of effects of substituents on the electrical conductivity of anils, Gooden [78] found a correlation between conductivity and the Hammett substituent constant for both the meta and para series of substituents.

The dependence of the conductivity on the degree of crystallinity differs from one polymer to another [79]. It has been shown in polyacetylene [80,81] that a highly crystalline polymer has a conductivity four orders of magnitude greater than that of an amorphous polymer. However, conductivity of polytrifluoroethylene or polyethylene decreases on transition from amorphous to crystalline [82,83].

There are reports of study of the effect of molecular weight on the conductivity of polymers [84-86]. However, the relationship between molecular weight and conductivity has not yet been quantitatively determined. Increased mol. wt. of polyhydroquinone, polystyrene and poly(vinyl acetate) showed an increase in conductivity. Increased mol. wt. of cis-polyacetylene showed no change in conductivity and increased mol. wt. of trans-polyacetylene showed a decrease in conductivity [84].

Induced orientation of the macromolecules affects the conductivity of polymers in a complex manner. For instance, the conductivity of polyacrylonitrile increased [87] while that of polyvinyl alcohol remains unchanged [88] and that of polyethylene terephthalate decreased [89].
Considerable interest has been devoted to the problem of change in conductivity of polymers due to intentional doping with low mol. wt. compounds [90]. The carrier mobility can be greatly influenced by impregnating the polymer with suitable dopants [91]. Depending on their chemical structure and the way in which they react with the macromolecular matrix, doping substance increases the conductivity of the polymer to different degrees.

The doping of polymers is usually accomplished by chemical [92] or electrochemical [93] means. It has been suggested that the conduction mechanism in polyacetylene is independent of the method of doping [94].

3.11 MODELS EXPLAINING STEADY CONDUCTION

The steady state current is generated due to intrinsically generated charge carriers and charge injection from contacts. These phenomenon can be explained by the following model/theory/effects.

(a) Block band theory:

Charge transport in the solids having a negative temperature coefficient of carrier drift mobility is usually described in terms of Bloch band theory. The basic assumptions of the band theory are:

(i) Use of one electron in the periodic potential one electron approximation,
(ii) Neglect of multiple structure on individual atoms, and
(iii) Treatment of electron lattice interaction as small perturbation.
The basic mechanism of charge transport in solids depends on nature of the electron exchange interactions and the electron phonon interactions. In inorganic semiconductors the electron exchange interactions are much larger than the electron phonon interactions, so that the electron behaves as a quasi free particle occasionally scattered by phonons and, therefore, the charge transport is coherent [95]. In polymeric substances the electron exchange interactions are much smaller than the inorganic solids, so that there is always a possibility that the electron phenomena on interactions may dominate in such solids. Thus, the small mean free path and the small carrier mobility in polymeric solids make the assumption of coherent charge transport barely self consistent.

(b) The Tunnelling Method:

Another important model of charge transport is the tunnelling of charge carrier, proposed and discussed by Eley [96]. Tunnelling is the process in which charge carriers can cross the barrier without having energy equal to the barrier height. This model assumes that an electron in a π-molecular orbital on one molecule, when excited to a higher energy level, can tunnel through a potential barrier to an unoccupied state of a neighbouring molecule with energy conserved in the process. The electron in the excited state may tunnel to its neighbouring molecule or return to its ground state but, in general, the probability for the former is much greater than the latter.
Tunnelling process is shown in Fig. 3.2. For a square potential barrier, $E_T$ can be assumed to be the ionization potential of the molecule. In reality, the tunnelling electron would experience a potential which is the sum of the approximate coulomb potential attracting the electron to a positive ion and the potential of electron affinity of the originally neutral molecule. These potentials vary smoothly and are more correctly approximated by a triangular rather than a square barrier. Perhaps the triangular barrier shape facilitates the intermolecular electron transport as the barrier width becomes smaller for the excited electron at a higher level.

(c) The Hopping Model:

The charge transport can also be described in terms of the hopping model which may be preferable to the band model under certain circumstances. A carrier can move from one molecule to another by jumping over the barrier via an excited state as shown in Fig. 3.3. The criterion to determine whether the charge transport in the molecular crystals takes place coherently according to the band model or by random jumps according to the hopping model depends on the electron lattice interactions. It depends on whether the strongest coupling exists with intermolecular (lattice) or intramolecular (nuclear) vibrations, it is linear or quadratic in the phonon coordinates and it is strong or weak compared with the intermolecular electron exchange interactions. The vibration period are typically $10^{-12}$ sec for intermolecular modes and $10^{-11}$ sec for
intramolecular period and intermolecular vibration period by $\tau$, $\tau v_i$ and $\tau v_\eta$, respectively, we have the following two important cases:

**Case I**: $\tau < \tau v_\eta < \tau v_i$:

In this case the electron motion is so rapid that the vibration motion can be regarded as stationary and as a perturbation to the motion of the electrons. The electron can be thought of travelling over several lattice sites before being scattered. The band model is applicable to this case.

**Case II**: $\tau v_\eta < \tau < \tau v_i$:

In this case the molecule vibrates (intermolecular vibration) while the electron remains on a particular lattice site. This implies that during the time when electron remains on the lattice site, the nuclei of the molecule on this particular lattice site moves to a new equilibrium position. This gives rise to the formation of a polaron. The interaction of electron and phonon in the lattice site may lead to self-trapping in which the electron polarises the molecule and is trapped in self induced potential well. This case may lead either to random hopping transport or to coherent band transport. For the former, the electron trapped in such a potential well requires an activation energy to surmount a barrier of height equal to the binding energy of the polaron in order to move to the neighbouring site. Thus, for the hopping transport the electron-phonon interaction must be strong.
Richardson-Schottky Effect:

The observable conduction in polymeric solids is usually explained in terms of charge injection from the metal contacts. Injection current which is smaller than the bulk current is observed due to Schottky field emission (i.e., electrode limited current flows with heteropolar space charge and depletion layer formation in front of electrode).

Schottky emission of electrons may occur from the metal contact of negative potential into conduction band of the dielectric. The fact that the electrons are emitted into the dielectric instead of vacuum is taken care of by multiplying the Richardson’s formula for thermionic emission of electrons with the dielectric constant of solids. At very low voltage the conduction is due to field assisted thermionic emission of electrons from negative biased electrode (or holes from positively biased electrodes) over the interfacial barrier. The presence of electric field at the barrier modifies the emission current as it reduces the work function (as shown in Fig. 3.4) separating the two materials and is known as Schottky effect. For a trap free insulator the current density $J$ is given by [97,98]

$$J = AT^2 \exp(-\phi_s/kT) \exp(\beta_s V^{1/2}/kT) \quad \ldots (3.76)$$

where $\beta_s$, known as Schottky coefficient = $(e^{3/4} \varepsilon \varepsilon_0 d)^{1/2}$, $d$ is the thickness, $\varepsilon_0$ is the permittivity of free space, $\varepsilon$ is the dielectric constant, $e$ is electronic charge, $A$ (Richardson Dushman constant) = $4 \pi m e k^2/h^3$, $T$ is the absolute temperature, $\phi_s$ is the metal dielectric potential barrier height, $V$ is the applied voltage and $k$ is the Boltzmann’s constant.
The above equation predicts a linear relationship between $\ln J$ and $V^{1/2}$ of slope $\beta_s/kT$ at constant temperature. To a first approximation, a plot of $\ln (J/T^2)$ versus $1/T$ for a constant voltage can yield $\phi_s$, the barrier height.

Thus, Schottky emission is the thermionic emission of electron under the application of electric field due to the lowering of constant barrier height, leading to a strong temperature dependent Schottky current.

(e) **Poole-Frenkel Effect**

The application of an electric field on the dielectric material will either change the rate of carrier generation or injection, or change the distribution function and the mobility of the carriers. Sometimes both changes occur. The former change causes 'Electrode Effect' due to the Schottky type thermionic emission, and the latter produces "Bulk Effects" caused by the field dependent carrier mobility due to various scatterings and also by the field dependent carrier density due to field dependent detrapping process which is known as the "Poole-Frenkel Effect".

Poole-Frenkel Effect (abbreviated as P-F effect) sometimes called internal Schottky effect describes the electron transfer by field enhanced thermal excitation (or detrapping) of trapped electrons into the conduction band of the dielectric. The interaction between the positively charged trap and electron gives rise to the Coulombic barrier [99], the P-F effect (field assisted thermal ionisation) is the lowering of this Coulombic potential.
barrier when it interacts with an electric field. This is usually associated with the lowering of trap barrier in the bulk of dielectric.

The P-F bulk limited conductivity is given by the following equation [100,101].

\[ J = AT \exp(-\phi_{PF}/kT) \exp(\beta_{PF} V^{1/2}/kT) \]  \( \quad (3.77) \)

where \( \phi_{PF} \) is the barrier associated with the promotion of an electron from a donor level to the conduction state or alternatively, with the promotion of an electron from a valence state to an acceptor level, \( A \) is a constant, \( V \) is the applied potential, \( k \) is the Boltzmann's constant, \( \beta_{PF} \) is P-F the coefficient and \( T \) is the absolute temperature.

The factor \( (\beta_{PF} V^{1/2}) \) in the above equation is the amount by which the coulombic barrier is lowered due to its interaction with the field.

Usually \( \beta_{PF} = 2 \beta_s \), it can, however, become comparable to \( \beta_s \) under certain conditions [102,103]. Hence, quite often it becomes difficult to distinguish between the R-S and P-F type of conduction from the analysis of J-V characteristics. However, the use of different electrode materials modifies significantly the R-S current but not the P-F current [104].

(f) **Space Charge Limited Current (SCLC):**

This mode of conduction can have a pronounced effect on the electrical properties of insulators. Space charge limited current is important because the injected current is independent of the mechanism of carrier
generation and their trapping within the solid. Space charge is generally referred to as the space field with a net positive or negative charge and appears in a variety of insulators. Space charge polarisation occurs in the direction of the field and also due to direct injection of charge carriers from the electrodes at high field.

There are, in fact, several variation of space charge limited flow depending on whether the current is due to electrons only (i.e., single injection), or electrons and holes both (i.e., double injection) and whether the traps and recombination centres are present.

Single carrier injection currents are necessarily space charge limited. In a perfect trap free insulator, all the injected carriers remain free. They contribute to the space charge and the current flow is exactly analogous to that in a vacuum diode. Under double injection, i.e., with electrons, injected from cathode and holes injected from anode, space charge conditions are partially overcome and for intermediate injection level charge neutrality can be assumed throughout the insulator. However, at high and low injection levels, the space charge again becomes important.

The magnitude of current response and the actual form of the current-voltage characteristics are determined by the interaction of the injected carriers with localized defect states, which can trap and store charge in equilibrium with the free charge. In fact, some injected charge is trapped at these localized defects. Therefore, due to reduction of injected
current through trapping, the appearance of SCLC is inhibited until a sufficiently large field is applied. Further, the transition from ohmic region to SCLC region depends mainly on the distribution of trapping levels.

The role of traps in study of SCLC was realised by Rose [105] and Lampert [106]. As long as the concentration of traps is not very large, an increase in the applied field and so in the concentration of carriers injected into the dielectric will shift the equilibrium between occupied and unoccupied traps and in case of unipolar SCLC the current density is given by [107]

\[ J = \sqrt{2} \mu \theta (\varepsilon \varepsilon_0 / d^3) \]  ... (3.78)


where \( J \) is the current density, \( d \) is the thickness of the sample, \( V \) is the applied potential, \( \varepsilon \) is the dielectric constant, \( \mu \) is the carrier mobility, \( \varepsilon_0 \) is the permittivity of free space and \( q = n_0/n_t \), where \( n_0 \) is the effective density of free carriers and \( n_t \) is the effective density of the trapped carriers.

Assuming that carriers are trapped at shallow levels of average depth \( E_t \), that remains in the thermal equilibrium with the concerned energy band, we have

\[ q = n_0/n_t = N_C/N_t \exp(-E_t/kT) \]  ... (3.79)

where \( N_C \) is the density of states in the conduction band and \( N_t \) is the density of shallow traps within the quadratic region of SCLC, the current density is given by:

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\[ J = v^2 \mu \left( \varepsilon \varepsilon_0 / d^3 \right) (N_c/N_t) \exp(-E_t/kT) \] ... (3.80)

or \[ J = V_2 \mu_0 \left( \varepsilon \varepsilon_0 / d^3 \right) (N_c/N_t) \exp[-(E_t - E_{\mu})/kT] \] ... (3.81)

where \( \mu = \mu_0 \exp E_{\mu}/kT \) is the temperature activated carrier mobility.

Deviation from eqn. (3.81) and dependence of \( J \) on some higher power of \( V \) has been described as due to existence of deep traps and continuous distribution of trapping levels in the forbidden gap [105-108]. The slope of \( \log J \) and \( 1/T \) plot gives \(-E_t/k\) while the intercept for the limit \( 1/T \to 0 \) gives \((m \varepsilon \varepsilon_0 \sqrt{v^2/d^3}) (N_c/N_t)\), from which \((mN_c/N_t)\) and \(N_t\) can be calculated.

The fact that only few organic solids show an ohmic region [109,110] has led to the belief that the conduction in organic solids is mainly extrinsic. The hole [111] and electron injection in organic solids have been achieved using special electrodes and their correlation with ionization energies have been studied [112].

### 3.12 DIELECTRIC MEASUREMENT

When solid polymeric materials are subjected to an electric field, an induced electric moment is produced. This induced electric moment persists, whenever the field is present. In case, when the permanent dipoles are present, an electric field brings about their orientation and polarizes the material. The displacement of polar groups require some time and is thus dependent on frequency and temperature, which lead to different dispersion [113,114] phenomena. Actually at frequencies and
temperatures where dispersion occurs, only a part of electrical energy is stored, while some of it is dissipated as heat.

There are different types of polarization has already been described in Chapter 1. Dipolar polarization occurs in the frequency range 10 to $10^6$ Hz. Atomic and electronic polarizations are observed in the IR and optical frequency ranges.

The displacement of polar group of polymers requires some time and is thus dependent on the frequency and temperature which lead to different dispersion phenomena according to the segmental motion of the polymer chain or orientation of the polar side groups.

The loss factor exhibits a maximum at frequencies at which dielectric permittivity shows a dispersion (Fig. 3.8). The maxima in dielectric loss occurs at temperatures at which motion of large segments of polymer chain or different side groups begins. Dielectric behaviour of polymers is characterized by distribution in relaxation times. The detailed study of dielectric behaviour of polymers has given valuable insight into their macromolecular motion.

3.12-i DIELECTRIC RELAXATION IN POLYMERS

Valuable informations could be obtained from the dielectric relaxation [115-144] studies, made in polar and non polar linear polymers using various techniques. Various mechanism for the charge storage in polymers could be easily classified as a result of these studies.
Figure 3.6 Behavior of dielectric constant ($\varepsilon'$) and loss factor ($\varepsilon''$) for polar polymers as a function of frequency (broadening of loss curve is caused by multiple relaxation times and is shown by the dotted line).

- $\varepsilon'_s$ - Static dielectric constant
- $\varepsilon'_{eq}$ - High frequency dielectric constant
- $\tau$ - Dielectric relaxation time.
- $1$ - Dipole contribution
- $2$ - Electronic contribution
It has been observed that total charge stored in a polymer electret [145] and the different mechanism which contribute to this charge are very sensitive to the structure of the forming material. It was also observed that charge can be produced by making some structural changes in the polymer matrix itself by doping with certain impurities [146-148].

Polymers are complex dielectric materials. The use of polymers as dielectrics is being increasingly important. Choice of the polymeric dielectric for each concrete case depends on its dielectric and other physical properties over a wide range of temperatures, electric field and frequencies [149-160]. Investigation of dielectric properties is one of the most convenient and sensitive methods of studying polymer structure. Dielectric studies in polymers provide vital [161-172] information on the molecular configuration of a system; for example - movement of dipoles, losses of energy, segmental motion, conduction mechanism, latent heat, etc. It is, therefore, important that their dielectric behaviour should be fully understood. Dielectric properties of several polymers [173-179], polar and non-polar have been investigated.

3.12-ii DIELECTRIC PROPERTIES [180-193]

(a) MACROSCOPIC DESCRIPTION OF STATIC DIELECTRIC CONSTANT [194]

As an introduction to the concept of the static dielectric constant of a substance, consider the following well-known experimental result.
Two plane parallel plates of area \( A \) and separated by \( d \) cm are charged with a surface charge density \( q \), one plate being positive and other negative. If the space between the plates is evacuated and if \( d \) is small compared with the dimensions of the plates, this will result a homogeneous electric field between the plates, the field strength being given by

\[
E_{\text{vac}} = 4\pi q = D
\]

... (3.82)

in e.s.u. is called the electric displacement or flux density. The potential difference between the plates is equal to

\[
f_{\text{vac}} = E_{\text{vac}} \cdot d
\]

... (3.83)

and the capacitance of the system is defined by

\[
C_{\text{vac}} = \frac{A \cdot q}{\phi_{\text{vac}}} = \frac{\phi}{\phi_{\text{vac}}}
\]

... (3.84)

Suppose now that the space between the plates is filled with an insulating substance, the charge of the plates being kept constant. It is observed that the new potential difference \( \phi \) is lower than \( \phi_{\text{vac}} \) and similarly the capacitance \( C \) of the system is increased. The static dielectric constant \( \varepsilon_s \) is then defined by

\[
\varepsilon_s = \frac{\phi_{\text{vac}}}{\phi} = \frac{C}{C_{\text{vac}}}
\]

... (3.85)

Thus, as a result of introducing the substance, the field strength is reduced from the value \( E_{\text{vac}} \) to the value \( E \), where

\[
E_{\text{vac}} = D = \varepsilon_s
\]

... (3.86)
In other words, the effective surface charge density on the plates is now 
$q' = E/4\pi$ rather than $q = E_{vac}/4\pi$, and one may say that introducing the
dielectric is equivalent to reducing the surface charge density by an amount

$$P = q - q' = (E_{vac}/4\pi)(1 - 1/\varepsilon_s) = (\varepsilon_s - 1)E/4\pi$$

... (3.87)

Thus, under the influence of the external field, the dielectric facing the
positive charge acquires a negative induced surface-charge density $P$ and
vice versa. This is illustrated in Fig. 3.7. $P$ is called the polarisation of the
substance. One may write

$$D = E - 4\pi P = \varepsilon_s E$$

... (3.88)

3.12-iii DIELECTRIC PROPERTIES OF INSULATORS IN
ALTERNATING FIELDS

When an ideal dielectric is subjected to an alternating field, current -
I, would be ahead of voltage - V, precisely by $90^\circ$ and current would be
purely reactive. In actual fact, the phase angle $\phi$ is slightly less than $90^\circ$;
total current through the capacitor can be resolved into two components -
active $I_a$ and reactive $I_r$ currents, we see that

$$\delta = 90^\circ - \phi$$

... (3.89)

where $\delta$ is called the dielectric loss angle.

3.13 THE COMPLEX DIELECTRIC CONSTANT AND
DIELECTRIC LOSSES [194]

When a dielectric is subjected to an alternating field, the polarisation
$P$, also varies periodically with time and so does the displacement $D$. In
Fig. 3.7: SCHEMATIC ILLUSTRATION OF CHARGES INDUCED AT THE SURFACE OF A DIELECTRIC.
general, however, $P$ and $D$ may lag behind in phase-relative to $E$, so that, for example if

$$E = E_0 \cos \omega t \quad \ldots \ (3.90)$$

we have

$$D = D_0 \cos (\omega t - \delta)$$

$$= D_1 \cos \omega t + D_2 \sin \omega t \quad \ldots \ (3.91)$$

Clearly, $D_1 = D_0 \cos \delta$

and $D_2 = D_0 \sin \delta$

For most dielectric $D_0$ is proportional to $E_0$, but the ratio $D_0/E_0$ is generally frequency-dependent. To describe this situation, one may thus introduce two frequency dependent dielectric constants:

$$\varepsilon' (\omega) = D_1/E_0 = (D_0/E_0) \cos \delta \quad \ldots \ (3.92)$$

$$\varepsilon'' (\omega) = D_2/E_0 = (D_0/E_0) \sin \delta \quad \ldots \ (3.93)$$

It is frequently convenient to lump these two constants into a single complex dielectric constant,

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \quad \ldots \ (3.94)$$

because the relation between $D$ and $E$, both expressed as complex quantities, is then simply

$$D = \varepsilon^* E_0 e^{i\omega t} \quad \ldots \ (3.95)$$

as may readily be verified.
It may be noted that according to equation (3.92) and (3.93), there exists the relation

$$\tan \delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} \quad \ldots \quad (3.96)$$

and because both $\varepsilon'$ and $\varepsilon''$ are frequency-dependent, the phase angle $\delta$ is frequency-dependent. $\varepsilon''(\omega)$ represents the losses in the system of bound charges exactly in the same way as the free charges are responsible for the conductivity losses [195]. Now, it will be shown that the energy dissipated in the dielectric in the form of heat is proportional to $\varepsilon''$.

**3.14  DIELECTRIC LOSSES AND RELAXATION TIME**

Let us consider a dielectric for which the total polarisation $P_s$ in a static field is determined by three contributions

$$P_s = P_e + P_a + P_d \quad \ldots \quad (3.97)$$

where the subscripts e, a and d refer respectively to electronic, atomic and dipolar polarisation. It will be assumed that values of $P_e$ and $P_a$ are attained instantaneously. Let $P_{ds}$ denote the saturation value of $P_d$ obtained after a static field $E$ has been applied for a long time. It will be assumed that the value of $P_d$ as a function of time after the field has been switched on is given by

$$P_d(t) = P_{ds} \left(1 - e^{-t/\tau}\right) \quad \ldots \quad (3.98)$$

Hence,

$$\frac{dP_d}{dt} = \frac{1}{\tau} \left[ P_{ds} - P_d(t) \right] \quad \ldots \quad (3.99)$$
In the case of an alternating field \( E = E_0 e^{i\omega t} \), eqn. (3.89) may be employed if we make the following change.

\( P_{ds} \) must be replaced by a function of time \( P_{ds}(t) \) representing the saturation value which would be obtained in a static field and is equal to instantaneous value \( E(t) \). Hence, for alternating fields we shall employ the differential equation

\[
\frac{dP_d}{dt} = \frac{1}{\tau} [P_{ds}(\varepsilon) P_d]
\]

we shall define the "instantaneous" dielectric constant \( \varepsilon_{ea} \) by

\[
P_e + P_a = \frac{\varepsilon_{ea} - 1}{4\pi} E
\]

We may then write

\[
P_{ds} = P_s - (P_e + P_a)
\]

\[
= \frac{\varepsilon_s - \varepsilon_{ea}}{4\pi} E
\]

This yields

\[
\frac{dP_d}{dt} = \frac{1}{\tau} \left( \frac{\varepsilon_s - \varepsilon_{ea}}{4\pi} E_0 e^{i\omega t} P_d \right)
\]

Solving this equation, we obtain

\[
P_d(t) = C e^{-t/\tau} + \frac{1}{4\pi} \frac{\varepsilon_s - \varepsilon_{ea}}{1 + \omega \tau} E_0 e^{i\omega t}
\]

The total polarization is now also a function of time and is given by \( P_e + P_a + P_d(t) \).

Hence, for displacement one obtained

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\[ D(t) = \varepsilon^* E(t) \]
\[ = E(t) + 4\pi P(t) \quad \ldots (3.105) \]

From the last two equations and from the definition \( \varepsilon^* = \varepsilon' - i\varepsilon'' \) the following expressions result:

\[ \varepsilon'(\omega) = \varepsilon_{ea} + \frac{\varepsilon_s - \varepsilon_{ea}}{1 + \omega^2 \tau^2} \quad \ldots (3.106) \]

\[ \varepsilon''(\omega) = (\varepsilon_s - \varepsilon_{ea}) \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad \ldots (3.107) \]

These equations are frequently referred to as the Debye equations.

When the dielectric polarisation is studied as a function at frequency, it is found that at low frequencies all the three polarisation contribution and \( \varepsilon' \) at such frequencies represent the static dielectric constant (Fig. 3.8). At higher frequencies, the orientation polarisation stops contributing the \( \varepsilon' \) and only contribution is from electronic and atomic polarisation. Above IR frequencies, even atomic polarisation stops contributing (Fig. 3.9).

**3.15 DIFFERENT TYPE OF RELAXATION IN POLYMERS**

In polymers normally two types of relaxations \( \alpha \) and \( \beta \) are observed. The \( \alpha \)-relaxation is due to the reorientation of the segmental groups and it takes place at temperatures around and above glass transition temperature (Tg) and is very much dependent on the intra and inter-molecular interactions. The \( \beta \)-relaxation is due to the micro-Brownian motion of the dipoles in the side groups attached to the main chain and it occurs at
Fig. 3.8: Debye curves for $\epsilon'$ and $\epsilon''$ as functions of frequency for a dielectric with a single relaxation time.
Fig. 3.9: (a) Variation of permittivity with frequency for simple dielectric

(b) Variation of loss tangent with frequency for simple dielectric.
temperatures below $T_g$. In polymers like poly(methyl methacrylate) (PMMA), both $\alpha$ and $\beta$ relaxation coalesce to give single relaxation and is known as $\beta$-relaxation process [196].

3.16 FACTORS AFFECTING DIELECTRIC BEHAVIOUR OF POLYMERS

(a) Effects of Polar Groups:

The $\alpha$-relaxation is basically dependent on the intra- and inter-molecular interactions. The greater the inter-molecular interaction the less mobile are the molecules and higher is the relaxation temperature at which loss maximum occurs and longer is the relaxation time. Exchange of non-polar substitutes increases dipole-dipole interaction.

(b) Effect of Substituents:

Introduction of very bulky substituents into the side chains or increasing the side chains decreases the mobility sharply. Introduction of chlorine considerably increases the magnitude of $\alpha$-relaxation in poly(methyl $\alpha$-chloroacrylate) but it has not altered $\beta$-relaxation [197].

(c) Effect of Side Group Isomerism:

The magnitude of $\alpha$- and $\beta$-relaxations of isomers have been significantly different. For example, the magnitude of $\alpha$-relaxation for poly(vinyl acetate) (PVAC) is much higher than that of poly(methyl acrylate) (PMA), whereas the magnitude of $\beta$-relaxation of PMA is seven times
higher than that of PVAc [198,199]. This arises because of the attachment of ester oxygen to the main chain in PVAc.

(d) **Effect of Stereoregularity :**

The dielectric properties of polymers are substantially dependent on the stereoregular nature of the polymer because the percentage, the length and quantitative proportion of syndiotactic and isotactic sections have a significant effect on the molecular mobility of polymers [200]. The molecular mobility of syndiotactic polymers is more restricted than of isotactic polymers [200,201].

(e) **Effect of Plasticizers :**

Dielectric relaxation of polymers shift towards lower temperature side on the addition of plasticizers. This is because plasticizers

(i) increase molecular mobility

(ii) increase free volume

(iii) decrease Tg of the polymer

Effect of plasticizer on dielectric relaxation of polymers reveals that at low concentrations of plasticizers the loss peak occurs mainly from the motions of polymers segment as modified by the plasticizer molecules which are bound to the polymer molecules by the dipole-dipole interactions, till the critical composition is achieved. Beyond that the loss peak arises largely from the plasticizer molecules [200,202].
(f) **Effect of copolymerization:**

Dielectric properties of copolymers vary according to the constitution/composition and the ratio of the monomeric units [203-205].

(g) **Effect of CrossLinking:**

Cross-linking always decreases molecules mobility and increases temperature and relaxation time of $\alpha$-process [200].

(h) **Effect of Pressure:**

Pressure influences the relaxation times of the process in which the inter-molecular interaction plays an important role. Thus, increasing the pressure results in the increase of $\alpha$-relaxation process and that of $\beta$-process to a lesser degree [196].

### 3.17 PARAMETERS AFFECTING DIELECTRIC CONSTANT

(a) **Temperature [206-229]:**

According to the classical mechanics, the total molecular polarizability $\alpha$ is the sum of electronic polarizability $\alpha_e$ and polarizability arising due to molecular motion $P^2/3kT$ and is given by

$$\alpha = \alpha_e + \frac{P_{perm}^2}{3kT} \quad \ldots (3.108)$$

where $P_{perm}$ is the permanent dipole moment, $k$ is Boltzman constant and $T$ the absolute temperature. The dielectric constant of simple elemental dielectrics show relatively small temperature dependence since there occurs very small change in electronic structure. For ionic dielectrics, substantial increase in dielectric constant is brought about at high
temperature because of the loosening of the bonds which hold the ions in place.

Debye's equation relating the dielectric constant $\varepsilon$ with structure and temperature of a substance is

$$\frac{\varepsilon - 1}{\varepsilon - 2} = \frac{4\pi N}{3} \left( \alpha_o + \frac{\mu^2}{3kT} \right) \ldots (3.109)$$

where,

$N$ = No. of molecules per c.c.

$\alpha_o$ = Polarizability of the molecule

$\mu$ = Permanent electric dipole moment of the molecule.

This suggests that the dielectric constant of polar substance is temperature dependent and that of non-polar substances temperature independent.

(b) Frequency [230-241]:

One of the most striking features of the dielectric is the relationship between dielectric constant, dielectric losses and frequency. Each type of polarization has a particular frequency range at which it responds quickly. Only in this range they show proper variations in dielectric constants and losses.

When a dielectric is subjected to an alternating field, the polarization and displacement vectors vary periodically but due to absorption they lag
behind in phase with the applied field resulting in the complex form of dielectric constant. We know that

\[ \tan \delta = \varepsilon''/\varepsilon' \]  ... (3.110)

where \( \delta \) is the phase angle between displacement and field. The energy dissipated in the dielectric in the form of heat is proportional to \( \varepsilon'' \) and, therefore, \( \tan \delta \) is termed loss tangent and \( \delta \) as loss angle.

In eqns. (3.96) and (3.97) if \( \omega \ll 1/\tau \), then \( \varepsilon' \) approaches \( \varepsilon_s \) and \( \omega \ll 1/\tau \) then \( \varepsilon' \) approaches \( \varepsilon_{ea} \) which follows that the dipoles are no longer able to follow the field. Thus, with increase in frequency the relaxation spectrum is characterised by a constant value followed by a slow fall of \( \varepsilon' \) to a low value and \( \varepsilon'' \) shows a broad peak.

(c) **Field [242-248]**:

An electric field orients the dipoles of the polar dielectric in all possible directions, parallel, antiparallel or others, depending upon the applied field strength. High dielectric constant and high dielectric losses appear when dipoles align parallel to the field. However, their perpendicular alignment with field produces almost no dielectric constant.

(d) **Humidity**:

Water molecules present inside the dielectric configuration increase the dielectric constant to a considerable amount [249]. Chatterjee [250] has done a detailed study on the variation of dielectric constant with varying amount of moisture in the ebonite and fibre specimens in frequency range
of 214 to 750 mc/s. Bhargava [233] has also reported increase in dielectric constant of polystyrene with humidity in low temperature region.

(e) Impurity:

Impurity in polymer produces changes in dielectric constant and dielectric losses of the polymer. Effect of chloronil on polystyrene is observed by Shrivastava and Kulshetra [251]. Relaxation behaviour of doped polycarbonate their film has been studied by Mahendru and Agarwal [252].

(f) Nature of the Polymer:

Polymer can be divided as polar and non-polar materials. For non-polar substances containing no ionic impurities, the measured loss factor is very small but it is not actually zero in the liquid state and rather it increases with frequency in micro wave region.

The dielectric constant exhibits a sharp drop when transition from liquid to the solid state occurs in the polar substances. Dielectric losses are also approximately zero for such non-rotating polar molecules.
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