CHAPTER III
Chapter-III

Electrical Conduction

3.1 Introduction:

Most of the polymers are considered to be insulators because they show low conductivity, low dielectric loss and high breakdown strength\textsuperscript{171}. However, recent research in the field of polymers has led to the development of special type of high molecular weight materials which exhibit a conductance high enough to class them as semiconductors (specific conductivity = $10^{-12}$ to $10^{12}$ ohm$^{-1}$ cm$^{-1}$) or even in some cases as conductors\textsuperscript{172}.

In the past several years, a good amount of work has been reported on electrical conduction in polymeric materials\textsuperscript{173-175} and various mechanisms such as ionic conduction\textsuperscript{176-178}, Schottky emission\textsuperscript{179-181}, space charge limited conduction\textsuperscript{182,183}, tunnelling\textsuperscript{184}, Poole-Frentiel mechanism\textsuperscript{185}, Charge hopping\textsuperscript{186} and small polaron mechanism\textsuperscript{187} have been proposed to explain the experimental results.

Electric current in an ordered (i.e., having a definite direction) motion of electric charges in space. Current appears in matter under the effect of applied voltage, the charge material particles of the matter being brought into the state of ordered motion by the force of an electric field. Thus any matter will be conducting if it contains free charge carriers. When ions move in an electric field, electrolysis takes place. Dielectrics with ionic conduction are also subjected to electrolysis but it is not so
pronounced due to their high resistivity. A large quantity of electricity can be passed through them only during a long period of time if a rather high voltage is applied. Electrolysis in dielectrics is more prominent at increased temperatures when the resistivity of matter is reduced. The molecules of most of organic polymers can not be ionised nut ionic conduction still takes place due to presence of impurities. Nonohmic conduction at high fields in ionic model is explained by diffusion over field perturbed potential barriers, by internal heating and by polymer structure modification by the field. The experimental temperature dependence and disproportionality between current and voltage are usually explained on the basis of temperature and field dependence of mobility. In that case, current-voltage curves follow a hyperbolic sine function. But it is not a definite proof of ionic conduction. In polymers with hologens in their molecular\textsuperscript{172} structure, electrical conduction is qualitatively proved to be ionic\textsuperscript{177}.

The fact that electronic conduction plays a role in polymers was established experimentally by Seanor\textsuperscript{188}. To discuss electronic conduction it is necessary to investigate the generation of free carriers and their transport through the material. Several books and reviews\textsuperscript{189-193} deal with the problem of carrier generation. Contact limited emission was first studied for the metal vacuum interface. In this case three mechanisms of current flow may be distinguished. Thermionic emission\textsuperscript{194} (Schottky emission) occurs in the
low-field high-temperature limit. Field emission\textsuperscript{195,196} (Fowler-Nordheim Tunnelling) occurs in the high-field low-temperature limit and is the direct quantum mechanical tunnelling of electrons from allowed states below the Fermi-level in a metal into allowed states in vacuum. Thermal field emission\textsuperscript{197-199} occurs when the dominant contribution to the observed currents arises from the tunnelling of thermally excited electrons through the narrow upper region of the image-force-lowered work-function-barrier. Murphy and Good\textsuperscript{200} showed that each of those mechanism is limiting approximation observed under appropriate conditions at applied field and temperature.

In polymers at or below room temperature, the density of free charge carriers is extremely low and with an electric field, non-equilibrium conditions can be achieved, which can be easily enhanced by injecting a charge through an ohmic contact. If the contact is equivalent to sufficiently large reserve of free charges, the current-voltage characteristic does not depend on the manner in which the charges are generated but is strictly connected with the charge transport mechanism. Current-voltage curve is generally nonlinear on account of the two basic causes. At high fields the charges are accumulated between the electrodes\textsuperscript{201}. The presence of traps within the forbidden gap reduces the free charge density and produces a localized charge density within the polymer. The density, energy distribution and the nature of the traps have a determining influence on current-voltage characteristic which also
depends on the type of charges involved in the conduction process\textsuperscript{202}. Space charge limited current theory of Rose\textsuperscript{203} has been modified by Lampert\textsuperscript{204}. Trapping sites exert a strong influence on the current flow i.e., the concentration of free carriers and their mobility. Mobility values in polymers are very low suggesting strong trapping. Phenyl rings and alopohatic or aromatic groups may be active traps. The trapping ability of unsaturation sides in the chain and the chain ends of pure polymer is confirmed. Similar conclusions are obtained by Perlman and Unger\textsuperscript{205} in the studies of electron traps in irradiated polyethylene and teflon. Mobility values of polyethylene satisfy the relation for carrier hopping between localized sites. If the activation values of hopping are low 0.2 - 0.3 ev, hopping is connected with charge jumps brought about by motions of chain elements and the process is related to so-called chain hopping mechanism while of greater values (0.5 ev) the so-called trap hopping mechanism is involved. Martin and Hirsch\textsuperscript{206} proposed energy traps 0.2 - 0.75 ev for polystyrene 0.2 - 0.3 ev for polyethylene terephthalate, showing that both the mechanisms play a significant part. Life time of carriers in traps depends on the field. Thus band model with traps of various depths explains experimental results reasonably. However, the nature of charge carriers and trapping sites has not yet been settled conclusively.

In polymers when H-atoms in the backbone chains are replaced by larger aromatic groups with \texttau electrons, the
highest field and the lowest empty molecular orbits are formed from the substituents and the charge transfer occur within the pendent groups where charge carrier density is higher due to higher affinity to electrodes or holes. The role of backbone chain is less important. Taking into consideration that the overlapping of \( \pi \) systems is small, the band width must be narrow. The band width depends on the method used but does not exceed 0.1 ev. This narrow band width is responsible for the fact that the electrons are for quite a long time connected with the particular \( \pi \) system which exceeds the vibrational and the high frequency dielectrical relaxation time. This results in deformation of electron density in the \( \pi \) system and in induced polarization of the neighbouring \( \pi \) systems. The bonding energy of an electron to the potential well can be calculated. Thermal energy (phonons) can be transferred to electrons, including thermally assisted hopping. This mechanism is called small polaron mechanism\textsuperscript{207}. In polymers conduction can be explained in terms of small polaron mechanism and in some cases as intrinsic phenomenon.

The trapping capability of a polymer can be greatly modified by doping it with certain impurities. Carrier mobility in polymeric materials is increased by small molecules such as iodine\textsuperscript{208}. Recently Srivastava and co-workers\textsuperscript{137-138} doped polystyrene with several impurities and found that the conductivity of the polymer is greatly enhanced due to doping of the matrix with iodine\textsuperscript{137}. The
enhanced conductivity of the polymer has been interpreted in terms of charge-transfer complexes.

This chapter describes transient behaviour of current, current-voltage characteristics and temperature dependence of current in pure and Ph doped PS films.

3.2 Results:

Generally polymers gives a current on application of a voltage at a particular temperature. These currents are known as transient currents. Transient currents in PS and doped PS films were investigated. To measure the current substrate was biased positively and the upper electrode was connected to the electrometer. Current-time curves were investigated in the voltage range 9-90V and temperature range 40-90°C in pure and doped PS films of 20 um thickness.

Figure 3.1 shows current time curves on a double log graph at 9, 27, 63, 72, 81 and 90V at 20°C for PS. The same graph for doped PS has been plotted in figure 3.2 at 9, 27, 63, 72, and 81V at 20°C. In this way the effect of voltage on transient currents was studied at 20°C. The effect of temperature on transient currents in the range 40-90°C was also studied. The bias voltage was kept constant at 9V. Transient currents at 40, 60, 80, and 90°C for PS has been shown in figure 3.3 while those for doped PS in the same temperature range are shown in figure 3.4.

Conductivity of a sample is studied in two different ways. First by varying the voltage at a constant temperature and secondly by varying the temperature keeping the bias
voltage constant. Plots in two different ways has been obtained. Current-voltage characteristics of PS in the voltage range 1.5 - 90V have been plotted at 30, 40, 50, 60, 70, 80 and 90°C in figure 3.5. The same plots for doped PS films are shown in figure 3.6.

Effect of film thickness on current-voltage characteristics of pure and doped PS was investigated. Figure 3.7 exhibits the effect on PS samples were films of 20, 10, 5, 3 and 2 μm thickness has been used. The same plots for Ph doped PS have been illustrated in figure 3.8.

Electrode plays an important role in the mechanism of conduction because the charge carriers may be injected from the electrode into the polymer specimen. Current-voltage characteristics of pure and doped PS films in the form metal-polymer-Al sandwich were studied at 50°C. Metal used were Al, Ni, Pb, Cu and Zn. The plots in the form of J-V1/2 are shown in figure 3.9 for pure films and in figure 3.10 for doped films. The plots of doped films are quite straight while those of pure samples are not quite straight.

To investigate the effect of doping on conductivity of PS, the doped films at 5, 10, 20 and 30 g l⁻¹ were used. The voltage was kept constant and the films were heated at a very small rate of heating. The current at various temperature was noted. From the current the conductivity of the films was calculated and the plots of conductivity VS. 10³/T (K⁻¹) are exhibited in figure 3.11. The values noted on the plots give the activation energy. It is 1.05 ev for
Fig. 3.1 Current-Time characteristics of 20μm thick PS films at 20°C for different bias voltages.
Fig. 3.2 Current-Time characteristics of 20μm thick doped PS films at 20°C for different bias voltages.
Fig. 3.3 Current–Time characteristics of 20μm thick PS films at 9V for various temperatures
Fig. 3.4 Current–Time characteristics of 20μm thick doped PS films at 9V for various temperatures.
Fig. 3.5 Current–Voltage characteristics of 20μm thick PS films
pure PS and 1.32, 1.66, 1.53 and 1.52 ev for the films doped at 5, 10, 20 and 30 gl·¹ respectively.

3.3 Discussion:

Electronic conduction may be due to the motion of free carriers, electrons in the conduction band and holes in the valance band or alternatively to the motion of quasi-localized carriers which is otherwise described as hopping of bound carriers between localized sites²⁰⁹ in the dielectric. The former process requires an activation energy in order to excite a carrier into the relevant band and this energy can normally be supplied thermally or by other free carriers which have acquired a high energy in an electric field, leading to an avalanche process. The activation energy may be affected by electric field as in the case of Poole-Frenkel effect²¹⁰.

The hopping process required less energy than the activation into the free band and this energy may, in the limit of very high density of localized centres, tend to zero as in the case of impurity band conduction in semiconductors²¹¹. This process is favoured in the case of heavily disordered solids, such as amorphous and glassy dielectric films²¹².

Some dielectrics show a region of linear current voltage characteristics i.e., ohmic conduction at low fields²¹³, specialty at elevated temperature although more often this region can not be seen at the limit of detection. It is difficult to establish conclusively whether ohmic
conduction is due to ionic or electronic processes but ionic conduction would appear more likely.

In interpreting the properties of dielectric films, one frequently employs concepts taken over from the physics of crystalline media. In this way one refers to trapping levels and donor and acceptor levels at discrete energy values. One speaks of energy barriers due to ionized impurities and, in the case of Poole-Frenkel effect one employs the model of hydrogenic impurities in which the bound electron is characterized by a definite effective mass and a ground state orbit of a diameter corresponding to several interactioning spacings. These concepts may be valid to a greater or lesser extent in the case of poly crystalline and micro crystalline films, although allowance may have to be made for the presence of interfacial barriers. It would be very difficult to justify their use in application to amorphous and glassy films. It is appropriate to recall here the salient features of the theory of amorphous conductors as it applies to dielectric films. The general consensus of opinion is that the basic features of the band structure, such as the width of the forbidden gap, are determined primarily by the short-range order i.e., by the relative disposition of the nearest neighbours in the solid. Since these dispositions are similar in amorphous and crystalline solids, the broad features are preserved on transition from crystalline to amorphous structure. The disappearance of medium and large range order does influence the detailed shape of the band structure; however, in that case it causes
a considerable blurring of the edges of the conduction and valence bands, and gives rise to a distribution of deep localized levels in the forbidden gap.

In a crystalline solid, there exists a clear distinction between the propagating bands—conduction, valence and forbidden. In the former the carriers propagate freely except for collisions on thermal vibrations and other lattice imperfections which determine a mean free path which is greater, usually considerably greater than the lattice spacing. In the forbidden gap, the energy levels that may exist due to imperfections are strictly localized and an electron has to be excited from one of these levels to the conduction band before being able to move on. Special case arise when the localized levels are spaced so closely that their wave functions overlap and give rise to the formation of the so-called impurity band, leading to metallic properties with zero activation energy. Alternatively, the spacing may not be as close as is necessary for the formation of impurity band, but sufficient for phonon-assisted tunnelling between neighbouring centres, the so-called hopping conduction. Hopping is characterized by an activation energy which is only a fraction of the normal ionisation energy of the carrier from the centre into the band is often accompanied by a rather complicated frequency dependence.

The significance of blurred band edges is that there is no sharp distinction between the propagating and forbidden gap but instead partly localized levels are formed leading
to a conduction by a process intermediate between impurity band and hopping conduction in which the propagation of the carriers is characterized by a small mobility. The deeper the levels, the more localized their character, until the deep tail states may be considered as proper trapping sites, unlike traps in crystalline materials, however, these deep states would not possess any clearly defined activation energy.

Poole-Frenkel mechanism is frequently invoked in the interpretation of electric current in dielectric films at reasonably high electric fields. The physical basis of Poole-Frenkel mechanism is analogous to the Schottky emission.

O'Dwyer in a theoretical paper considers a detailed electronic model of a dielectric with traps with Schottky emission from an injecting electrode and with Fowler-Nordheim correction for tunnelling through the top of the barrier at high fields. In a recent review of Poole-Frenkel mechanism Simmons\textsuperscript{215} pointed out that experimental data apparently favouring the Schottky mechanism can be more compatible with Poole-Frenkel mechanism if it is postulated that shallow neutral traps are present in the dielectric together with deep lying donors. Franks and Simmons\textsuperscript{216} consider further the effect of space charge on Poole-Frenkel process.

A consequence of the phenomenon of carrier injection is the formation of space charge cloud\textsuperscript{217} of carriers in the vicinity of contacts. Mutual repulsion between the
individual carriers limits the total injected charge in the film and the resulting current is said to be space charge limited. Trapping sites reduce the magnitude of current. The mobile charge carriers are continually interacting with the lattice. A thermodynamical equilibrium is maintained between the space charge and lattice so that there is a special relationship between the electric field and the drift velocity of the carriers. The trapping sites accentuate this difference even further. Holes or electrons can be injected according to the choice of electrode material\textsuperscript{218}. This then brings in the added complication of recombination.

3.3 (a) Transient Current :

When a di field is applied to a finite thickness of a dielectric sandwiched between two parallel electrodes, there is besides the rapidly charging current and steady state conduction current, a long term slowly decaying current. Similarly, on removal of the voltage and the electrodes short-circuited, the fast component of the current is followed by a long term slowly decaying current. This long term current is known as the anomalous current or absorption current\textsuperscript{219}. Provided the principle of superposition holds, the behaviour of charge in current with time for the charging and discharging events are equivalent and their numerical analysis are identical. The discharge current manifests itself in the familiar absorption of the charging experiment. Dielectric relaxations which occur in the frequency range 0.1 Hz are normally studied by their
contributions to the current decay of a charged dielectric on discharge\textsuperscript{220}.

Dasgupta and Joyner\textsuperscript{219} reported absorption current in polyethylene terephthalate and polypropylene by varying field, temperature, time, electrode material and thickness and identified the mechanism from the possibilities - electrode polarization, dipole orientation, charge storage leading to trapped space charge effect, tunnelling of charge carriers from the electrodes and hopping of charge carriers through localized states. The behaviour of absorption current in PS is observed to be similar to that of polypropylene. A sudden increase in voltage causes the current to transiently increase to high values. In a matter of minutes, the current subsides to a much smaller stationery value. The interpretation is that the sudden increase in voltage forced a corresponding increase of charge in the conduction band. In the course of minutes, most of this free charge settles into traps and one observes the rapid decay of current. The time required for the transient current to subside is a direct measure of the capture cross-section of traps for free carriers.

The transient current $J$ versus time $t$ on a double log scale yields a straight line (figure 3.1 and 3.2) showing that the decaying current obeys the usual $t^{-n}$ law ($n$ : an exponent; $0<n<1$) before reaching a steady state. The field dependence of the current (figure 3.1) may be expressed by the relation.

$$J(t) = K(t) E^p \quad \ldots \quad (3.1)$$
where $K$ is a decay factor independent of the field $E$ and $p$ is found to be 0.9 at low applied fields. The value of $p$ decreases with the increase of voltage. The temperature dependence of the current (figure 3.3 and 3.4) may be considered by

$$J(t) = A(t) t^{-n} \quad \ldots \quad (3.2)$$

where $A$ is a temperature dependent term. The absorption current shows a marked increase with temperature. The observed magnitude of $n$ in the temperature range and the absence of any thickness dependence and any significant electrode material effect (not shown) rule out tunnelling, electrode polarisation and charge injection forming trapped space charge as possible mechanisms for absorption currents. The observed behaviour of absorption current in the temperature range may be explained either by the mechanism of dipolar relaxation in the bulk with the wide distribution of relaxation times or by a charge carrier hopping process through localized states. A relaxation of dipoles may also be ruled out as a relevant mechanism because the absorption current was not found to be inversely proportional to the sample thickness$^{221}$.

3.3 (b) Current-Voltage Characteristics :

Current-Voltage ($J$-$V$) characteristic of 20 $\mu$m thick PS films in the temperature range $30 - 90^\circ$C have been plotted in figure 3.5. They are all linear. When the charge carriers are supplied from the electrode and all of them are transported ohm's law holds and the current is proportional to the voltage. The current in the case is limited by the
electrode. When the electric field is low, the mobility of the carriers or the presence of traps can limit the current observed in the system. In the absence of traps only mobility limits the current and one has a super linear J-V curve$^{23-25}$. The plots of figure 3.5 have been replotted in $J-V^{1/2}$ form in figure 3.12 for applied voltage in between 36 - 99V. The plots are seen to be linear. It is a well established experimental fact that for fields in excess of some 10 KV cm$^{-1}$ many dielectric films exhibit current-voltage characteristics of the form:

$$J = \exp \left( \frac{eB E^{1/2}}{K T} \right) \quad \text{...... (3.3)}$$

where $e$ is electronic charge, $E$ the field, $K$ Boltzmann's constant and $B$ a coefficient. This is naturally taken as evidence of either Schottky or Poole-Frenkel mechanism and since the coefficient $B$ for either of these is given by essentially fundamental constants, it is claimed that it should be possible to decide between the two mechanisms from the numerical value of the coefficients. The expression for Schottky emission is

$$J = J_0 \exp \left[ \frac{e (B_s E^{1/2} - V_g)}{K T} \right] \quad \text{...... (3.4)}$$

where $J_0$ is pre-exponential factor, $V_g$ the potential barrier and $B_s$ Schottky field lowering coefficient which is given by
Fig. 3.6 Current–Voltage characteristics of 20μm thick doped PS films
Fig. 3.7 CURRENT-VOLTAGE CHARACTERISTICS OF PS AS A FUNCTION OF THICKNESS AT 50°C
Fig. 3.8 Current—Voltage characteristics of doped PS as a function of thickness at 50°C
Fig. 3.9  \( J - V^{1/2} \) CHARACTERISTICS OF PS ON DIFFERENT METALS AT 50°C
Fig. 3.10 $J - V^{1/2}$ characteristics of doped PS on different metals at 50°C
Fig. 3.11 EFFECT OF DOPING ON CONDUCTIVITY OF PS
Fig. 3.12 Current Vs square root voltage of 20µm thick PS films at various temperatures
\[ \beta_s = \left( \frac{e}{4\pi \varepsilon_0 \varepsilon} \right)^{1/2} \quad \ldots \quad (3.5) \]

where \( \varepsilon_0 \) is the dielectric constant of free space and that of the material. The filed lowering of the barrier height for Poole-Frenkel effect is given by \( B_{PF} E^2 \) where \( B_{PF} = 2\beta_s \). The theoretical and experimental values of \( B \) show marked departures. This complicates the interpretation in terms of either of the simple models because a temperature dependence is not provided in both the Schottky and Poole-Frenkel mechanism.

Scher and Montroll\(^{209}\) recently advanced the phenomenological relationship for hopping conduction in which the field and temperature dependence of the mobility \( \mu \) is described by the following equation:

\[ \mu = \mu_0 \exp \left[ \left( \frac{a}{kT} \right) \left( E^n - E_0^n \right) \left( 1/T - 1/T_0 \right) \right] \quad \ldots \quad (3.6) \]

where \( \mu_0 \) is pre-exponential factor, \( a, E_0 \) and \( T_0 \) are parameters and \( \sqrt{n}^{1/2} \). In figure 3.12 the square root voltage dependence of current is shown for various temperatures. The straight lines when extended have a common intercept. The values of current and voltage at the intercept are found to be \( 5.8 \times 10^{-10} \) A and 1648V respectively. The same results are reported in figure 3.13 as a function of \( 10^3 / T \) in between 30 - 60°C at 36, 54, 72 and 90V. The curves bend heavily beyond 40°C. This behaviour is believed to be associated with the glass-transition temperature of the polymer. The plots before 40°C extended to have the common intercept. The values of current and temperature at the intercept are found to be \( 3.8 \times 10^{-10} \) A and 60°C respectively. The values for
Fig. 3.13 Current Vs $10^3/T$ of 20µm thick PS films at various voltages
Fig. 3.14 Current Vs square root voltage of 20μm thick doped films at various temperatures
Fig. 3.15 Current vs $10^3/T$ of 20μm thick doped films at various voltages.
Fig. 3.16 Zero field current density Vs. work function for pure and doped films
Fig. 3.17 Current density Vs reciprocal thickness cube for pure and doped PS at 50°C
current obtained from the two intercept are in very good agreement. Therefore, the current and hence, the mobility is described by equation (3.6)

3.3 (c) Effect of Doping on Current-Voltage Characteristics:

Current-Voltage characteristics of Ph doped PS films at 30, 40, 50 and 60°C are shown in figure 3.6. In figure 3.14 the square root voltage dependence of current is shown for various temperatures. The straight lines are extended to join at the common intercept. The values of current and voltage at the intercept are found to be 3.4 x 10^{-9} A and 1406V respectively. the same results are replotted in figure 3.15 as a function of 10^{3}/T in between 30-60°C at 36, 54, 72 and 90V. the curves bend heavily above 50°C. The straight lines meet at the common intercept. The values of current and temperature at the intercept are found to be 3.4 x 10^{-9} A and 63°C respectively. The values for current obtained from the two intercepts are in good agreement. So the current and hence the mobility in Ph doped PS film is also described adequately by equation (3.6). The values of current at the intercept for PS film is obtained to be 5.8 x 10^{-10} A while that for Ph doped PS film is determined to be 3.4 x 10^{-9} A. Hence, the carrier mobility is enhanced due to doping of polymer matrix with Ph. A linear voltage dependence of the activation energy is exhibited by pure and doped PS but the slope of the plot for doped film is greater than that for the pure one. This indicates that due to doping the activation energy becomes more voltage dependent.
3.3 (d) Electrode Material Effect:

Charge transfer from metal depends on electron levels in which the carriers shift freely under the influence of field. The energy on this level \( E_b \) may be given by:

\[
E_b = E_g = (I_g - P^+) - (A_c + P^-) = I_c - A_c \quad \ldots \quad (3.7)
\]

where \( I_g \) is ionisation energy, \( A_c \) electron affinity, \( P^+ \) and \( P^- \) polarisation energies and \( I_c \) ionisation energy of a molecule of the material, \( E_b \) corresponds to energy gap \( E_g \). In case of polystyrene \( E_g = 4 - 5 \) ev

while for polyethylene \( E_g \approx 8 \) ev \( (P^+ = P^- \approx 1.5 \) ev \)

From these data intrinsic generation of free carriers resulting from Boltzmann's factor \( \exp (-E_g/KT) \) is negligible at temperatures below polymer decomposition. It gives more emphasis to the importance of metal-electrode contact which is the origin of carriers responsible for conduction.

The contact is said to be ideal if the distance between metal and dielectric is 10Å. If no excess ions or other energy states appear in the dielectric, the fermilevel is midway between conduction and valence band. The fermilevel is away from the vacuum level by \( \phi \) \( (\phi \) corresponds to work function of electron detached from the metal). When the metal comes into contact with the dielectric, there is a tendency towards equalization of levels at the point of contact. If the fermi level is higher in the dielectric than in the metal, then electrons are transferred to the metal and in this way a levelling of potentials takes place. In the case of organic compounds, there are no excess charges even if there are defects, they are deep and therefore can
not go ionization under the influence of thermal energy, the same applies to impurities from the other organic molecules. Electrostatic equilibrium is established only due to transfer of carriers from metal. Electron overcomes the potential barrier

\[ X^- = \phi - A \] \hspace{1cm} \ldots \hspace{1cm} (3.8) \\

while holes

\[ X^+ = I_c - \phi \] \hspace{1cm} \ldots \hspace{1cm} (3.9) \\

In this way emission current arises as described by Richardson's equation:

\[ J = AT^2 \exp \left( -\frac{X^-}{kT} \right) \] \hspace{1cm} \ldots \hspace{1cm} (3.10)

A similar equation holds for holes. Such an injected charge is captured in neutral traps which are always present. Figure 3.16 shows zero field current density versus work function for pure and Ph doped PS films. The plot for doped PS is straight showing some charge due to doping.

3.3 (e) Effect of Dopant Concentration on Temperature Dependence of Conductivity:

The interpretation of the temperature dependence of conductivity is polymers is far from consistent. Some hypotheses have postulated that conductivity above and below the inflection is ionic and electronic in nature respectively and yet others are based on the analogy with some intrinsic conduction exists above inflection and impurity conductivity below inflection. Shishkin and Vershinina and Warfield and Petree connect the inflection with glass transition of the polymer. They explain
the inflection at glass transition by charge in environmental conditions for ion mobility at the transition from the glassy state into a highly elastic one. Herwig and Jenckel\textsuperscript{228} and Raddish\textsuperscript{229} suppose that the inflection appears as a result of the super-position of polarisation effects on the conductivity process at temperatures below the glass transition temperature, at which the relaxation times becomes long. Adamec and Mateova\textsuperscript{230} concluded that the inflection on $\sigma(T)$ curve does not necessarily correspond to the glass transition temperature of the polymer, even though the inherent conductivity becomes a predominating component in the vicinity of glass transition.

Incorporation of Ph in 5 gl\textsuperscript{-1} exhibits two regions in temperature dependence of conductivity of the polymer, one below and the other above 45°C. With the increase in dopnat concentration the two regions become more prominent and at a concentration of 30 gl\textsuperscript{-1} the two regions terminate into one. The value of activation energy for different regions was calculated from Arrhenius relation:

$$\sigma - \sigma^0 \exp \left( \frac{H}{KT} \right) \quad \ldots \ldots \ldots \ldots (3.11)$$

where $\sigma^0$ is pre-exponential factor and $H$ the activation energy. The low temperature tail below 45°C in conductivity curves of the doped films may be attributed to impurity conduction. The activation energy 1.05 ev of pure PS is increased due to doping of the polymer. The activation energies of 5, 10, 20, 30 gl\textsuperscript{-1} Ph doped films come out to be 1.32, 1.66, 1.53 and 1.52 ev respectively. High activation arises from intrinsic conduction, the difference
in activation energies is due to higher dissociation energy to form the carriers for intrinsic conduction. Similar types of doping have been reported due to doping of poly vinyl fluoride$^{231}$ and polystyrene$^{136}$.

Below 45°C the activation energy is described with the increase in Ph concentration. The conductivity is enhanced considerably, which may be associated with the increase in mobility due to doping. The strong concentration dependence of conductivity of the polymer helps to interpret that transport in Ph doped PS films occurs via a hopping process among sites associated with the dopant molecule. A rather detailed theoretical background exists for hopping transport with a discrete activation energy. Theoretical refinements are in progress to include distribution of hopping energies and to describe alternative transport mechanisms such as multiple trapping and trap-controlled hopping$^{232-236}$. Although these extensions of the theoretical concept will narrow the range of possible interpretation of the transport mechanisms, a clear identification would require the experimental modifications of materials parameters specific to the proposed transport model, such as the densities of hopping or trapping sites. In this respect, the concept of doping of organic polymers is extremely powerful.

3.3 (f) Thickness Dependence:

It is of importance to be able to distinguish between non-ohmic behaviour due to space charge and that arising from other physical process. The obvious method is to investigate the dependence on thickness of a set of current-
voltage curves current-voltage characteristics of 2, 3, 5, 10 and 20 μm thick films at 50°C are shown in figure 3.7 and for doped films in figure 3.8. Thin film gives more current. It is the evidence of space charge accumulation. Pulfrey et al.\textsuperscript{237} consider electronic conduction and space charge in amorphous insulating films and conclude that at small thicknesses Schottky law is more probable while at large thickness the Poole-Frenkel law is expected. Thus, if one makes films of various thicknesses, one would expect Schottky mechanism for thinner samples and Poole-Frenkel for thicker specimens, i.e., the typical transition between interface control with thin films and typical macroscopic conduction in electrically neutral material, changing at higher currents, to space-charge limited current with the free carriers providing the space-charge. Current density versus reciprocal thickness curve has been plotted in figure 3.17.

3.4 Conclusions:

The above discussion on electrical conduction in pure and Ph doped PS films enable to draw the following conclusions:

1. The transient current in PS decays according to \( t^{-n} \) law before reaching a steady state. The observed magnitude of \( n \) and the lack of thickness and electrode material dependence of transient current indicate carrier hopping process.

2. The absence of any significant electrode effect on current-voltage characteristics of the polymer films rule out the Schottky thermionic emission of charge carriers.
3. Thickness variation on current-voltage curve of PS reveals space charge build up.

4. In low field regime Ohm's law seems to be valid in pure and Ph doped PS films.

5. At high field values the linearity of current with square root of voltage for pure and doped films indicates Schottky or Poole-Frenkel mechanism. But the Poole-Frenkel mechanism is more logical because comparatively thick (20 μm) films have been used in the investigation.

6. The experimental value of Poole-Frenkel coefficient is calculated to be very low in comparison to the theoretical value. This complicates the interpretation of current-voltage characteristics in terms of Poole-Frenkel mechanism and shows a temperature dependence which is not provided in the simple model for Poole-Frenkel mechanism.

7. The values of current for pure and Ph doped films determined from the common intercept of current versus square root voltage at various temperatures agrees well with the value determined from the common intercept of current versus 10³ at various voltages. This shows that the field and temperature dependence of mobility in the two types of films can be described adequately according the equation

\[ \mu = \mu_0 \exp\left( \left( \frac{q}{kT} \right) \left( E^n - E^0 \right) \left( \frac{1}{F} - \frac{1}{F_0} \right) \right) \]

The above equation in the phenomenological relationship for hopping conduction as described by Scher and Montroll.

8. Due to doping of the polymer with Ph in 10 g l⁻¹ concentration, the value of current at the common intercept
is enhanced to $8.6 \times 10^{-5}$A from $5.8 \times 10^{-6}$A. The increase in current is associated with the increase in carrier mobility.

9. Temperature dependence of conductivity of pure and Ph incorporated films reveal that doping of the PS matrix with Ph enhances the conductivity of the polymer. The increase in conductivity is due to the increase in mobility of charge carriers due to impregnation of the matrix with Ph.