Chapter-3

Electrical Conductivity
ELECTRICAL CONDUCTIVITY

3.1 Introduction

Most of the polymers are considered to be insulators because they show low conductivity. (211-216) low dielectric loss and high break down strength (217). However, recent research in the field of polymers has led to the development of special type of high molecular weight materials which exhibits a conductance high enough to classify them as semiconductors (specific conductivity $= 10^{-12}$ to $10^{12}$ ohm$^{-1}$cm$^{-1}$) or even in some cases as conductors (218).

In the past several years, a good amount of work has been reported on electrical conductioon in polymeric materials (219-222) and various mechanisms (223-232) such as ionic conduction (233-235), Schottky emission (236-239). space charge limited conduction (239, 240) tunnelling (241). Poole-Frenkel mechanism (242), charge hopping (243, 244) and small polaron mechanism (245) have been proposed to explain the experimental results.

Electric current is 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 charged material particles of the matter are 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 temperature when the resistivity of matter is reduced. The molecules of most of organic polymers can not be ionised but 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 halogens in their molecular (218)
structure, electrical conduction is qualitatively proved to be ionic (234).

The fact that electronic conduction plays a role in polymers was established experimentally by Seanor (246). To discuss electronic conduction, it is necessary to investigate the generation of free carriers and their transport through the material. Several books and reviews (247-251) 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 (252) (Schottky emission) occurs in the low field high temperature limit. Field emission (253, 254) (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 (255-256) 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 (258) showed that each of these mechanisms in limiting approximation is observed under appropriate conditions of 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 charge, 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 non linear on account of the two basic causes. At high fields the charges are accumulated between the electrodes (259). 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 (260). Space charge limited current theory of Jose (261) has been modified by Lampert (262). Trapping sites exert a strong influence on the current flow i.e. on the concentration of free carriers and their mobility. Mobility values in polymers are very low suggesting strong trapping.
Phenyl rings and aliphatic 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 conclusion are obtained by Perlman and Unger (263) 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 (264) proposed energy traps 0.2-0.75 eV for polystyrene and 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 th field. Thus band model with traps of various depths explains experimental results reasonably. However, the nature of charge carriers and trapping site has not yet been settled conclusively.

In polymers when H-atoms in the backbone chains are replaced by larger aromatic groups with \( \pi \)-electrons, the highest filled and the lowest empty molecular orbits are formed
from the substituents and the charge transfer occurs within the pendent groups where charge carrier density is higher due to higher affinity to electrons or holes. The role of backbone chain is less important. Taking into consideration that the overlapping of π-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 π-system. 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 (265). 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 (266-277). Carrier mobility in polymeric materials is increased by small molecules such as iodine (263). Recently Srivastava and co-workers (68,69) doped polystyrene with several impurities and found that the conductivity of the polymer is greatly enhanced due to doping of
Fig. 3.1, Effect of temperature, voltage and iodine concentration on transient currents in PS
the matrix with iodine (68). 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 iodine doped PS films.

3.2 Results

Application of a voltage to a polymer film causes current which is found to decrease first rapidly and then slowly. Transient behaviour of current was investigated in 20 μm thick films of PS, I₁ and I₃. At 50°C, I₁ gives ten times more current than PS. I₃ also gives more current but this increase is less. Current also depends upon applied voltage but the temperature dependence is more pronounced.

Current (J) versus time (t) on a double log plot yielded a straight line, the current may be described by

\[ J(t) = A(T) t^{-b} \] .... (3.1)

When \( b \) is an exponent and \( A(T) \) a temperature dependent factor. Fig. 3.1 exhibits the effect of temperature, voltage and iodine concentration on transient behaviour of current.
Fig. 3.2. Electrode effect on Schottky plots of $I_1$ at 50°C, effect of temperature on $J-V^{1/2}$ plots of $I_1$, and effect of iodine concentration on $J-V^{1/2}$ plots at 50°C.
For different plots b ranged between 1.5-2.2.

Voltage dependence of current may be described by

\[ J(t) = K(t) V^p \] \hspace{1cm} \ldots (3.2)

\( p \) is an exponent and \( K \) is a decay factor independent of voltage. Transient current was also found to depend upon electrode material.

Contacts provide an important source of carrier injection in poly-meric materials. To investigate the role played by contacts, steady state current - voltage (J-V) characteristics were traced at 50°C for \( I_1 \) in the configuration Al-PS-Metal. Al, Cu, Ni and Zn metals were employed to obtain a range of work function. The replots of J-V in the form fo J-V^x (Schottky plots) are shown in Fig. 3.2. The figure also shows the effects of concentration and temperature. The plots when extrapolated in the backward direction seem to originate from the same point. Therefore electrode dependence is rather weak.

Fig 3.3 illustrates the effect of thickness on J-V characteristics of \( I_1 \) at a constant temperature of 50°C. For the thicknesses of 20, 10 and 5 \( \mu \)m the J-V plots are linear. It is seen that slope of J-V plots increases with the decrease in the film
Fig. 3.3, Effect of Thickness on Current-Voltage Characteristics of I, at 50°C
Fig. 3.4, Current Vs reciprocal Thickness Cube of $l_1$, at 50°C
Voltage indicated on the plots
Fig. 3.5, Effect of iodine concentration on Current-Voltage Characteristics of PS

50°C

10^8

10^6

10^4

10^2

Current (A)

PS

Voltage (V)

10^1

3 10 100
Fig. 3.6. Current-Voltage Characteristics of I, at different temperatures.
thickness. Current density at the same voltage plotted against reciprocal thickness cube of the film gave a straight line. Fig. 3.4 shows these plots for the applied voltages 1.5, 4.5, 9, 45 and 90V.

Fig. 3.5 Compares the steady state conduction currents obtained by applying a voltage in the range 3-99V at a temperature of 50°C to the PS. $I_1$, $I_2$, $I_3$, $I_4$ and $I_{10}$ films. They are all linear on double log scale. Currents and hence the conductivities of the doped film are greater than those of pure PS film at all the voltages applied. At a particular voltage, as the iodine concentration is increased, the current is also increased. Slope of pure PS plot is greatest and it is decreased with the increase in iodine concentration. At a lower voltage the current differ more than at higher voltage i.e. as the voltage is increased, the difference in the currents of various samples becomes smaller and smaller.

Current voltage characteristics of $I_1$ at 30, 40, 50, 60 and 70°C have been plotted in Fig 3.6. Similar plots were also obtained for other concentrations of iodine. Slopes of these lines are seen to decrease with the increase in temperature. The
Fig. 3.7, Effect of iodine concentration on current Vs $10^3/T$
Voltage being 18V and heating rate 1°C min⁻¹ Activation energy noted on the plot
Fig. 3.8, Effect of iodine concentration on conductivity Vs $10^3/T$

Activation energy noted on the plots.
difference in current at various temperatures is greater at smaller voltages and is smaller at greater voltages.

The temperature variation of current in the range 30-100°C was studied by heating the film at a constant rate of 1°C min⁻¹ and applying a voltage of 18V. This is shown in fig 3.7. The conductivity was evaluated from the measured value of current. The conductivity curves (σ Vs 10¹/T) of pure PS film and imregnated with iodine (I₁-I₁₀) are shown in fig 3.8. The conductivity of PS film increases linearly with temperature from 30°C to about 70°C beyond which a strong bend is observed. Similar plots are seen for doped films. At all temperatures, conductivity of doped film is greater than that of pure PS. Due to increase in iodine concentration, the conductivity is further enhanced. Activation energy E was calculated from

\[ \sigma = \sigma_0 \exp \left( \frac{E}{kT} \right) \]

where \( k = \) Boltzmann’s Constant

The value of activation energy is noted on the corresponding plot. The value of activation energy decreases due to doping which is further decreased due to increase in iodine concentration.
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 sites (278) in the dielectric. The former process requires an activation energy in order to excite a carrier into 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 effect (279).

The hopping process requires 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 semiconductors (280). This process is favoured in the case of heavily disordered solids, such as amorphous and glassy dielectric films (281).

Some dielectrics show a region of linear current voltage characteristics i.e., ohmic conduction at low fields (282),
specially 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 interacting 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 (283). 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 carrier 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 arises 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 (284) 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 (285) 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 (286) consider further the effect of space charge on Poole-Frenkel process.

A consequence of a phenomenon of carrier injection is the formation of space charge cloud (287, 288) 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 (289). This then brings in the added complication of recombination.

3.3 (a) Transient Current:

When a DC 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 (290). Provided the principle of superposition holds, the behaviour of change in current with time for the charging and discharging events are equivalent and their numerical analysis are identical. The discharge current manifests itself in a 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 (291).

Das Gupta and Joyner (290) 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 iodine doped 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 stationary 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 (Fig 3.1) showing that the decaying current obeys the usual $t^b$ law ($b$ an eponenet; $0 < b < 1$) before reaching a steady state.

The absorption current shows a marked increase with temperature. The observed magnitude of $b$ in the temperature range and the absence of any thickness dependence and any significant electrode material effect (not shown) rule out tunnelling, electrode polarization 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 (292).

3.3 (b) Effect of Electrode Material:

Charge transfer from metal depends on electron
levels in which the carriers shift freely under the influence of field. The energy on this level (293) may be given by

\[ E_b = E_g = (I_g - P) - (A_c + P) = I_e - A_c \]

Where \( I_g \) is ionisation energy, \( A_c \) electron affinity, \( P \) and \( P' \) polarization energies and \( I_c \) ionisation energy of a molecule of the material, \( E_b \) corresponds to energy gap \( E_g \). In case of PS \( E_b = E_g = 4 - 5 \) eV, from this data intrinsic generation of free carriers resulting from Boltzmann's factor 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 10A. If no excess ions or other energy states appear in the dielectric, the Fermi level is midway between conduction and valence band. The Fermi level 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 over comes the potential barrier (designated by $\chi$)

$$\chi = \phi - A_c \quad \ldots 3.4$$

while holes must overcome the potential barrier

$$\chi^+ = I_c - \phi \quad \ldots 3.5$$

Where $\phi$ is the metal work function. In this way emission current arises as described by Richardson's equation:

$$J = AT^2 \exp(-\chi/kT) \quad \ldots 3.6$$

Where $J$ is the current density, $A$ is a constant, $T$ is the absolute temperature and $k$ is Boltzmann's constant.

In the light of above discussion, $J-V$ plot (fig 3.2) may be interpreted in terms of Richardson-Schottky (RS) field assisted thermionic injection of carriers from metal electrodes.
The RS mechanism has also been suggested in other studies on polyethylene terephthalate, polytetrafluorethylene and poly N-vinyl carbazole (294, 295). The simple RS theory does not give a good fit to the experimental data and various explanations have been advanced to explain this. Schug et al. (296) have concluded that the electric field in the RS effect is determined by the trapped space charge moderated by Poole-Frenkel effect (285). Taylor and Lewis (297) have assumed a more generalised form of the potential barrier rather than the Coulombic barrier usually employed in treatments of the RS effect. They obtained consistent agreement with experimental results in studies on polyethylene and polyethylene terephthalate and concluded that the potential barrier chosen referred to the cathode-dielectric interface and is probably determined by a space-charge layer in the dielectric. It has been suggested that such space-charge layers are charged up by the absorption current (298, 299). The classical RS effect predicts a current-voltage relationship of the form:

\[ J = AT^2 \exp \left( -\frac{x}{kT} \right) \exp \left( \beta V^{1/2} \right) \]

...3.7

with \[ \beta = \frac{e}{kT} \left( \frac{e}{4}\pi \varepsilon_0 \varepsilon d \right)^{1/2} \]

...3.8

Where, \( d \) is the film thickness, \( \varepsilon \) is the dielectric constant, \( \varepsilon_0 \) is
the permittivity of free space and \( e \) is the electronic charge. For zero field, this equation reduces to the previous one and the current density depends on the potential barrier at a constant temperature. Zero field current density does not vary with metal work function.

**3.3 (C) Thickness Dependence:**

A consequence of the phenomenon of carrier injection is the formation of a space charge due to their trapping in different trapping sites. Mutual repulsion between the individual carriers limits the total charge injected in the sample and the resulting current is said to be space charge limited current (SCLC). Certain requirements are to be fulfilled for such a flow of injected charge to take place and be detected. The first stringent condition is that the electrodes furnish ohmic contacts to the solid. Secondly the insulator should be relatively free from trapping defects and the contribution of thermally generated carriers be small.

The complete mathematical analysis of time independent SCLC in solids is so complex that no explicit expressions have yet been obtained relating the current and
voltage. Mott and Gurney (300) were the first to emphasize the importance of an injecting contact between a metal and an insulator and they provided an approximate expression relating the current, voltage and thickness in a trap free insulator. A slight modification of their theory results in the following relationship between current, voltage and thickness for a SCLC.

\[ J = \frac{9\theta \varepsilon \mu v^2}{8d^3} \]

... 3.9

In this equation \( \mu \) is the mobility of carriers, \( \varepsilon \) and \( d \) are the permittivity and thickness of the sample and \( \theta \) is the fraction of total carriers (all electrons above the Fermi level) which are free.

The above equation is a special case of the general scaling law for bulk space currents in a homogeneous medium which is:

\[ J \propto d (V/d^2)^n \]

... 3.10

Where \( n \) is a constant which need not necessarily be an integer. For example in the trap free insulator case, \( n=2 \), while for double injection, \( n=3 \) and for recombinative space-charge
injection, \( n = 1/2 \) (301, 302).

The introduction of deep trapping centres in the solid can result in a higher power dependence of current on voltage than the square law relation. It is evident that as more and more electrons are injected into a solid, the traps will gradually get filled up and eventually no more injected electrons are trapped. The first approximate treatment of this problem was by Lampert (262) who considered a model containing a set of defect states at a single discrete energy level.

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 (3.8). Thin films give more current. It is the evidence of space charge accumulation. Pulfray et al. (303) 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. Linearity of current density versus reciprocal thickness cube plots (fig. 3.4) is the ample proof of SCLC in iodine doped PS-matrix.
3.3 (d) Current Voltage Characteristics:

Current-voltage characteristics (fig. 3.5 and 3.6) are linear. When the charge carriers are supplied from the electrode and all of them are transported, Ohmic 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 curves (304, 305)

The plots of fig. 3.6 have been replotted in J-V\(\frac{1}{2}\) form in fig 3.9. The plots are seen to be linear. This is naturally taken as evidence of either Schottky or Poole-Frenkel mechanism. The theoretical and experimental values of constants in Schottky and Poole-Frenkel equations 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 mechanisms.

Scher and Montorll (278) recently advanced the phenomenolgical relationship for hopping conduction in which the voltage and temperature dependence of the mobility \(\mu\) is described
Fig. 3.9. Replots of fig 3.6 in J-V^{1/2} form. Temperature Noted on plot.
Fig. 3.10. Replots of fig 3.6 in J-10^{1/2}/T form Voltage
Noted on the plot
by the following equation

\[ \mu = \mu_0 \exp \left( \frac{a}{k} \right) (V^n - V_0^n) \left( \frac{1}{T} - \frac{1}{T_0} \right) \] ....3.11

Where \( \mu_0 \) is pre-exponential factor, \( a \), \( V_0 \) and \( T_0 \) are parameters and \( n \) approximates to 1/2. In Fig. 3.9 the square root voltage dependence of current is shown for temperatures 30, 40, 50, 60 and 70\(^o\)C. The straight lines when extended have a common intercept. The values of current and voltage at the intercept are found to be 7.4 \times 10^{-8} \text{ A} and 1190 \text{ V} respectively. The same results are replotted in Fig. 3.10 as a function of \( 10^3/T \) for voltages 18, 36, 63 and 99 \text{ V}. The straight lines when extended have a common intercept. The values of current temperature at the intercept are found to be 7.6 \times 10^{-8} \text{ A} and 92\(^o\)C respectively. The values of current obtained from the two intercepts are in very good agreement. Therefore the current and hence, the mobility is described by the above equation in iodine doped PS films.

3.3 (e) Effect of dopant concentration on temperature dependence of conductivity -

The interpretation of the temperature dependence of conductivity in 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 other are based on the analogy with some intrinsic conduction exists above inflection and impurity conductivity below inflection. Shishkin and Vershinina (306) and Warfield and Petree (307) connect the inflection with glass transition of the polymer. They explain the inflection at glass transition by change in environmental condition for ion mobility at the transition from the glassy state into a highly elastic one. Herwig and Jenckel (308) and Raddish (309) suppose that the inflection appears as a result of the superposition of polarization effects on the conductivity process at temperature below the glass transition temperature, at which the relaxation time becomes long. Adamec and Mateova (310) concluded that the inflection on $J(T)$ 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.

High activation (Fig. 3.6) arises from intrinsic conduction. The difference in activation energies is due to higher dissociation energy to form the carriers for intrinsic conduction. Similar results of doping have been reported for polyvinyl fluoride (311) and polystyrene (180). 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 iodine 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 the distribution of hopping energies and to describe alternative transport mechanisms such as multiple trapping and trap-controlled hopping (312-316), although these extensions of the theoretical concept will narrow the range of possible interpretation 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.

3.4 Conclusions:

The above discussion on electrical conduction in iodine doped PS films enable to draw the following conclusions.

1. The transient current decays according to t-b law before reaching a steady state. The observed magnitude of b and the
lack of thickness and electrode material dependence of transient current indicate carrier hopping process.

2. Electrode effect on current-voltage characteristics of the films indicates the Schottky thermionic emission of charge carriers.

3. Thickness variation on current voltage curve of doped PS reveals space charge build-up.

4. In low field regime Ohm’s law seems to be valid in iodine doped PS films.

5. At high field values, the linearity of current with square root of voltage indicated Schottky or Poole-Frenkel mechanism. But the poole-Frenkel mechanism is more logical because comparatively thick (20μ m) 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 value of current for iodine 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 $10^3/T$ at various voltages. This shows that the field and temperature dependence of mobility in the films can be described adequately according the equation.

$$\mu = \mu_o \exp \left( \frac{a}{k} (V^* - V^*o) (1/T - 1/T_o) \right)$$

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

8. Temperature dependence of conductivity of pure and iodine incorporated films reveals that doping of the PS matrix with iodine 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 iodine.

9. Iodine is a strong electron acceptor impurity. It forms charge transfer complexes (CTC) and so the conductivity is enhanced.

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