CHAPTER III

THERMALLY STIMULATED DISCHARGE CURRENT
3.1 INTRODUCTION

The electric polarization of the polymer originates from dipole orientation, migration of charge carriers over a microscopic distance, space charge effects and from surface charging. It is quite possible that one or more types of polarization mechanisms stated above are operative in bringing about the polarization in a polymer. Knowledge of specific polymer and the charging process often allows one to distinguish between these possibilities. Identification of polarization effects is also possible by comparing TSD measurements with electric data\(^1\). However, in making such comparisons, it should be borne in mind that the dielectric relaxations are measured in different ways. TSD typically is a non-isothermal measurement in which time and temperature are varied simultaneously, while dielectric measurements are traditionally done either at a constant frequency or at a constant temperature. The height and position of the relaxation peaks may therefore be quite different.

In polymers various types of molecular relaxations are possible\(^2\). The only motions possible at low temperatures are local motions of the molecular groups, e.g. rotation of the side groups (\(\beta\)-relaxation) or internal motions within side groups (\(\gamma\)-relaxation). At high temperatures, segments of the main chain become mobile. The main chains then become flexible so that the polymer softens and becomes rubbery. The temperature at which these conformational re-arrangements of the main chain segments set in, is therefore called the glass transition temperature.
In this chapter the theory of Thermally Stimulated Discharge Current (TSDC) for discrete as well as distributed relaxation processes is discussed. Also the theoretical details of charge transport processes in polymeric materials are given.

3.2 THEORY OF THERMALLY STIMULATED DISCHARGE CURRENT (TSD)

The TSD studies in polymers include discrete as well as the distributed relaxation processes. The discrete relaxation process is characterized by a particular value of relaxation time $T$ and activation energy $E$, whereas distributed relaxation process may have a distribution either in $T$ or in $E$ or in both $^3$. The generalized theory of TSD was developed by Gross$^4$, Perlman$^5,6$ Turnhout$^7$ and others$^8,9$ from the theory of ionic thermo-currents developed by Bucci et. al$^{10}$. This generalized theory is very much similar to that of thermoluminescence$^{11,12}$ or electrical glow$^{13,14}$.

3.2-1 THEORY OF TSD FOR DISCRETE RELAXATION PROCESS

In TSD technique, the sample is first polarized at a static field $E_P$, for a time $t$ and with temperature $T_P$. The sample is cooled down to room temperature $T_r$ and $T_P$ and is subsequently warmed up at a linear rate, $b^{15}$. The polarization build up at temperature $T_P$ can be described as

$$P(t) = P_0 \left[1 - \exp\left(-t/c\right)\right]$$  \hspace{1cm} (3.1)

where $P_0$ is the initial polarization formed at $E_P$ and $T_P$ and its value in the case of freely rotating dipoles is given by

$$P_0 = \left(N/\mu^2 E_P^3 kT_P\right)$$  \hspace{1cm} (3.2)

In eqn. (3.2) $N$ is the dipole concentration, $\mu$ is the dipole moment and $k$ is the Boltzmann's constant. The term $c$ in equ.
(3.1) is the relaxation time and the temperature variation of T can be represented by Arrhenius type equation.\(^{16}\)

\[ \tau(T) = \tau_0 \exp \left( \frac{E}{kT} \right) \quad \cdots \quad (3.3) \]

where \(\tau_0\) is the relaxation time at infinite temperature and \(E\) is the activation energy. Eqn. (3.1) can be rewritten as

\[ P(t) = P_0 \left[ 1 - \exp \left( - \int_0^t - \frac{dt}{\tau(t)} \right) \right] \quad \cdots \quad (3.4) \]

By substituting the temperature varying factor \(\tau(T)\) eqn. (3.4) becomes,

\[ P(t) = P_0 \left[ 1 - \exp \left( - \int_0^t \frac{\text{exp}(-E/kT)}{\tau_0} dt \right) \right] \quad \cdots \quad (3.5) \]

The discharge current is simply the rate of change of polarization

\[ I(t) = - \frac{dp(t)}{dt} \quad \cdots \quad (3.6) \]

The temperature of the sample is increased at a constant rate so that the following explicit relationship exists between temperature and time

\[ T = bt + T_0 \quad \cdots \quad (3.7) \]

where \(b = \frac{dT}{dt}\) is the heating rate and \(T_0\) is a constant.

Taking into account eqns (3.2), (3.3), (3.6) and (3.7) one gets an expression for TSD curve as

\[ I(T) = \frac{Nnu^2Ep}{3kT_T} \exp \left[ - \frac{E}{kT} - \frac{1}{bT_0} \int_0^T \exp \left( -\frac{E}{kT} \right) dt \right] \quad \cdots \quad (3.8) \]

where \(T_T\) is the room temperature at which the heating of the sample commences. According to eqn.(3.8) the current intensity at any temperature is directly proportional to the polarizing field \(E_p\).
In case of polymers containing trapped charges, it may be shown that under the conditions of uniform polarization, the expression for the discharge current versus temperature, arising from charges released from traps is more or less the same as eqn. (3.8) except for the constant factor prior to the exceptional term. The actual expression is given by 6

\[ I(T) = a' \exp \left[ - \frac{E}{kT} - b' \int_{T_0}^{T} \exp \left( - \frac{E}{kT} \right) dT \right] \]  

...(3.9)

where \( E \), in this case, is the trap depth and constants \( a' \) and \( b' \) are given as

\[ a' = \frac{(n_{to})^2 (\mu \tau)}{2 \epsilon d_{co}} \quad \text{and} \quad b' = \frac{2}{b_{co}} \]  

...(3.10)

where \( n_{to} \) is the initial charge density of traps, \( (\mu \tau) \) is the charge mobility life time product, \( e \) is the electronic charge, \( \sigma \) the depth of penetration of charge, \( \epsilon \) the dielectric constant and \( d \) is the thickness of the dielectric material. By making use of eqn (3.8) and (3.9) we can find the following:

(I) An expression of \( T_M \) at which the maximum of TSD current occurs, can be obtained by applying the condition \( dI(T)/dt = 0 \), which yields \( \tau_o \) as

\[ \tau_o = \frac{kT_M^2}{bE} \exp \left( \frac{E}{kT_M} \right) \]  

...(3.11)

and the corresponding relaxation time \( \tau_M \) is given as

\[ \tau_M = \frac{kT_M^2}{bE} \]  

...(3.12)

(II) The total charge released to the external circuit is given by

\[ Q = \int_{0}^{\infty} I(t) \, dt \]  

...(3.13)
(III) The low temperature tail of the distribution in eqn. (3.8) can be written as

\[ \ln I(T) = \text{Const.} \left( -\frac{E}{kT} \right) \]  \hspace{1cm} \ldots \ (3.14) 

Hence the activation energy \( E \) can be calculated from the semilogarithmic plots of \( \ln I(T) \) versus \( 1/T \).

for Bucci's graphical interaction method,

\[ T - 154.5^2 \]

\[ \ln I(T) = \ln \left[ \int_{t(t')} I(t') dt' \right] - \ln I(T), \quad = \ln \tau_0 + \frac{E}{kT} \ldots (3.15) \]

or \[ \ln I(T) = \ln \frac{Q_r}{I(T)} \ldots (3.16) \]

where \( Q_r \) is the remaining charge of the isolated peak and \( I(T) \) is the instantaneous current of the TSD peak at time \( t(T) \).

3.2-2 THEORY OF TSD FOR DISTRIBUTED RELAXATION PROCESSES

Distributed relaxation process either in relaxation times or in activation energies or in both have been observed in many polymers and the above described theory of discrete relaxation process is inadequate to describe such processes. A more generalised theory for dealing with distributed relaxation process can be derived by taking into account of Frohlich's\(^{17}\) bistable model of dipolar reorientation. Let there be \( nE \) \( dE \) dipoles in the energy range of \( E \) and \( E+dE \). The total dipole concentration is then given by

\[ N = \int_{E}^{\infty} n(E) dE \] \hspace{1cm} \ldots (3.17) 

The polarization is now a function of \( E \) and \( t \) follows the differential equation.

\[ \frac{dP(E,t)}{dt} + \frac{P(E,t) dE}{dE} = P_m(E) dE \] \hspace{1cm} \ldots (3.18) 

55
where $c$ is the relaxation time described in equation (3.3). $P_m(E)$ is the maximum polarization due to reorientation of the dipoles, i.e., polarization for $t \rightarrow \infty$ and is given as

$$P_m(E)dE = n(E)\left[\frac{E^2_{pP}}{3kT_P}\right] ... (3.19)$$

The general solution of the equation (3.18) can be written as

$$P(E,t) = f(E) \cdot \phi(t) ... (3.20)$$

where

$$f(E) = \frac{E^2_{pP}}{3kT_P} ; \quad \phi(t) = \exp\left[\int_0^t dt/c\right] ... (3.21)$$

for time $t = t_1$ up to which the isothermal polarization of the sample is carried out at $E_p$ and $T_p$ the solution is given by

$$P_1(E) dE = \frac{E^2_{pP}n(E)}{3kT_P} \left[1-\exp\left\{-t_1/c(E)\right\}\right] dE ... (3.22)$$

Since prior to TSD measurement the sample is kept shorted for time $t = t_2$, the polarization attained by the sample just before heating it for TSD measurements is given as

$$P_2(E) dE = P_1(E) dE \cdot \phi(t_2) ... (3.23)$$

The discharge current is simply the rate of change of polarization and the value of current in the case of distributed polarization is obtained by summing over the entire range of activation energy, i.e.

$$I = \int_{E=0}^{E=\infty} \left[\frac{P_2(E)/\phi(t)}{dE} dE \right] ... (3.24)$$

or

$$I = \int_{E=0}^{E=\infty} \left[\frac{P_2(E)/c \cdot \phi(t)}{dE} dE \right] ... (3.25)$$

by using equation (3.21) we have

$$\frac{d}{dt} [\phi(t)]^{-1} = -\frac{1}{c} \cdot [\phi(t)]^{-1}$$

56
\[ I = \int_{E=0}^{E=\infty} \frac{P_2(E)}{\tau} \exp \left( -\int_t^T \frac{dT}{\tau} \right) dE \quad \ldots \ldots (3.26) \]

The sample is heated at a constant heating rate \( b = \frac{dT}{dt} \), then the current density in the case of distributed polarization becomes,

\[ I = \int_{E=0}^{E=\infty} \frac{P_2(E)}{b \tau} \exp \left( -\int_t^T \frac{dT}{\tau} \right) dE \quad \ldots \ldots (3.27) \]

It can be seen that equation (3.27) is identical to eqn. (3.8) of discrete relaxation processes. Further, it has been shown that \( P_2(E) \, dE \) and \( n(E) \, dE \) are related by 8

\[ P_2(E) \, dE \propto \frac{n(E)}{E} \, dE \quad \ldots \ldots (3.28) \]

Using eqn. (3.28) the expression (3.27) takes the form

\[ I \propto \int_{E = E_{\text{min}}}^{E_{\text{max}}} \frac{n(E)}{E} \, g(E,T) \, dE \quad \ldots \ldots (3.29) \]

where \( g(E,T) = (b/\tau) \, \exp \left( -\int_t^T \frac{dT}{\tau} \right) \)

and \( E_{\text{min}}, E_{\text{max}} \) are determined by \( T_r \) and \( T \).

The value of \( g(E,T) \) can be approximately solved on the basis of theory suggested by Simmon et al. 19 on the distribution of electronic traps.

The current reaches its maximum at the temperature \( T_M \), which is related to \( E_M \) and \( g_0 \) by the equation

\[ K T_M^2 = b E_M c(T_M) = b E_M c_0 \exp(E_M/k T_M) \quad \ldots \ldots (3.30) \]

3.3 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.

3.3-1 EFFECT OF POLING TEMPERATURE (\(T_p\))

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\(^{20,21}\). 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.

3.3-2 EFFECT OF POLING FIELD (\(E_p\))

The distinction between uniform and non-uniform polarizations can be made with variation of poling field (\(E_p\)). For uniform polarizations, charge increases linearly\(^{22}\) while for non-uniform polarizations charge increases non-linearly\(^{23}\) 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 Frankel effect\(^{24}\) 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\textsuperscript{25}. This has been attributed to the lowering of barrier height of the charge traps with the increase in $E_p$. Shrivastava etal\textsuperscript{26} 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.

3.3-3 EFFECT OF POLING TIME ($t_p$)

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\textsuperscript{26}.

3.3-4 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\textsuperscript{26-30}. Both inorganic and organic doping agents have been used for this purpose.

Life and charge stability of polymer electrets increases with doping\textsuperscript{31}. 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 etal\textsuperscript{26}. 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\textsuperscript{32} which has been attributed to the formation of charge transfer complexes between dopant and the main molecular chain of polymer.
3.4 PRESENT AND LAST DECADE'S WORK

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, formation and aggregation of impurity vacancy complexes, phase transitions, photographic response of silver halides etc.

Studies on thermoelectrets started as early as in 1922 by Eguchi\textsuperscript{33} on Carnuba wax. Since then various dielectrics both plastic and ceramics have been studied extensively by different workers. Excellent reviews on this subject both theoretical and experimental have appeared in the literature\textsuperscript{34,35} Some of the work recently reported in literature on polymer thermoelectrets is briefly reviewed below to get a comprehensive picture of the present state of research on this subject.

Thermally stimulated discharge currents (TSDC) in carnuaba
wax electrets were studied by Perlman\textsuperscript{36} using a linear heating rate for various polarizing fields, temperatures, times and thicknesses of the sample. Three peaks were observed at 47, 59 and 69 C respectively. Microscopic displacement of ions with trapping was proposed as the possible mechanism for the TSDC.

Caserta and Serra\textsuperscript{37} have made simultaneous measurements of current-voltage characteristics, isothermal discharge currents and thermally stimulated discharge currents to determine the mechanism of formation of electrets in carnuba wax. Homocharge from the electrodes and hetero charge with the material are found to be responsible for TSDC.

The electret effect in shellac wax was investigated by thermally stimulated discharge current (TSDC) technique by Pillai et al\textsuperscript{38} prepared under different polarizing conditions. They observed only one peak for the TSDC spectra. They have attributed the TSDC spectra to the dipolar orientation and microscopic displacement of charges with trapping.

Jain et al\textsuperscript{39} studied thermally stimulated discharge currents in solution grown polyvinyl butyral films as a function of the polarization field (1750 to 25000 V/cm) and iodine dopant concentration. Polarized polyvinyl butyral films exhibited two glow discharge peak one at 350 K and the other at 430 K corresponding to activation energies of 0.19 and 0.53 eV respectively. It was observed that the first-peak disappeared at low polarizing fields (1750 V/cm). The second-peak was attributed to the depolarization of the aligned dipoles connected to the main chain whereas the first peak due to the local motion or
twisting of the side groups connected to main chain. On doping with iodine, both un-polarized films exhibited TSD currents. This is attributed to the formation of charge complexes.

Mahendru et al.\textsuperscript{40} studied thermally stimulated discharge currents in polyvinyl acetate thin films as a function of polarizing field (0-9 kV/cm) and thickness (1000-7000 Å). They reported three peaks at 326, 389 and 468 K. The peaks at 326 and 389 K were attributed to the motion of the side groups and the orientation of the dipoles of the main polymer chain respectively, whereas the peak at 368 K was related to the relaxation process which was due to the release of the trapped space charges.

Mahendru et al.\textsuperscript{41} studied electret effects in polyvinyl fluoride thin films. They observed only one peak in the TSDC spectra. The results of these studies were explained in terms of the disorientation of dipoles and/or the migration of charges over microscopic distances with trapping.

Thermally stimulated discharge currents from polyacrylonitrile were studied by Comstock et al.\textsuperscript{42}. Electrically polarized films of stretched and unstretched polyacrylonitrile was measured with the thermally stimulated discharge technique. Preferential orientation of nitrile side groups in polarized specimens was inferred from birefrigence and X-ray diffraction experiments but the contribution of observed persistent electrical polarization appeared to be small. The major contribution was found to be due to trapped space charges, some part of which was associated with residual solvent molecules. Small ordered regions within polyacrylonitrile were expected to
play a role in development of each contribution to the final persistent electrical polarization.

Thermo stimulated currents from poly-chlorotrifluoro-ethylene electrets were studied by Latour and Murphy\textsuperscript{43}. Thermostimulated current profiles were obtained for electrets of chlorotrifluoroe-ethylene poled under various conditions of field strengths, temperature and electrode contact. The principal current peak was located at 145 C for electrets poled at an elevated temperature (100-178 C) and at 125 C for electrets poled at room temperature (20 C). Increase in the poling field from 3 to 300 KV/cm produced continuous variations in the discharge current profile consistent with a transition from hetero-charge to homo-charge. Both hetero-charge and homo-charge appeared to be released simultaneously at the principal current peak. Similar curves were obtained for samples poled with corona.

Studies on electron traps in polyethylene terephthalate by thermally stimulated current and photostimulated detrapping current analysis was made by Takai et.al\textsuperscript{43}. A broad peak of TSDC was observed around -100 C at which the motion of the COO group was released. The apparent activation energy of the former peak was estimated at about 0.23 eV by the partial heating technique. On the other hand TSDC spectra at -185 C showed an existence of deep traps at 2.3 eV, which could be thermally cleaned by heating only upto -70\textdegree C. These facts clearly showed the effect of molecular motions on the carrier detrapping process during heating.

Thermally stimulated depolarization studies of EC polymer
electrets were made by Talwar and Sharma. Thermally stimulated depolarization (TSDC) of polyvinyl chloride thermoelectrets prepared at polarizing temperatures of 80, 100 and 120 °C with field strengths of 10, 12.5 and 14 kV/cm was studied. A sharp peak appeared at 97 °C and was associated with the activation energy of the trap at a depth of 0.44 ± 0.03 eV.

Miyairi and Yanagisawa studied thermally stimulated current in polyethylene terephthalate in the high temperature region. Electrical conduction in polyethylene terephthalate (PET) at high temperature was dominated by ionic process.

Thermally stimulated depolarization current (TSDC) of polypyromellitimide film was measured by Tanaka et al. in order to obtain knowledge of the charging and discharging mechanisms of carriers in polypyromellitimide. Two peaks were observed one at 173 °C, and the other at 50 °C in the dried film. The peak showed electrode material dependence also.

Kojima and Maeda studied thermally stimulated currents from polyethylene terephthalate due to injected charges. Thermally stimulated currents from polyethylene terephthalate (PET) electrets was investigated in the temperature range from --190 to +120 °C. Both dependences of TSC on electrode metals (Au, Al) and the polarity of an applied field were remarkable in the temperature range above -40 °C. The results indicated the electrons injected from the Al cathode greatly contributed to the TSC above 40 °C and that the TSCs below -40 °C for Al electrode and at all temperatures for Au electrodes were mainly induced by the depolarization of dipoles.
Bhargava and Srivastava\textsuperscript{48} investigated thermally stimulated discharge currents in polystyrene thin films grown by the solution growth technique. Films in the thickness range (2000-10000 Å) were polarized at 130 °C under the influence of different field strengths (2 - 10 KV/cm). Two relaxation peaks were observed at 77 °C and 112 °C. The occurrence of 112 °C peak was explained in terms of space charge injection from electrode and ionic effect. The occurrence of 77 °C peak was shown to be due to release of trapped charges due to local movements of polystyrene molecular chains.

TSDC study of pyrene picrate charge transfer complex was made by Srivastava and Mathur\textsuperscript{49}. They observed two peaks. The first peak was attributed to bulk polarization whereas the second peak due to Maxwell Wagner charging. Iqbal and Hogarth\textsuperscript{50} studied the trap depth in evaporated polypropylene from measurements of thermally stimulated currents. The occurrence of thermally stimulated currents in thin evaporated films of polypropylene was demonstrated and an analysis of the curve gave an electron trap depth of 0.33 eV in this material.

Jain et al.\textsuperscript{51} studied the charge storage properties in solution grown polyvinyl butyral (PVB) thin films as a function of poling field (2.50 x 10\textsuperscript{4} - 400 x 10\textsuperscript{6} V/m), temperature (333-398 K), time (5.40 x 10\textsuperscript{3} - 1.44 x 10\textsuperscript{4}) such thickness of the films (0.8 - 4.5 μm) and heating rates of depolarization (2.8 - 10 K/min) by the TSDC technique. Two relaxation processes one at 47 K and other at 423 K were observed having activation energies of 0.36 ± 0.02 eV and 0.66 ± 0.02 eV respectively. The peak at 347 K was found to be due to the deorientation of the aligned
dipoles involving the acetate/hydroxyl groups. The peak at 423 K was attributed to the release of trapped electrons/holes. The increase in the activation energy associated with the peak at 423 K and the shift in its position towards higher temperatures with increase in the poling time and temperature suggested the peak was associated with a distribution of relaxation times.

Srivastava et al.\textsuperscript{52} studied electrical polarization in polystyrene films of thickness 20 \( \mu \text{m} \) by measuring the TSDC at different polarizing fields, temperatures, and heating rates. One peak was observed at 150 C which was oriented by a change in the field. The occurrence of peak was due to a mechanism involving dipole orientation process.

Narasimha Rao and Narsingh Das\textsuperscript{53} studied the TSDC in polyacrylic acid polymer films. Polyacrylic acid films of thickness 15 \( \mu \text{m} \) were grown by the solution growth technique. Thermally stimulated discharge currents (TSDC) were studied on these polymer films is a function of polarizing field strength and polarizing temperature at a constant heating rate of 0.08 Ks\textsuperscript{-1} in all these studies, one TSDC peak was observed and the temperature corresponding to this peak was found to shift to higher temperatures as the polarizing temperature increases. But for given polarizing temperature, the temperature corresponding to the peak was independent of polarizing field strength. The activation energies and relaxation parameters were evaluated. The origin of the TSDC was attributed to the dipolar orientation process.
Narasimha Rao and Kalpalatha studied thermally stimulated discharge currents in polyvinyl pyrrolidone polymer films. Polyvinyl pyrrolidone films of thickness 17.6 μm were grown by the isothermal solution growth technique. Thermally stimulated discharge currents were studied on these films as a function of polarizing field strength and polarizing temperature at a constant rising rate of 0.14 KS⁻¹. In all these studies only one TSDC peak was observed and it was attributed to the space charge process.

Verma and Sinha studied TSDC in bakeline (polyphenol formaldehyde) thermolectrets. Ω and Ψ peaks were obtained for different poling temperatures and fields. Dou-Yol Kang et al. studied TSC in polypyromellitumide polyimide). They observed three peaks A, B and C. The C peak was shown to be created due to the polarization of ionic space charge which was measured as a function of forming time, forming temperature, forming voltage. Chand and Kumar studied the effect of doping of TSD relaxation in polyvinylidene fluoride (PVF₂) films. TSD spectra of both pure and methylene blue dye doped PVF₂ films showed two relaxation peaks; however, in the latter case the peak positions, peak currents and charges depend strongly on the concentration of the dopant. TSC peaks in undoped poly (p-phenylene vinylene) were observed by Onoda et al. Akutemy and Hirch reported TSD and TSC measurements on PVK films over the temperature range 85-530 K and the corresponding activation energy was deduced to be 0.55 ± 0.05 eV. Thermally stimulated depolarization current (TSDC) spectra of polychlorotrifluoroethylene with relatively low crystallinity were measured by Shimizu and Nakayama. These TSDC
peaks were observed in the range of 85 to 400 K.

Narasimha Rao and Subba Rao\textsuperscript{61} studied the thermally stimulated depolarization currents in polyacrylamide polymer films between polarizing field strengths $0.48 \times 10^6 \text{ Vm}^{-1}$ to $24.1 \times 10^6 \text{ Vm}^{-1}$ and temperature range from 305 to 368 K for different heating rates and polarizing times. The spectra showed only one peak at low polarization temperatures whereas two peaks at high polarization temperatures. The origin of TSDC peak I was attributed to the dipolar orientation and peak II was attributed to the space charge polarization with the injection of charge carriers from the electrode and subsequent trapping and detrapping. Thermally stimulated discharge current from various pure, doped polymers and polyblend were studied by Khare et al\textsuperscript{62-80}

3.5 EVALUATION OF RELAXATION PARAMETERS

The value of relaxation parameters such as activation energy and relaxation time ($\tau$) can be evaluated using different techniques as discussed below:

3.5.1 EVALUATION OF RELAXATION PARAMETERS USING TSD

Several methods have been used for the evaluation of activation energy and other relaxation parameters of the different TSD peaks\textsuperscript{81-86}. In the present studies, however, the initial rise method and Bucci's whole curve method have been used for the evaluation of these parameters.

(I) INITIAL RISE METHOD

The low temperature part of the current as defined by eqn. (3.14) in Sec. 3.1 represents the initial rise portion of the relaxation peak occurring in the TSD spectra. Therefore, if a
semilogarithmic graph of 1(T) versus 1/T is plotted, a straight line is obtained, the slope of which gives the value of activation energy (E). Knowing the value of E, peak temperature (T_M) of the TSD peak and the heating rate (b) the values of other relaxation parameters such as g_o, g_M and g_300 can be evaluated by using eqns. (3.11), (3.12) and (3.1) respectively.

(II) BUCCI'S WHOLE CURVE METHOD

In this method, whole of the TSD curve is taken into consideration for evaluating the activation energy and other relaxation parameters. As given in Sec. 3.1, when a semilogarithmic graph of Q_r/I(T) against 1/T is plotted, where Q_r is the remaining charge and I(T), the current at a particular temperature, a straight line is obtained. The slope of this graph gives the activation energy and its intercept on the log Q_r/I(T) axis yields the value of relaxation time (τ_o).

The total charge (Q) liberated in a particular relaxation process is measured by the area under the curve. Then the charge upto a certain arbitrarily chosen temperature is calculated in a similar way by measuring the area under that portion of the curve. The difference of these two charges gives the value of remaining charge (Q_r). Such values of Q_r are estimated at different temperatures. Knowing the values of I(T) at different temperatures, relaxation parameters were evaluated from the graph of log Q_r/I(T) versus 1/T.

3.6 PRESENT EXPERIMENTAL TECHNIQUE (TSDC MEASUREMENT)

In order to heat the sample, a measuring cell with desired specifications was fabricated. A copper cavity was taken and a heating element was bound on both sides of the cavity with the
help of an asbestos rope. This cavity was then fixed at the centre of the aluminium box (12x12x12 cm$^3$). The extended part of the cavity remained out of the box and was used for earthing. To achieve an insulation between the cavity and the box, the empty space of the box surrounding the cavity was filled with asbestos powder. The terminals of the heating element were brought out on the top of the box and electrical contacts were made by shielding wires through BNC connectors having teflon insulation.

The schematic diagram of the experimental set-up for the measurement of TSD from the poled sample is shown in Fig. 3.0. The poled sample clamped between two mica sheets, was placed inside a specially designed measuring cell. Heating was done by means of a variac controlled resistance wound heating element. This element gave almost linear rate of temperature increase which could be varied over the range 1-15 K/min. The temperature of the sample was measured by means of a calibrated copper constantan thermocouple and the thermocouple emf was fed to the X-axis of the recorder (Riken Densi, Japan, Model F-42 CP). The current released from the sample to the external circuit was recorded as a function of temperature fed through a Keithely Electrometer.

3.6-1 PRESENT EXPERIMENTAL DETAILS

The present investigation has been carried out on the solution grown EC, PMMA and their blend samples. The measurements were made with samples charged with fields of well made with samples at temperature with fields of for each measurements a fresh sample was taken.
Fig. 3.1: Time-temperature and time-field scheme, showing the relevant times, temperatures and fields, during formation, storage and TSD of electrets.
3.7 RESULT AND DISCUSSION (TSDC)

The polarization in a thermally charged specimen may arise due to various mechanisms, the important amongst these are orientational or dipolar polarization, the translational or space charge polarization and interfacial polarization. Several distinct dielectric and space charge relaxations are usually present in a polarized specimen. This multiplicity is seen most easily in the study of depolarization current as a function of temperature. As the temperature rises molecular mobilities of various types become successively energised exhibiting their characteristic peaks during the thermally stimulated depolarization cycle.

Figure 3.1 shows thermally stimulated discharge current (TSDC) thermograms of pure ethyl cellulose (EC) films polarized with field of 10 kV/cm at temperature 30, 40, 60 and 80 °C respectively. The curves exhibit two peaks. The first peak was located around 75±5 °C. The second peak was centred around 112±2 °C. On increasing the polarizing temperature magnitude of current increases. Figure 3.2 exhibits TSDC thermograms of EC films polarized with higher poling field (i.e. 100 kV/cm) Similar behaviour has been found as described for figure 3.1. With increase in poling field current value has been found to be little higher.

The thermally stimulated discharge current (TSDC) thermograms for the EC films polarized with various fields (i.e. 10, 25, 50 and 100 kV/cm) at temperature 30 and 80 °C have been shown in figures 3.3 and 3.4 respectively. All the thermograms exhibit two peaks located at temperatures between 70-80 and 115-125 °C respectively.

71
FIG 3.1- T S D C Spectra of EO Films at different polarizing temperatures (Tp)

FIG-INITIAL RISE PLOTS OF TSDC SPECTRA
FIG. 9.2 - T S D C Spectra of EC Films at different polarizing temperatures (T_p)

FIG: INITIAL RISE PLOTS OF TSCD SPECTRA

Ep=100kV/CM.
FIG. 3.3 - T S D C Spectra of EC Films at different polarizing fields (E_p)

FIG. - INITIALRISE PLOTS OF TSDC SPECTRA
FIG. 3.4 - T S D O Spectra of EO Films at different polarizing Fields (E_p)

FIG. - INITIAL RISE PLOTS OF TSDO SPECTRA
In the case of $T_p=30$°C, the depolarization current was found to correspond always to hetero-charge for all the poling field. It is observed that for samples polarized with lower fields at higher temperature ($80$°C) initially the current is anomalous (current flowing in the same direction as that of the charging current) over a certain temperature range in the early part of the thermogram, however, for other cases the observed current is normal (current has been found to be of the polarity opposite to that of the charging current). So far as the effect of poling field on the peak, characteristics of the observed peaks are concerned it is observed that the peak current of both the peaks have been found to increase and position of both the peaks shifted towards higher temperature with rise in poling field value.

TSDC thermogram of PMMA polarized with field ($10, 25, 50$ and $100$ kV/cm) have been shown in figures 3.5 - 3.8 respectively. The behaviour of all the thermograms for PMMA films have been found to be very similar to those observed for pure EC samples. The main characteristics of the thermograms are-

(1) all the thermograms figures (3.5-3.8) consists of to well-defined peaks located at lower and higher temperature region.

(2) with the increase in the poling field and poling temperature the depolarising current increase, and position of peaks tends to shift towards higher temperature side.

The charge originated in TSRC measurements due to dipole orientation or trapping of space charge in defect or
FIG: 3.5 - T S D C Spectra of PMMA Films at different polarizing temperatures (Tp)

FIG: INITIAL RISE PLOTS OF TSDC SPECTRA
FIG:3.6-T S D C Spectra of PMMA Films at different polarizing temperatures (Tp)

FIG:- INITIAL RISE PLOTS OF TSDC SPECTRA
FIG: 3.7 - T S D C Spectra of PMMAFilms at different polarizing fields (Ep)

7 - INITIAL RISE PLOTS OF TSDC SPECTRA OF
Fig. 3.6 - T & D C Spectra of PMMA Films at different polarizing fields (Ep)

Fig. - Initial Rise Plots of TSDO Spectra
dislocation sites is known to give rise to a uniform polarization which is a heterocharge on the other hand, space charge build up by migration of ions over microscopic distances gives a nonuniform heterocharge and trapped injected space charge results in a nonuniform home or hetero charge depending upon the work function of the metal electrodes.

PMMA is an amorphous polymer strongly polar in character. The TSDC thermograms of this polymer are reported to be characterized by a peak in the glass transition region (90-105 C) and another space charge peak in the higher temperature range 130 - 140 C. At lower temperature 30-40 C one more subsidiary relaxation associated with the rotation of side groups called B relaxation is also well documented in the literature.

Under the influence of electric field the irregularly distributed dipoles of side chains are mobilized / oriented in a certain direction. Thermal activation at a constant rate causes the release of charges due to their mobilization giving a peak at the site of maximum release of charge. The increase in current magnitude with field may be attributed to the increase in mobility of the charge carriers.

Ethyl cellulose is a weakly polar polymer. It's main chain is C-O-C but they differ in electronegative nature from the main chain. The electronegativity of the main chain bond arises from the difference in the electronegativity of carbon and oxygen atoms, however, the electronegativity of the side groups arises from the difference in electronegativity of H₂C=O-C₂H₅ and C-O-C₂H₅ bonds in the side chain. The slight polar nature of the polymer is due to the difference in electronegativity of the main
chain and the side groups.

Out of the two well resolved peaks appeared in TSDC thermogram for EC samples, first peak correspond to the orientation of strongly attached ethoxy group in the side chain. The relaxation processes has been found to be associated with an activation energy of 0.20 eV. The dipoler relaxation is maximum around the glass transition temperature which is reported\textsuperscript{87} to be 60-75 C. The shifting of first peak over a particular range and the increase in the broadness with increasing value of poling field indicates, that at low field the polarization is not saturated and increasing value of polarizing field leads to be completion of dipolar polarization. The peak current of high temperature peak (i.e. 110 C) has also been found to increase with increasing value of poling field. Activation energy indicates that this peak may be a space charge peak arising from the relaxation of various electronic charge trapped in energy aticcey and spatially distributed trapping side in the polymer.

PMMA has polar side group COOCH\textsubscript{3}, which can rotate with and without the main chain segments C-CH\textsubscript{2}. Three peaks have been reported\textsuperscript{88} in pure PMMA known as B, O and C peaks. Since the experiments in the present study have been done at higher temperature, the B-peak (associated with the motion of carbonyl side group ) has not been observed. The TSDC thermograms recorded in the present investigation were charactrized with two peaks at 95 and 116 C respectively. The lower temperature peak observed at 95 C in the present investigation can be considered to arise due to relaxation process associated with the microbrownian motion
of the main chain segments near the \( T_g \) of the polymer. Presence of dipolar motions in PMMA around \( T_g \) has already been reported. From the various curves showing the effect of polarizing temperature it is evident that the peak current position for the low temperature peak shifts towards the higher temperature with increase in the polarizing temperature. Further, the peak height increases almost linearly with an increase in the forming field. The total charge released associated with this peak was also found to increase linearly with the forming field. These characteristics further support our argument that the low temperature peak observed in the present investigation may be considered to arise due to dipolar motions in PMMA with distribution in relaxation frequencies. As the temperature is increased more and more dipoles are rendered free, which are oriented by the field. Hence the peak position must shift towards higher temperature side as is observed in the present case.

The variation of the total charge released with the polarizing field for the second peak, observed at a higher temperature is shown in fig 3.21 and 3.22. The total charge was found to increase nonlinearly with the polarizing field.

The three blends samples prepared were 90:10, 93:7 and 95:5 by weight proportion of ethyl cellulose and PMMA, designated as \( P_1, P_2 \) and \( P_3 \) respectively. Figures (3.9-3.20) show the TSDC thermogram for \( P_1, P_2 \) and \( P_3 \) blends. The effect of polarizing fields and polarizing temperatures on the TSDC characteristics of these blend samples is as under -
FIGURE 3.21: PEAK CURRENT VS POLING FIELD
3.21: FOR PURE EC & PMMA AT DIFFERENT TEMPERATURES FOR (4) PEAK
1. Effect of polarizing field :-

The TSDC spectra for the specimen polarized with fields of 10, 25, 50 and 100 kV/cm at fixed temperature of 30 and 80 C are illustrated in figures (3.11, 3.12; 3.15, 3.16; 3.19, 3.20). The following inferences can be obtained from these figures.

(A) $P_1$ sample (EC: PMMA=90:10)

1. The specimen polarized at 30 C show anomalous current peak at 80 and $115 \pm 5$ C for all the poling fields. Initially the current observed is normal over a certain temperature range and becomes anomalous during the later part of the cycle.

2. The specimen polarized at 80 C show anomalous peak for the various poling fields. Initially current observed with the polarity opposite to that of the charging current and becomes anomalous for the remaining temperature range. For the sample polarized with a field of 50 kV/cm shows a decreasing anomalous current behavior, which becomes normal passing through a maximum with increasing temperature and finally becomes anomalous. For entire temperature range, the sample polarized with 100 kV/cm the current flows in the anomalous direction.

(B) $P_2$ samples (EC: PMMA-93:7)

1. The sample polarized with higher fields (i.e. 50 and 100 kV/cm) shows an anomalous current behavior over the entire cycle. However for samples poled with 10 and 25 kV/cm initially a normal current was found which becomes anomalous with increasing temperature.

2. The specimen polarized at 80 C show a current following in the anomalous sense through for the polarizing fields of 10, 25, 50 and 100 kV/cm. Anomalous current behavior has been observed in the initial and later part of the cycle for 25 kV/cm. The
location of the peaks were observed at 65±5°C and 115±5°C respectively for all the samples. It is evident from various thermograms that with increasing fields the magnitude of the current increases.

3. With increasing PMMA content in the EC:PMMA matrix, the current has been found to increase. All the thermogram clearly indicates the coexistence of hetero and homo charges.

(C) P₃ samples (EC:PMMA-95:5)

1. The specimen polarized with the fields 10, 25 and 50 kV/cm show a normal current behavior which in the later part of the TSD current becomes anomalous. For the fields of 50 and 100 kV/cm current again changes sign and finally becomes normal for all the fields. We have observed two anomalous current peaks.

2. A very similar behavior for the specimen polarized with the fields (i.e. 10, 25, 50 and 100 kV/cm) at 80°C has been observed as that of samples polarized at 30°C.

Effect of Polarizing Temperature :-

Figures (3.9, 3.10; 3.13, 3.14; 3.17, 3.18) show the typical thermograms for the samples polarized at 30, 40, 60 and 80°C with poling field of 10 and 100 kV/cm. The curve are characterized with two homocharge peaks located in the temperature range 65±5 and 115±5°C respectively.

(A) P₄ samples :-

Figures 3.9 and 3.10 represent the TSDC thermogram for the samples polarized with the field of 10 and 100 kV/cm. The initial current for the sample polarized at 30 and 40°C corresponds to normal current. The current changes sign and
becomes anomalous Similar behaviour has been observed for the sample poled with 100 kV/cm. The magnitude of current increases with polarizing temperature and field.

(B) $P_2$ samples :-

The TSDC thermograms for samples polarized with the field of 10 and 100 kV/cm are shown in figures 3.13 and 3.14 respectively. The sample poled at 30 C with 10 kV/cm show an initial normal current and becomes positive at 45 C. After giving two anomalous peaks finally it again becomes normal in the latter part of the cycle, however, for the samples poled at 60 and 80 C normal behaviour in the entire cycle along with two well resolved peaks has been observed. The thermograms for the samples poled with 100 kV/cm at temperature 30, 40 and 80 C are characterized with two peaks and the current corresponds to homocharge. With increasing poling temperature the magnitude of current increases.

$P_3$ samples :-

The curves for the sample polarized with fields of 10 and 100 kV/cm are shown in 3.17 and 3.18 respectively. In the case of samples poled with 10 kV/cm at 40 and 60 C current initially starts with negative polarity, changes sign at 40 C to exhibit peaks at 70 and 120 C and finally becomes normal. However, for the temperatures 30 and 80 C no change of sign in the polarity of current has been found. The samples poled with 100 kV/cm at 30 C, current starts with negative polarity and changes sign at 45 C and remains positive for the rest of the TSDC run. However samples poled at 40, 60 and 80 C exhibit two well resolved anomalous peaks at 60 and 100 C.
It is evident from the above summerized results that the magnitude of current has been influenced with the polarizing temperature, polarizing field and blend contents. With increase in all these factors an increase in current has been observed.

The classical theory of Gubkin Perlman and others, for the decay of charge of an electret, assumes the superposition of homocharge and heterocharge. Homocharge is the space charge consisting of ions and electrons and produced by the discharge in air gap between poling electrode and samples, Hetro charge on the other hand, is volume charge produced by either the rotation of dipoles or the separation of ions. Since the total charge is the sum of homocharge and heterocharge, then if the observed TSDC is due to dipole disorientation or ion displacement during heating process, the sign of the discharge current is expected to be of opposite polarity to that of the charging current. On the other hand, if it is due to dissipation of space charges, the sign of the TSDC is expected to be the same as charging current or positive in polarity.

In the present case TSDC's of both polarities have been observed depending upon the forming conditions. This experimental observation, in the first instance, indicates that in the present case the mechanisms leading to heterocharge formation along with one or more of those leading to homocharge formation are contributing to the net polarization.

The TSDC's for the samples polarized at low temperature with low fields have been observed to be negative. This indicates that the major contribution to the polarization should be
due to the dipole orientation or it may be Maxwell - Wagner type polarization. The TSD current of positive polarity for the samples polarized at higher temperatures with higher fields indicates that the mechanisms resulting in homocharge formation dominate those leading to heterocharge formation under high polarization temperatures and high field conditions.

All polymers are known to contain excess charges inherently introduced during synthesis. The motion of these excess charges under space charge limited drift and diffusion also generates a discharge current opposite to the charging current.

The existence of homocharge in the present investigation, particularly, in the case of the samples polarized at high temperatures and high forming fields indicates that the electrets contain an anomalous amount of space charges. A dielectric never insulates perfectly, particularly not at high temperatures, when an increasing number of thermal carriers are generated. During polarization these carriers will move under the applied field and when the dielectric is cooled, some of them will be trapped. Existence of various types of traps in polymers is well documented. Owing to this process, thermally formed electrets usually contain a space charge polarization.

Space charges can also be injected from the electrodes, especially, at high field strengths. The decay of such space charges during depolarization results in a current that corresponds to homocharge. In the present investigation electrets formed at high temperatures and with the high polarizing fields show a current that corresponds to homocharge for the entire TSDC cycle. Thus, it can be safely concluded that a considerable
# PURE EC

## 1. POLING FIELD (Ep = 100 KV/cm)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>POLARIZ TEMP.</th>
<th>PEAK TEMPERATURE</th>
<th>PEAK CURRENT (A)</th>
<th>ACTIVATION ENERGY (ev)</th>
<th>CHARGE RELEASED (Coul)</th>
<th>RELAXATION TIME (To)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tp – C Peak I</td>
<td>Peak II</td>
<td>Peak I Peak II</td>
<td>1st 2nd</td>
<td>1st 2nd</td>
<td>1st 2nd</td>
</tr>
<tr>
<td>1.</td>
<td>30 80</td>
<td>110</td>
<td>7.6 15.6</td>
<td>0.15 0.33</td>
<td>6.781 3.52</td>
<td>6.88 3.98</td>
</tr>
<tr>
<td>2.</td>
<td>40 80</td>
<td>110</td>
<td>10.6 18</td>
<td>0.16 0.30</td>
<td>8.512 3.874</td>
<td>7.32 4.78</td>
</tr>
<tr>
<td>3.</td>
<td>60 80</td>
<td>110</td>
<td>12.8 21</td>
<td>0.14 0.31</td>
<td>8.997 7.971</td>
<td>7.79 4.98</td>
</tr>
<tr>
<td>4.</td>
<td>80</td>
<td>110</td>
<td>22.8</td>
<td>0.17 0.32</td>
<td>9.114 10.24</td>
<td>8.72 5.64</td>
</tr>
</tbody>
</table>

## 2. POLING FIELD (Ep = 10 KV/cm)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>POLARIZ TEMP.</th>
<th>PEAK TEMPERATURE</th>
<th>PEAK CURRENT (A)</th>
<th>ACTIVATION ENERGY (ev)</th>
<th>CHARGE RELEASED (Coul)</th>
<th>RELAXATION TIME (To)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tp – C Peak I</td>
<td>Peak II</td>
<td>Peak I Peak II</td>
<td>1st 2nd</td>
<td>1st 2nd</td>
<td>1st 2nd</td>
</tr>
<tr>
<td>1.</td>
<td>30 70</td>
<td>110</td>
<td>11.4 15.1</td>
<td>0.14 0.28</td>
<td>8.125 4.456</td>
<td>6.93 4.88</td>
</tr>
<tr>
<td>2.</td>
<td>40 70</td>
<td>110</td>
<td>12.2 15.8</td>
<td>0.15 0.29</td>
<td>8.877 4.878</td>
<td>7.77 5.012</td>
</tr>
<tr>
<td>3.</td>
<td>60 70</td>
<td>110</td>
<td>13.1 16.9</td>
<td>0.17 0.27</td>
<td>9.123 5.113</td>
<td>7.82 5.08</td>
</tr>
<tr>
<td>4.</td>
<td>80 70</td>
<td>110</td>
<td>14.2 17.7</td>
<td>0.16 0.31</td>
<td>9.997 5.224</td>
<td>9.62 5.43</td>
</tr>
</tbody>
</table>

## 3. POLARIZING TEMPERATURE (Tp = 80 C)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>POLING FIELD(Ep)</th>
<th>PEAK TEMPERATURE</th>
<th>PEAK CURRENT (A)</th>
<th>ACTIVATION ENERGY (ev)</th>
<th>CHARGE RELEASED (Coul)</th>
<th>RELAXATION TIME (To)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KV/cm Peak I Peak II Peak I Peak II 1st 2nd</td>
<td>1st 2nd</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>10 70 110</td>
<td>10.3 17.4</td>
<td>0.17 0.29</td>
<td>7.875 5.342</td>
<td>7.10 4.32</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>25 70 110</td>
<td>12.6 19.8</td>
<td>0.18 0.31</td>
<td>8.617 6.732</td>
<td>7.20 4.72</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>50 75 110</td>
<td>14.2 22</td>
<td>0.19 0.32</td>
<td>9.772 7.432</td>
<td>7.60 5.09</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>100 75 110</td>
<td>15 23</td>
<td>0.16 0.33</td>
<td>10.13 7.777</td>
<td>7.73 5.35</td>
<td></td>
</tr>
</tbody>
</table>

## 4. POLARIZING TEMPERATURE (Tp = 30 C)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>POLING FIELD(Ep)</th>
<th>PEAK TEMPERATURE</th>
<th>PEAK CURRENT (A)</th>
<th>ACTIVATION ENERGY (ev)</th>
<th>CHARGE RELEASED (Coul)</th>
<th>RELAXATION TIME (To)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KV/cm Peak I Peak II Peak I Peak II 1st 2nd</td>
<td>1st 2nd</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>10 70 130</td>
<td>11.2 18.4</td>
<td>0.15 0.28</td>
<td>8.347 4.357</td>
<td>4.28 2.98</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>25 70 130</td>
<td>16.2 22.6</td>
<td>0.17 0.33</td>
<td>8.925 4.667</td>
<td>4.57 3.04</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>50 70 130</td>
<td>18 24.2</td>
<td>0.18 0.34</td>
<td>9.111 4.777</td>
<td>4.98 3.07</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>100 70 130</td>
<td>19.8 26.8</td>
<td>0.20 0.30</td>
<td>9.907 4.887</td>
<td>5.36 3.14</td>
<td></td>
</tr>
</tbody>
</table>

Table - 3.1
# PURE PMMA

## 1. POLING FIELD (Ep = 100 KV/cm)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>POLARIZ. TEMP. (°C)</th>
<th>PEAK TEMPERATURE</th>
<th>PEAK CURRENT (A)</th>
<th>ACTIVATION ENERGY (eV)</th>
<th>CHARGE RELEASED (Coul)</th>
<th>RELAXATION TIME (To)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tp = C</td>
<td>Peak I</td>
<td>Peak II</td>
<td>Peak I</td>
<td>Peak II</td>
<td>1st</td>
</tr>
<tr>
<td>1.</td>
<td>30</td>
<td>90</td>
<td>120</td>
<td>5.8</td>
<td>8.0</td>
<td>0.17</td>
</tr>
<tr>
<td>2.</td>
<td>40</td>
<td>90</td>
<td>130</td>
<td>7.0</td>
<td>10.0</td>
<td>0.16</td>
</tr>
<tr>
<td>3.</td>
<td>60</td>
<td>90</td>
<td>120</td>
<td>8.1</td>
<td>10.4</td>
<td>0.18</td>
</tr>
<tr>
<td>4.</td>
<td>80</td>
<td>90</td>
<td>120</td>
<td>8.7</td>
<td>11.1</td>
<td>0.19</td>
</tr>
</tbody>
</table>

## 2. POLING FIELD (Ep = 10 KV/cm)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>POLARIZ. TEMP. (°C)</th>
<th>PEAK TEMPERATURE</th>
<th>PEAK CURRENT (A)</th>
<th>ACTIVATION ENERGY (eV)</th>
<th>CHARGE RELEASED (Coul)</th>
<th>RELAXATION TIME (To)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tp = C</td>
<td>Peak I</td>
<td>Peak II</td>
<td>Peak I</td>
<td>Peak II</td>
<td>1st</td>
</tr>
<tr>
<td>1.</td>
<td>30</td>
<td>80</td>
<td>110</td>
<td>11</td>
<td>14.2</td>
<td>0.16</td>
</tr>
<tr>
<td>2.</td>
<td>40</td>
<td>80</td>
<td>110</td>
<td>12</td>
<td>15.0</td>
<td>0.15</td>
</tr>
<tr>
<td>3.</td>
<td>60</td>
<td>80</td>
<td>110</td>
<td>12.8</td>
<td>15.6</td>
<td>0.17</td>
</tr>
<tr>
<td>4.</td>
<td>80</td>
<td>80</td>
<td>120</td>
<td>13.5</td>
<td>16.3</td>
<td>0.18</td>
</tr>
</tbody>
</table>

## 3. POLARIZING TEMPERATURE (Tp = 80°C)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>POLING FIELD (Ep)</th>
<th>PEAK TEMPERATURE</th>
<th>PEAK CURRENT (A)</th>
<th>ACTIVATION ENERGY (eV)</th>
<th>CHARGE RELEASED (Coul)</th>
<th>RELAXATION TIME (To)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KV/cm</td>
<td>Peak I</td>
<td>Peak II</td>
<td>Peak I</td>
<td>Peak II</td>
<td>1st</td>
</tr>
<tr>
<td>1.</td>
<td>10</td>
<td>70</td>
<td>100</td>
<td>4.2</td>
<td>6.8</td>
<td>0.21</td>
</tr>
<tr>
<td>2.</td>
<td>25</td>
<td>70</td>
<td>100</td>
<td>4.8</td>
<td>8.0</td>
<td>0.22</td>
</tr>
<tr>
<td>3.</td>
<td>50</td>
<td>70</td>
<td>100</td>
<td>5.6</td>
<td>8.9</td>
<td>0.23</td>
</tr>
<tr>
<td>4.</td>
<td>100</td>
<td>70</td>
<td>100</td>
<td>6.3</td>
<td>9.8</td>
<td>0.24</td>
</tr>
</tbody>
</table>

## 4. POLARIZING TEMPERATURE (Tp = 30°C)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>POLING FIELD (Ep)</th>
<th>PEAK TEMPERATURE</th>
<th>PEAK CURRENT (A)</th>
<th>ACTIVATION ENERGY (eV)</th>
<th>CHARGE RELEASED (Coul)</th>
<th>RELAXATION TIME (To)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KV/cm</td>
<td>Peak I</td>
<td>Peak II</td>
<td>Peak I</td>
<td>Peak II</td>
<td>1st</td>
</tr>
<tr>
<td>1.</td>
<td>10</td>
<td>70</td>
<td>120</td>
<td>11.4</td>
<td>14.5</td>
<td>0.20</td>
</tr>
<tr>
<td>2.</td>
<td>25</td>
<td>70</td>
<td>120</td>
<td>12.4</td>
<td>15.5</td>
<td>0.18</td>
</tr>
<tr>
<td>3.</td>
<td>50</td>
<td>70</td>
<td>120</td>
<td>13.3</td>
<td>17.0</td>
<td>0.19</td>
</tr>
<tr>
<td>4.</td>
<td>100</td>
<td>70</td>
<td>120</td>
<td>14.2</td>
<td>17.7</td>
<td>0.21</td>
</tr>
</tbody>
</table>
## POLY BLEND SAMPLES (P1)

### 1. POLING FIELD (Ep = 100 KV/cm)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>POLARIZ. TEMP.</th>
<th>PEAK TEMPERATURE</th>
<th>PEAK CURRENT (A)</th>
<th>ACTIVATION ENERGY (ev)</th>
<th>CHARGE RELEASED (Coul)</th>
<th>RELAXATION TIME (To)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tp - C</td>
<td>Peak I</td>
<td>Peak II</td>
<td>Peak I</td>
<td>Peak II</td>
<td>1st</td>
</tr>
<tr>
<td>1.</td>
<td>30</td>
<td>70</td>
<td>110</td>
<td>12.2</td>
<td>17</td>
<td>0.15</td>
</tr>
<tr>
<td>2.</td>
<td>40</td>
<td>70</td>
<td>110</td>
<td>14.8</td>
<td>19.4</td>
<td>0.17</td>
</tr>
<tr>
<td>3.</td>
<td>60</td>
<td>70</td>
<td>110</td>
<td>15.8</td>
<td>26.2</td>
<td>0.16</td>
</tr>
<tr>
<td>4.</td>
<td>80</td>
<td>80</td>
<td>110</td>
<td>18.7</td>
<td>30.6</td>
<td>0.18</td>
</tr>
</tbody>
</table>

### 2. POLING FIELD (Ep = 10 KV/cm)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>POLARIZ. TEMP.</th>
<th>PEAK TEMPERATURE</th>
<th>PEAK CURRENT (A)</th>
<th>ACTIVATION ENERGY (ev)</th>
<th>CHARGE RELEASED (Coul)</th>
<th>RELAXATION TIME (To)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tp - C</td>
<td>Peak I</td>
<td>Peak II</td>
<td>Peak I</td>
<td>Peak II</td>
<td>1st</td>
</tr>
<tr>
<td>1.</td>
<td>30</td>
<td>60</td>
<td>120</td>
<td>4.3</td>
<td>8.1</td>
<td>0.17</td>
</tr>
<tr>
<td>2.</td>
<td>40</td>
<td>60</td>
<td>120</td>
<td>4.8</td>
<td>9.0</td>
<td>0.16</td>
</tr>
<tr>
<td>3.</td>
<td>60</td>
<td>60</td>
<td>120</td>
<td>5.5</td>
<td>9.5</td>
<td>0.18</td>
</tr>
<tr>
<td>4.</td>
<td>80</td>
<td>60</td>
<td>120</td>
<td>6.4</td>
<td>10.2</td>
<td>0.20</td>
</tr>
</tbody>
</table>

### 3. POLARIZING TEMPERATURE (Tp = 80 C)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>POLING FIELD (Ep)</th>
<th>PEAK TEMPERATURE</th>
<th>PEAK CURRENT (A)</th>
<th>ACTIVATION ENERGY (ev)</th>
<th>CHARGE RELEASED (Coul)</th>
<th>RELAXATION TIME (To)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KV/cm</td>
<td>Peak I</td>
<td>Peak II</td>
<td>Peak I</td>
<td>Peak II</td>
<td>1st</td>
</tr>
<tr>
<td>1.</td>
<td>10</td>
<td>75</td>
<td>120</td>
<td>13.8</td>
<td>25.8</td>
<td>0.19</td>
</tr>
<tr>
<td>2.</td>
<td>25</td>
<td>75</td>
<td>120</td>
<td>15.8</td>
<td>28.0</td>
<td>0.18</td>
</tr>
<tr>
<td>3.</td>
<td>50</td>
<td>75</td>
<td>115</td>
<td>17.2</td>
<td>29.5</td>
<td>0.19</td>
</tr>
<tr>
<td>4.</td>
<td>100</td>
<td>75</td>
<td>115</td>
<td>19.0</td>
<td>32.2</td>
<td>0.20</td>
</tr>
</tbody>
</table>

### 4. POLARIZING TEMPERATURE (Tp = 30 C)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>POLING FIELD (Ep)</th>
<th>PEAK TEMPERATURE</th>
<th>PEAK CURRENT (A)</th>
<th>ACTIVATION ENERGY (ev)</th>
<th>CHARGE RELEASED (Coul)</th>
<th>RELAXATION TIME (To)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KV/cm</td>
<td>Peak I</td>
<td>Peak II</td>
<td>Peak I</td>
<td>Peak II</td>
<td>1st</td>
</tr>
<tr>
<td>1.</td>
<td>10</td>
<td>80</td>
<td>110</td>
<td>4.5</td>
<td>7.0</td>
<td>0.18</td>
</tr>
<tr>
<td>2.</td>
<td>25</td>
<td>80</td>
<td>110</td>
<td>6.2</td>
<td>9.0</td>
<td>0.19</td>
</tr>
<tr>
<td>3.</td>
<td>50</td>
<td>80</td>
<td>120</td>
<td>7.0</td>
<td>9.8</td>
<td>0.20</td>
</tr>
<tr>
<td>4.</td>
<td>100</td>
<td>80</td>
<td>120</td>
<td>7.8</td>
<td>11.8</td>
<td>0.21</td>
</tr>
</tbody>
</table>
# POLY BLEND SAMPLES (P2)

1. POLING FIELD (Ep = 100 KV/cm)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>POLARIZ. TEMP.</th>
<th>PEAK TEMPERATURE</th>
<th>PEAK CURRENT (A)</th>
<th>ACTIVATION ENERGY (eV)</th>
<th>CHARGE RELEASED (Coul)</th>
<th>RELAXATION TIME (To)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tp – C Peak I</td>
<td>Peak II</td>
<td>Peak I Peak II</td>
<td>1st - 2nd</td>
<td>1st - 2nd</td>
<td>1st - 2nd</td>
</tr>
<tr>
<td>1.</td>
<td>30 70</td>
<td>110</td>
<td>15.6 25.4</td>
<td>0.17 0.43</td>
<td>8.123 9.173</td>
<td>8.907 6.278</td>
</tr>
<tr>
<td>2.</td>
<td>40 80</td>
<td>110</td>
<td>19.0 28.8</td>
<td>0.16 0.42</td>
<td>10.234 10.327</td>
<td>8.954 6.301</td>
</tr>
<tr>
<td>3.</td>
<td>60 80</td>
<td>110</td>
<td>22.0 30.5</td>
<td>0.15 0.40</td>
<td>11.345 10.997</td>
<td>9.001 6.317</td>
</tr>
<tr>
<td>4.</td>
<td>80 80</td>
<td>110</td>
<td>23.5 33.5</td>
<td>0.14 0.49</td>
<td>12.567 11.011</td>
<td>9.087 6.527</td>
</tr>
</tbody>
</table>

2. POLING FIELD (Ep = 10 KV/cm)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>POLARIZ. TEMP.</th>
<th>PEAK TEMPERATURE</th>
<th>PEAK CURRENT (A)</th>
<th>ACTIVATION ENERGY (eV)</th>
<th>CHARGE RELEASED (Coul)</th>
<th>RELAXATION TIME (To)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tp – C Peak I</td>
<td>Peak II</td>
<td>Peak I Peak II</td>
<td>1st - 2nd</td>
<td>1st - 2nd</td>
<td>1st - 2nd</td>
</tr>
<tr>
<td>1.</td>
<td>30 70</td>
<td>120</td>
<td>13.0 17.9</td>
<td>0.16 0.42</td>
<td>4.447 10.456</td>
<td>8.657 4.109</td>
</tr>
<tr>
<td>2.</td>
<td>40 70</td>
<td>120</td>
<td>15.2 19.8</td>
<td>0.17 0.43</td>
<td>5.324 10.567</td>
<td>8.754 4.298</td>
</tr>
<tr>
<td>3.</td>
<td>60 70</td>
<td>120</td>
<td>16.4 21.4</td>
<td>0.18 0.45</td>
<td>5.997 11.678</td>
<td>8.857 4.321</td>
</tr>
<tr>
<td>4.</td>
<td>80 70</td>
<td>130</td>
<td>17.8 22.4</td>
<td>0.19 0.46</td>
<td>6.212 11.879</td>
<td>8.997 4.576</td>
</tr>
</tbody>
</table>

3. POLARIZING TEMPERATURE (Tp = 80 C)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>POLING FIELD (Ep)</th>
<th>PEAK TEMPERATURE</th>
<th>PEAK CURRENT (A)</th>
<th>ACTIVATION ENERGY (eV)</th>
<th>CHARGE RELEASED (Coul)</th>
<th>RELAXATION TIME (To)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KV/cm Peak I Peak II</td>
<td>Peak I Peak II</td>
<td>1st - 2nd</td>
<td>1st - 2nd</td>
<td>1st - 2nd</td>
<td>1st - 2nd</td>
</tr>
<tr>
<td>1.</td>
<td>10 80 110</td>
<td>16.4 26.6</td>
<td>0.17 0.44</td>
<td>7.234 9.123</td>
<td>9.442 5.007</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>25 80 120</td>
<td>18.6 30.4</td>
<td>0.18 0.45</td>
<td>8.345 9.567</td>
<td>9.587 5.142</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>50 80 110</td>
<td>20.5 31.8</td>
<td>0.19 0.46</td>
<td>9.456 10.123</td>
<td>9.785 5.234</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>100 80 110</td>
<td>22.8 33.6</td>
<td>0.20 0.43</td>
<td>10.123 10.789</td>
<td>9.875 5.432</td>
<td></td>
</tr>
</tbody>
</table>

4. POLARIZING TEMPERATURE (Tp = 30 C)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>POLING FIELD (Ep)</th>
<th>PEAK TEMPERATURE</th>
<th>PEAK CURRENT (A)</th>
<th>ACTIVATION ENERGY (eV)</th>
<th>CHARGE RELEASED (Coul)</th>
<th>RELAXATION TIME (To)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KV/cm Peak I Peak II</td>
<td>Peak I Peak II</td>
<td>1st - 2nd</td>
<td>1st - 2nd</td>
<td>1st - 2nd</td>
<td>1st - 2nd</td>
</tr>
<tr>
<td>1.</td>
<td>10 70 130</td>
<td>10.5 15.0</td>
<td>0.18 0.43</td>
<td>4.456 2.345</td>
<td>8.002 4.007</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>25 70 130</td>
<td>11.6 15.8</td>
<td>0.19 0.42</td>
<td>5.567 3.456</td>
<td>8.017 4.019</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>50 70 130</td>
<td>12.5 15.7</td>
<td>0.20 0.44</td>
<td>6.678 4.789</td>
<td>8.235 4.299</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>100 70 110</td>
<td>13.2 17.0</td>
<td>0.22 0.43</td>
<td>7.789 5.623</td>
<td>8.337 4.992</td>
<td></td>
</tr>
</tbody>
</table>
### POLY BLEND SAMPLES (P3)

#### 1. POLING FIELD (Ep = 100 KV/cm)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>POLARIZ. TEMP.</th>
<th>PEAK TEMPERATURE</th>
<th>PEAK CURRENT (A)</th>
<th>ACTIVATION ENERGY (ev)</th>
<th>CHARGE RELEASED (Coul)</th>
<th>RELAXATION TIME (To)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tp - C</td>
<td>Peak I Peak II</td>
<td>Peak I Peak II</td>
<td>1st - 2nd</td>
<td>1st 2nd</td>
<td>1st 2nd</td>
</tr>
<tr>
<td>1.</td>
<td>30</td>
<td>60 100</td>
<td>6.2 14.6</td>
<td>0.17 0.57</td>
<td>9.789 10.123</td>
<td>16.879 8.766</td>
</tr>
<tr>
<td>2.</td>
<td>40</td>
<td>60 100</td>
<td>9.8 18.0</td>
<td>0.16 0.56</td>
<td>11.456 11.456</td>
<td>17.555 8.859</td>
</tr>
<tr>
<td>3.</td>
<td>60</td>
<td>60 100</td>
<td>11.2 22.0</td>
<td>0.18 0.58</td>
<td>12.345 11.567</td>
<td>17.876 9.017</td>
</tr>
<tr>
<td>4.</td>
<td>80</td>
<td>60 100</td>
<td>13.4 28.0</td>
<td>0.19 0.59</td>
<td>13.467 12.678</td>
<td>18.576 9.478</td>
</tr>
</tbody>
</table>

#### 2. POLING FIELD (Ep = 10 KV/cm)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>POLARIZ. TEMP.</th>
<th>PEAK TEMPERATURE</th>
<th>PEAK CURRENT (A)</th>
<th>ACTIVATION ENERGY (ev)</th>
<th>CHARGE RELEASED (Coul)</th>
<th>RELAXATION TIME (To)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tp - C</td>
<td>Peak I Peak II</td>
<td>Peak I Peak II</td>
<td>1st - 2nd</td>
<td>1st 2nd</td>
<td>1st 2nd</td>
</tr>
<tr>
<td>1.</td>
<td>30</td>
<td>70 120</td>
<td>2.5 6.7</td>
<td>0.18 0.56</td>
<td>5.557 11.123</td>
<td>12.078 6.875</td>
</tr>
<tr>
<td>2.</td>
<td>40</td>
<td>70 120</td>
<td>4.0 9.2</td>
<td>0.17 0.57</td>
<td>6.678 11.456</td>
<td>12.997 7.017</td>
</tr>
<tr>
<td>3.</td>
<td>60</td>
<td>70 120</td>
<td>5.3 10.0</td>
<td>0.19 0.58</td>
<td>7.742 12.567</td>
<td>13.353 7.497</td>
</tr>
<tr>
<td>4.</td>
<td>80</td>
<td>70 120</td>
<td>6.7 10.8</td>
<td>0.20 0.58</td>
<td>8.345 12.789</td>
<td>13.473 7.785</td>
</tr>
</tbody>
</table>

#### 3. POLARIZING TEMPERATURE (Tp = 80 C)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>POLING FIELD(Ep)</th>
<th>PEAK TEMPERATURE</th>
<th>PEAK CURRENT (A)</th>
<th>ACTIVATION ENERGY (ev)</th>
<th>CHARGE RELEASED (Coul)</th>
<th>RELAXATION TIME (To)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KV/cm</td>
<td>Peak I Peak II</td>
<td>Peak I Peak II</td>
<td>1st - 2nd</td>
<td>1st 2nd</td>
<td>1st 2nd</td>
</tr>
<tr>
<td>1.</td>
<td>10</td>
<td>60 100</td>
<td>10.0 20.0</td>
<td>0.16 0.55</td>
<td>8.246 10.234</td>
<td>15.070 8.192</td>
</tr>
<tr>
<td>2.</td>
<td>25</td>
<td>60 100</td>
<td>11.8 21.4</td>
<td>0.17 0.57</td>
<td>9.468 10.345</td>
<td>15.789 8.342</td>
</tr>
<tr>
<td>3.</td>
<td>50</td>
<td>60 100</td>
<td>14.8 25.0</td>
<td>0.18 0.59</td>
<td>10.268 11.456</td>
<td>16.379 8.757</td>
</tr>
<tr>
<td>4.</td>
<td>100</td>
<td>60 100</td>
<td>16.8 28.2</td>
<td>0.19 0.58</td>
<td>11.123 11.567</td>
<td>16.555 8.874</td>
</tr>
</tbody>
</table>

#### 4. POLARIZING TEMPERATURE (Tp = 30 C)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>POLING FIELD(Ep)</th>
<th>PEAK TEMPERATURE</th>
<th>PEAK CURRENT (A)</th>
<th>ACTIVATION ENERGY (ev)</th>
<th>CHARGE RELEASED (Coul)</th>
<th>RELAXATION TIME (To)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KV/cm</td>
<td>Peak I Peak II</td>
<td>Peak I Peak II</td>
<td>1st - 2nd</td>
<td>1st 2nd</td>
<td>1st 2nd</td>
</tr>
<tr>
<td>1.</td>
<td>10</td>
<td>60 120</td>
<td>10.9 14.6</td>
<td>0.19 0.54</td>
<td>5.657 9.787</td>
<td>11.991 5.998</td>
</tr>
<tr>
<td>2.</td>
<td>25</td>
<td>70 120</td>
<td>13.0 15.8</td>
<td>0.22 0.55</td>
<td>6.743 9.823</td>
<td>12.071 6.002</td>
</tr>
<tr>
<td>3.</td>
<td>50</td>
<td>70 120</td>
<td>14.0 17.4</td>
<td>0.20 0.58</td>
<td>7.678 10.452</td>
<td>12.982 6.197</td>
</tr>
<tr>
<td>4.</td>
<td>100</td>
<td>70 120</td>
<td>14.7 18.3</td>
<td>0.23 0.59</td>
<td>8.456 10.562</td>
<td>13.655 6.887</td>
</tr>
</tbody>
</table>
amount of contribution to the total polarization comes from charges injected from the electrodes. It is interesting to note that the tendency to homocharge formation is observed in all the cases. The conductivity increases with increase in temperature. Thus at higher temperature charges may be considered to be injected more easily.

From the observed results and discussion, it seems that homocharge formation is comparatively easy. The initial current corresponds to heterocharge in many cases which reverses in sign when all the dipoles have been oriented and ohmic conduction starts consuming the homocharges.

It is evident from the results of such measurements that the magnitude of the current is comparatively low during initial stages of TSDC; however, the magnitude of the current is quite high during the high temperature part of the TSDC cycle. In the absence of homocharging, we can assume that the electret contains only a dipole polarization. The dipoles will induce image charges on the adhering back metal electrode which makes the external field zero. Thus, the external field becomes zero and one has a neutral entity before the TSDC is started. When the electret is heated, dipoles are reoriented and part of the image charges are free to charge the capacitor formed by the electret. Thus, there appears a non-zero field in the air gap and the dipole reorientation generates a current. However, at high temperatures when ohmic conduction becomes high, the freed Ohmic charges will be dissipated. This dissipation will generate current of opposite polarity to that of the dipolar current.
Thus, the homocharge current is observed in the present case. As PMMA is blended with EC there results an increase in the net dipolar content. These dipoles are oriented by the field and the orientational effect of the field is more at higher temperature when the mobility of molecular sections is high. Further, it can also be understood in terms of the plasticization effect. The plasticization in known to increase the molecular mobility and free volume and lower glass transition temperature. Thus on blending there is sufficient free volume available for the polar groups in the blend to rotate and consequently there is a net increase in the dipolar polarization. As the field increases more and more dipoles are oriented resulting in increase in the total polarization as observed in the present case.

The contribution for polarization may also come from interfacial charging. This type of polarization is observed in the heterogeneous samples consisting of different components or phases. When the components have different dielectric constants and conductivities, charges accumulate near the interface leading to Maxwell-Wagner-Sillar (MWS) interfacial charging when the sample is heated and subjected to a field. During subsequent TSDC, these interfacial charges are destroyed because the local fields in the dissimilar part of the sample are reversed so that the neutralizing charges of opposite sign are conveyed to the interfaces by Ohmic conduction. In the present case PMMA has been blended with EC. This is expected to result in a net increase in the volume of crystalline-amorphous interfaces where the charges are trapped resulting in the MWS effect. The increase in the polarization with blending, therefore, may be considered due to
increased interfacial polarization effect. At higher temperature, melting of crystallites would lead to loss of trapping sites and therefore the polarization is decreased at high temperature. The charge carriers can be trapped at the crystalline amorphous interfaces forming a space charge. PMMA is a polar polymer largely amorphous in nature whereas EC is partial polar polymer. On blending with EC, there results a net increase in crystalline amorphous boundaries, where the space charges are trapped forming space charges. Release of these charges from the traps during subsequent TSDC gives rise to its depolarization current. The increase in the polarization on blending may be due to increased trapped space charges.

The peak current versus poling fields and released charge versus poling field plots associated with peak first are linear. This suggested that the peak is of dipolar nature and this phenomena can be attributed to the relaxation of the polar groups i.e. side chains from polarized state to one of equilibrium. This view is further supported by the observation that when the depolarized samples is reheated no current in the external circuit corresponding to peak first is observed.

Table 3.1 shows that the relaxation time (Peak I) decreases with increase in polarization temperature. This can easily be explained from the fact that the relaxation phenomenon is due to the internal friction of the polymer which depends exponentially on temperature. The time lag corresponding to the motions of permanent dipoles (ions, free and trapped charges) changes markedly with temperature. Heating accelerates the molecular
motion, thereby decreasing the time of that is the relaxation time.

The behaviour of peak current versus poling field for second peak in the higher field region indicates the space charge phenomena. The origin of second peak is not only due to single relaxation but seems to be complex and may arise due to, the release of the remaining part of the frozen dipoles by their cooperative motion with adjoining segment of the main polymer chain.

The closer examination of thermograms shows that the high temperature peak starts earlier for low polarizing temperature. Opposite behaviour is observed with this peak for samples polarized at fixed temperature with different polarizing fields. The shift of high temperature peak towards higher temperature with increasing value of poling temperature further indicates the trapping of electronic charges in energetically distributed traps existing in the polymer. These characteristics can be explained as follows.

Assuming that the trap structure is not influenced by heating, energetically different traps will be filled at elevated temperature rather than at room temperature. Assuming a discrete set of trapping levels, each represented by an activation energy "$U_i"$ and an attempt to escape frequency "$V_i"$ the detrapping time constant for each trapping level can be assumed to be of the form

$$\tau_i = [V_i]^{-1} \exp(\mu_i/kT) \quad (i = 1, \ldots, N_0) \quad \text{(3.31)}$$

where $N_0$ is the total number of trapping levels, $T_i$ the mean detrapping time for $i^{th}$ trapping level, $K$ the Boltzmann constant and $T$ the temperature.
For a trapping level to contribute to the charge motion in the sample during charging, $T_1$ has to be smaller than the charging time $T_c$. This means that with increasing temperature, the number of "active" (contributing to charge motion) trapping levels $N(T)$ increases whereas the number of inactive (not contributing to the charge motion) levels $(N_0 - N(T))$ decreases. These inactive levels store the charge delivered to the sample during charging process. In view of the above, the high temperature peak is expected to shift towards higher temperature with increase in poling temperature which is experimentally observed in the present case. This also explains the early initiation of the peak when the sample is poled at lower temperature.

In order to study the effect of the nature of the electrode materials on TSDC, the sample of EC, PMMA and polyblend samples ($P_1$ and $P_2$) with Al-Al, Al-Ag, and Al-Cu, electrode combinations, were polarized in identical conditions ($E_p=100$ kV/cm, $T_p=80$ C) and their TSDC spectra have been shown in figures $A_3$ and $B_3$ respectively. Two well resolved peaks has been observed for pure EC, PMMA as well as blended samples. In the case of pure sample the magnitude of current has been found to the higher for Al-Cu electrode configuration with respect to Al-Al and Al-Ag electrode configuration. However no systematic variation has been observed for $P_1$ and $P_2$ samples.

The primary source of charge carriers is the electrode contacts. Carriers are generated in the bulk on account of thermal ionization of impurities and absorbed water molecules. Nath and Kumar have shown injection of holes in cellulose film
and increase in charge mobility with iodine doping. Hole injection results in depletion of the layer of negative charges creating a field at the interface between the electrode and the film surface. We can understand our results better if we assume that a system consisting of dielectric sandwiches between electrodes is transferred from an initial state of pure capacitance to a final equilibrium state of pure resistance in series in the presence of charge carriers having different signs. The resistance of barrier layers and bulk material will be determined by the temperature.

When two metals are brought in close contact, a potential difference of work function $O_2-O_1$, is created between the two metals. The semi-insulating polymer differs from a metal, in that an electric field may exist, within the interior of the semiinsulator. For this reason the contact potential drop between the metal and the semi-insulator may take place within the material rather than at the contact interfaces. Along with the field, there may exit a depletion in the accumulation of charges in the surface layers. The work function of the polymeric material is higher compared to that of metals used for contacts, which creates an accumulation layer at the interfaces and leaves charged donors in the bulk. This in turn creates fields at the interfaces of the metal polymer system. The injection into the polymer film decreases with increase in work function. The number of injected carriers may be larger for metals with lower work function, such as Al and thus the field existing in the bulk may be partly compensated by the field created by injected charges at the interfaces. As the sample is heated, the charges
existing at the interfaces have to pass through the bulk, and may be trapped in the impurity centres and other trapping centres, such as chain coiling. The net charge injected from the electrodes are predominantly the majority carriers. The charges which essentially give rise to the field at the interfaces are mobilized and the field due to injected charge carriers is weakened, resulting in the release of partly compensated bulk field and the motion of charge carriers is then determined by the field in the bulk.
REFERENCES

23. G. Sawa, M. Kawade and M. Ieda, J. Appl. Phys., 44,


43. M. Latour, P.V. Murphy, J. Electrostat, 3 (1977) 163.


