CHAPTER V

THERMALLY STIMULATED DISCHARGE CURRENT AND PYROELECTRICITY

5.1 Introduction

In recent years much of our industrial progress is based on the use of polymers as insulator for both heat and electricity. However, our modern lifestyle increasingly demands more from the polymers than their traditional role of insulators for heat and electric current. Since the past two decades, the attention of many material scientists and engineers has been drawn to the preparation and characterization of polymer thin films.

The important use of electrostatic dissipating materials is in the packaging of electronic components. Electrostatic shock can often damage these components and therefore, it is necessary to ensure that electrostatic charge does not build up. The levels of conductivity required for this purpose is 10^{-4} to 10^{-8} S/cm and an uniform electronic conductivity. Polymers, in general, have a great capacity of storing charge.

Charge retention in thin polymer films has been extensively studied since the 1960's, when the first application of film electret microphones was reported [1]. The charge-transfer complex of the polymer-based systems have been used commercially as electrophotographic photoreceptors [2]. These properties make them suitable for applications, such as electret

microphones, thin film memory circuits, IR detectors, solid state batteries, etc [3].

When these thermoelectrets are subjected to a programmed heat treatment, they give rise to a current in the external circuit. This current, called TSDC, gives vital information about the charge storage capacity of the material. Similarly, pyroelectricity in materials has received great attention both theoretically and experimentally as some important practical devices like pyroelectric detectors can be fabricated from these materials.

The polarity of the thermo-electrets depends on the polarizing temperature, polarizing field and the characteristics of the materials. Recently, measurement of the thermally stimulated discharge current has become an important tool for studying various properties of materials.

Some of the reported works on TSDC and pyroelectricity studies are given below. Abd-Lefdil et al [4] studied the temperature dependence of electrical conductivity for oriented polyacetylene doped with iodine, molybdenum chloride and sulfuric acid. They reported that for the three dopants, in the same doping level range, the experimental results could be fitted using a variable range hopping model.

The two-charge theory put forwarded by Gross [5] explains the effect on polar dielectrics in terms of the orientation of the dipoles under the influence

of electrical and thermal activation. However, in the case of non-polar dielectrics additional factors such as trapping and accumulation of charge carriers have to be taken into account. Ionic and metallic impurities in polymers have been observed to give rise to the trapping of charge carriers at the trapping levels introduced by the doped impurities.

Bucci and Fieschi [6] have proposed an ionic thermal current method for the study of defects in ionic crystals. Because of its resolving power, it is particularly well suited to study the behaviour of complex dielectrics such as polymers. This theory was extended by Perlman [7] and Turnhout [8].

In the present study, Pani-EB and lightly doped acid Pani films were subjected to TSDC and pyroelectric studies and the details are given below :

5.2 Theory

5.2.1 Thermally Stimulated Discharge Current (TSDC)

The dipolar polarization at any temperature and instant in a solid is a result of simultaneous orientation action of the field and randomizing action of thermal vibrations. The rate at which the polarization 'P' decays with time can be expressed in terms of the polarization and a relaxation time 'T' as

$$dP/dt = -P/T. \qquad \text{................ (5.1)}$$

When the solid is warmed, 'T' is a function of temperature, which is in turn a function of time, and the solution to Equation (5.1) is

$$P = P_0 \ [1\text{-exp} \ (\text{-}t/\tau)]. \qquad \dots\dots\dots\dots \quad (5.2)$$

If the initial polarization P_0 has been formed by applying an electric field E_p at a temperature T_p, then for freely rotating dipoles, one has

$$P_0 = S \ N_d \ \mu^2 \ E_p \ / \ kT_p \qquad \dots\dots\dots\dots \quad (5.3)$$

where 'N_d' is the dipole concentration, μ is the dipole moment and k is the Boltzman constant. This is the familiar Langevin function. The discharge current is simply the rate of change of polarization; i.e.,

$$I \ = \ - [P_0/\tau] \ \text{exp} \ [\text{-}t/\tau]. \qquad \dots\dots\dots\dots \quad (5.4)$$

In solids, a reorientation of dipoles often involves the movement of ions from one equilibrium position to another. The jumping ion must overcome a potential barrier of energy U and the jumping probability per unit time is proportional to exp (-U/kT). The relaxation time is usually interpreted as the average time required for the jump or the reciprocal of the probability and so we have

$$\tau \ = \ \tau_0 \ \text{exp} \ [\text{-}U/kT] \qquad \dots\dots\dots\dots \quad (5.5)$$

where τ_0 is a constant. If the dielectric is warmed at a uniform rate, then

$$T = \alpha + \beta t \qquad \dots\dots\dots\dots (5.6)$$

where T is the temperature, t is the time, and α, β are constants. From Equations. 5.3 and 5.6 one has an expression for the glow peak, ie.,

$$I(T) = N \mu E_p / 3kT_p\tau_0 \exp(-U/kT) -1/\beta \tau_0 \int_{T_0}^{T} \exp(-U/kT)dT \dots\dots (5.7)$$

Grossweiner [9] has extended the TSC technique to find the capture cross section and also the attempt-to-escape frequency. The expression used are

$$\sigma_n = v/2.9 \times 10^{24} T_m^2 (m^2)$$

$$v = 3T'\beta /2T_m (T_m-T') [\exp(U/kT_m)] s^{-1}$$

where σ_n is the capture cross section, v is the attempt-to-escape frequency, β the heating rate, k the Boltzmann constant and T' the temperature at half maximum intensity on the low temperature side. Thus the TSC technique has become one of the most powerful tools for investigating the electrical properties of polymers and other dielectric materials.

5.2.2 Pyroelectricity

The pyroelectric effect concerns the change in the polarization of a crystal when it undergoes a change in temperature. Pyroelectricity is of two types:

(i) primary and (ii) secondary. If the sample temperature is changed without letting the sample change its shape and size, then it is primary pyroelectricity and would be observed in a completely clamped crystal. Secondary pyroelectricity is the direct result of pyroelectricity.

The pyroelectric effect defined broadly denoted changes in the internal polarization due to change of temperature. Although changes in the polarization of electrets with temperature are usually irreversible, they have been regarded as pyroelectric phenomena. On the other hand, pyroelectricity was believed to be a crystal property and was understood to occur in crystals belonging to pyroelectric symmetry groups [10]. In these cases, the pyroelectric current is reversible and not due to depolarization: i.e., the pyroelectric current is of opposite sign for heating and cooling.

The change in polarization dP of a crystal due to the change in its temperature dT is given by,

$$dP = P.dT \qquad \qquad \text{...........................(5.8)}$$

where the constant 'P' is called the pyroelectric coefficient of the crystal.

If a temperature change is caused by absorption of radiation, the observed pyroelectric effect is equivalent to the direction of the incident radiation. The

current 'I' in the external circuit depends on the area 'A' of the radiation receiving electrode and the rate of change of polarization with temperature is given by,

$$I = A \ dP/dT. \ dT/dt \qquad \dots\dots\dots\dots\dots (5.9)$$

The power 'W' absorbed by the crystal due to the change in the incident radiation is ,

$$W = J \ A \ x \ \rho \ Cp \ (dT/dt) \qquad \dots\dots\dots\dots (5.10)$$

where 'J' is the mechanical equivalent of heat, 'x' is the thickness of the crystal 'ρ' is the density and Cp is its specific heat at constant stress. Thus,

$$I/W = (dP/dT) / x \ \rho \ Cp \ J \qquad \dots\dots\dots\dots (5.11)$$

The above equation shows that the pyroelectric current should vary linearly with the incident radiation intensity and also as the reciprocal of the crystal thickness. It is also indicated that the pyroelectric material must have high volume resistivity, low density, low specific heat and minimum possible thickness for the dielectric materials, preferably less than the thermal diffusion length to ensure that the entire thickness of the detector is uniformly heated. Polymers, in general, have the desirable properties mentioned above. A polymer is a homogeneous mixture of crystalline and

amorphous regions on a macroscopic scale. However, polarization can be introduced by mechanical stretching and or by poling. Two physical models have been proposed to account for the appearance of pyroelectricity. They are (i) space charge model [10] and (ii) the dipolar model [11].

5.3. Experimental

5.3.1 Thermally stimulated discharge currents

The TSD currents were studied in an metal-Polymer-metal sandwich configuration obtained on glass slides. The films were annealed in a vacuum of 10^{-3} Torr by keeping them at 125 °C for one hour under a bias of 2 volts. Then the samples were polarised for 1 hour by keeping them in a specially constructed jig shown in Fig. 5.1. The jig was placed in an electrostatically shielded vessel which was evacuated to a vacuum of 10^{-3} Torr. The films were heated indirectly at a constant heating rate. All the connections were made with teflon amphenols for good insulation. To study the TSDC, the annealed films were cooled from high temperature in the presence of the electric field. At room temperature the samples were kept under short circuited for 5 minutes to remove any surface charges present. Now the samples were linearly heated up to a certain temperature with a uniform heating rate of 0.33 K/s and the currents were measured. Polarising temperatures of 308 and 333 K and polarising voltages of 2,4 and 6 volts were used. An EA 815 electrometer amplifier was used to
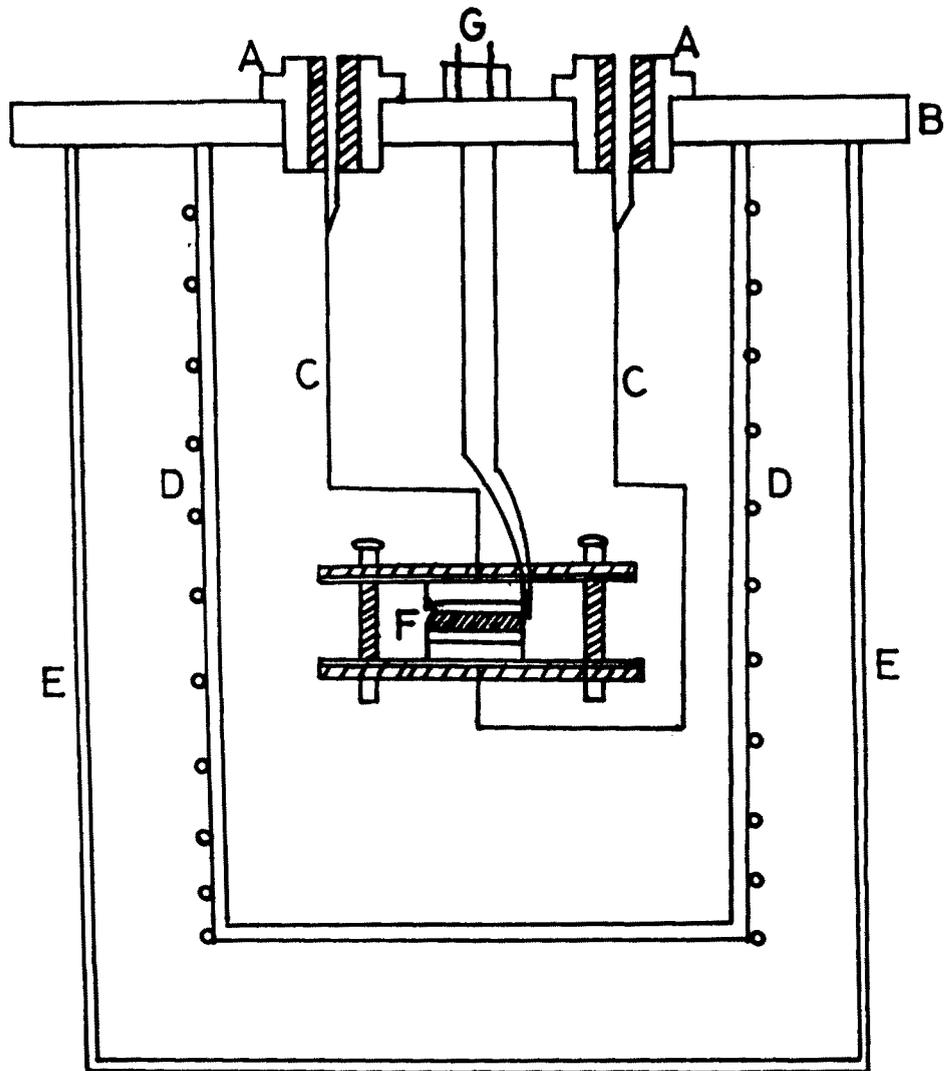
A-Teflon Amphenols

B- Detachable Aluminium Plate

C-Connecting Wires

D-Heating Element

E- Silver Chamber

F- Sample with Top & Bottom Electrode

G- Thermocouple Wires

Figure 5.1 Experimental Jig for TSDC and Pyroelectricity Studies

measure the depolarisation currents. Figure 5.2 shows the block diagram of experimental set up used for the TSDC study.

5.3.2 Pyroelectricity

The experimental set up used for measuring the pyroelectric current was same as that used for the TSDC measurements. The annealed films were polarised at different temperatures and fields for a fixed time of 1 hour. After poling , the films were cooled to room temperature and then short circuited for 5 minutes to allow for decay of any stray charges. The films were then heated at a constant rate of 0.33 K/s indirectly. The first thermal run, which is irreversible, is a measure of the absorbed charges during the poling process. All the subsequent thermal cycles give the reversible or true pyroelectric currents.

5.4 Results and discussion

Thermally stimulated discharge current spectra of polyaniline-EB and lightly acid doped polyaniline films at 308 and 333 K at different polarising fields are given in Fig. 5.3 (a & b).

In the case of polyaniline-EB [Fig.5.3(a)] film, a peak current was observed at 375 K for a polarising field strength of 4×10^5 V/m. No prominent peaks were observed on variation of the polarising field. But the
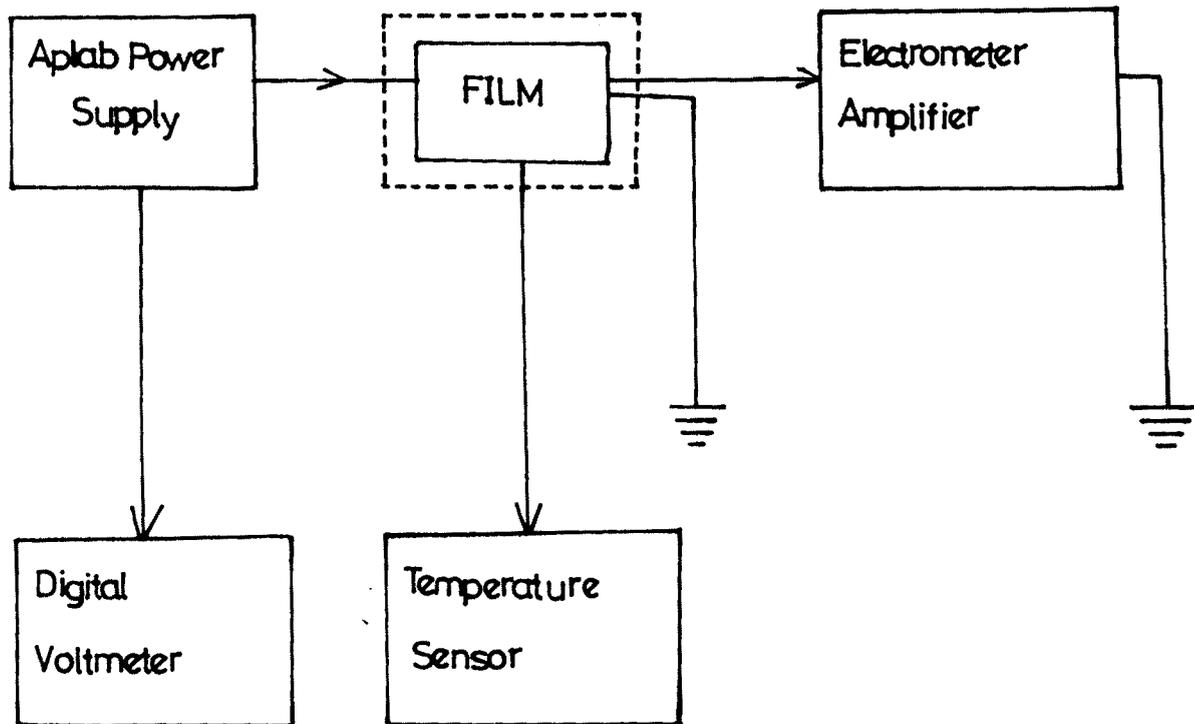
Fig. 5.2 Block diagram of experimental set-up used for TSDC and pyroelectricity studies
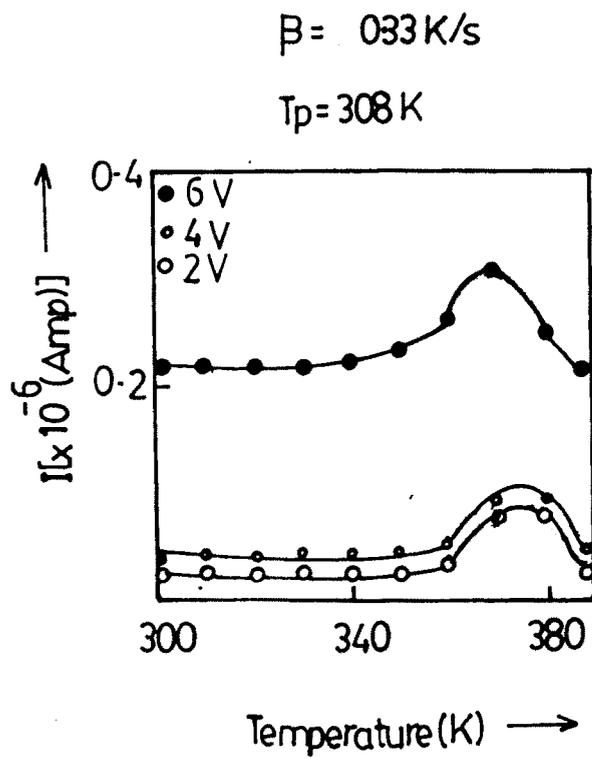
$\beta = \ 0.33 \, K/s$

$Tp = 308 \, K$

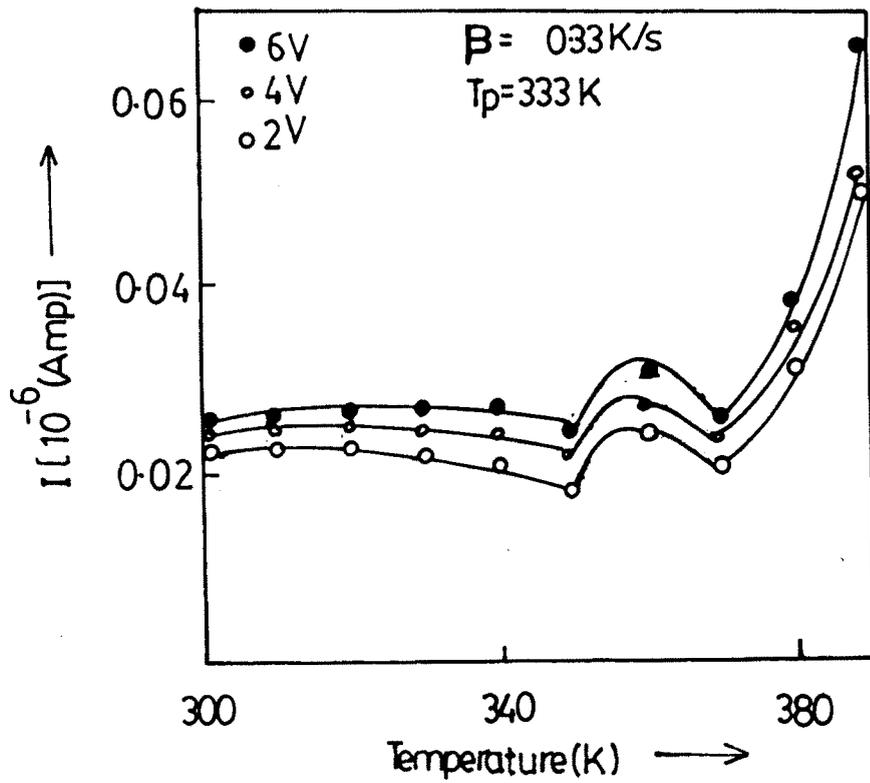Fig. 5.3(a) TSDC versus temperature of Pani-EB film polarised at 308 K

Fig. 5.3(b) TSDC versus temperature of Pani-EB film polarised at 333 K

value of current remains constant upto 366 K and decreased till 375 K after which there is a steady increase suggesting a possible peak at higher temperature outside the range of study. No prominent peaks were observed for the same film [Fig.5.3(b)] polarised at 333 K. The magnitude of current was found to decrease with increase in polarising field strength.

In the case of acid doped Pani [Fig.5.4(a)] film, a peak current was observed at 335 and 380 K for a polarising field strength of 2.8×10^5 V/m. No prominent peaks were observed on variation of the polarising field. Peaks were observed at 380 K for the same film [Fig.5.4(b)] polarised at 333 K. The magnitude of current was found to decrease with increase in polarising field strength.

Figs.5.5 (a & b) show the variation of pyroelectric coefficient for Pani-EB film polarised at two temperatures (308 & 380 K) for different polarising field strengths. For films polarised at low temperature (308 K), the transition temperature shifted to lower temperatures with increasing polarising field, while it shifted to higher temperatures for films polarised at high temperatures (380 K). Similar behaviour was observed for acid doped Pani film [Fig.5.6(a & b)].

The activation energy was calculated using 'initial rise' method of Garlick and Gibson [12] by isolating the individual peaks from the composite curves. Fig. 5.7 (a & b) shows the plot between log I versus 1/T. From the
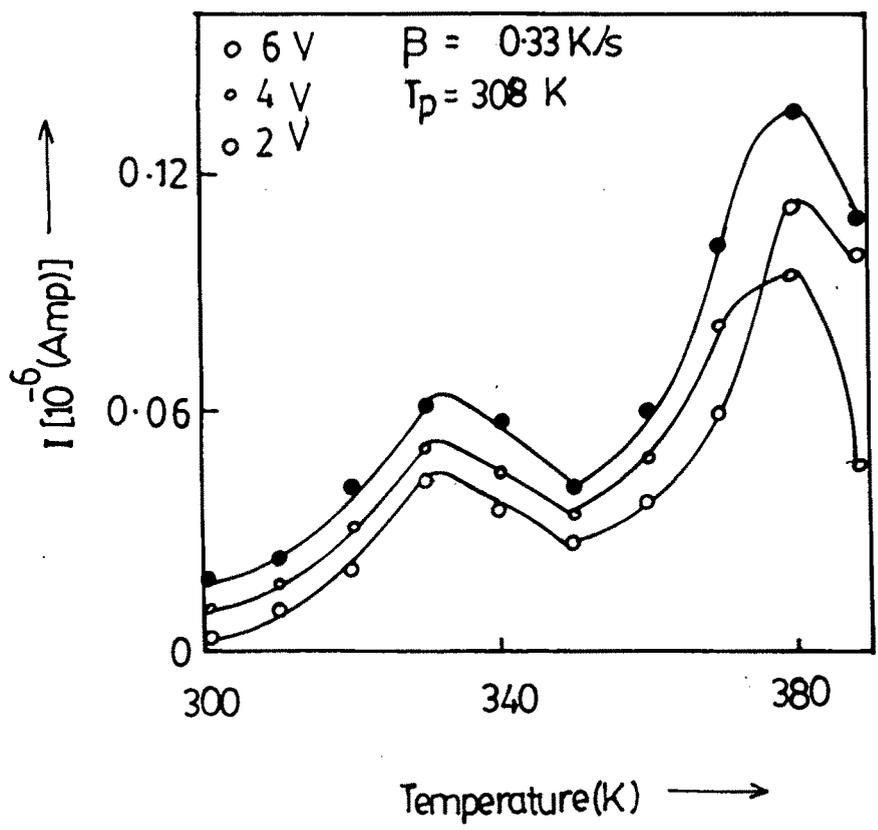
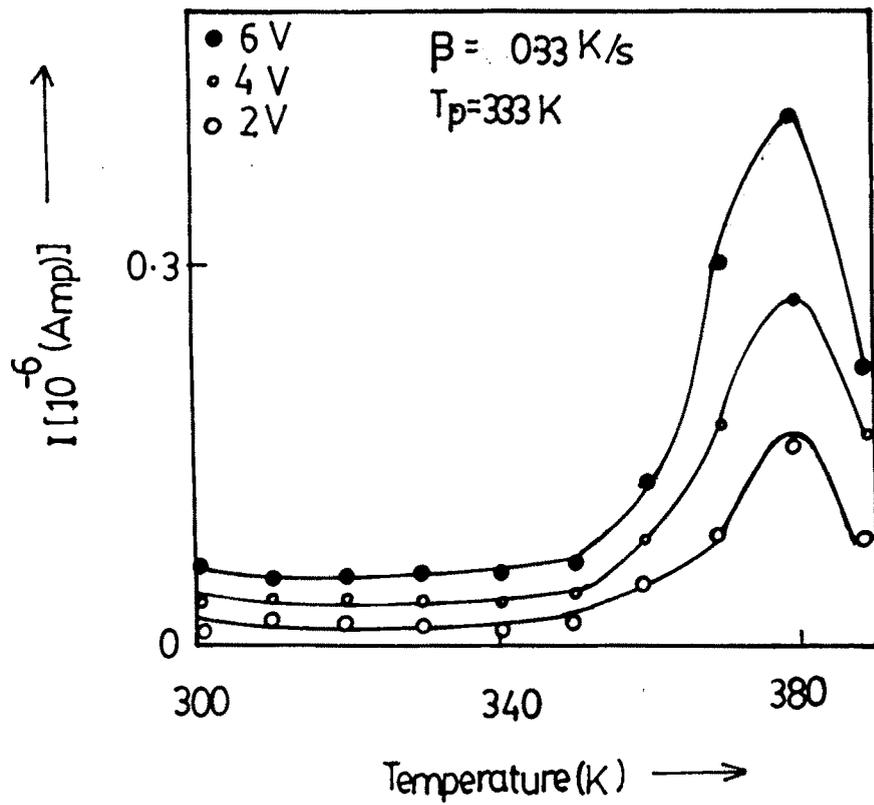Fig. 5.4(a) TSDC versus temperature of acid doped Pani film polarised at 308 K

Fig. 5.4(b) TSDC versus temperature of acid doped Pani film polarised at 333 K
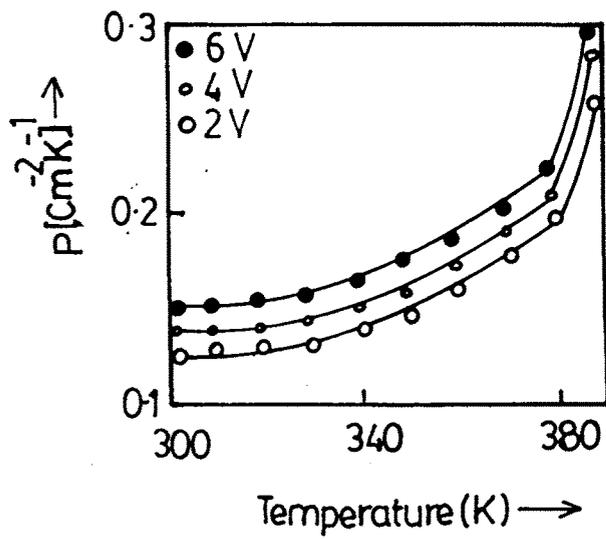
$\beta = 0.33 K/s$

$T_p = 308 K$

Fig. 5.5(a) Pyroelectric coefficient versus temperature of Pani-EB
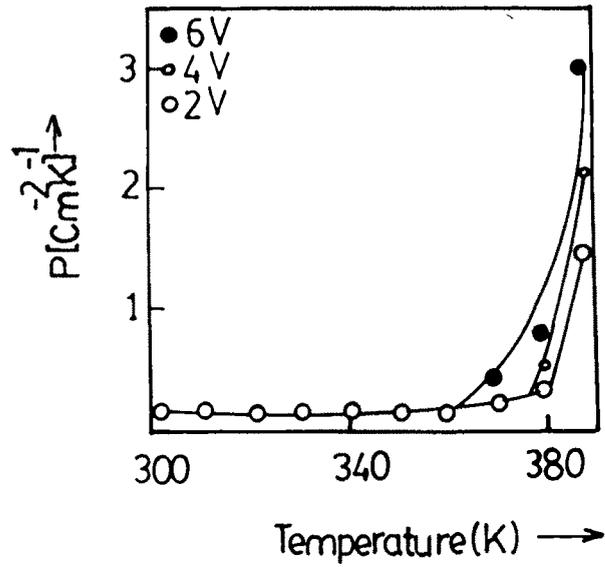film polarised 308 K

$\beta = 0.33 K/s$

$Tp = 333 K$

Fig. 5.5(b) Pyroelectric coefficient versus temperature of Pani-EB
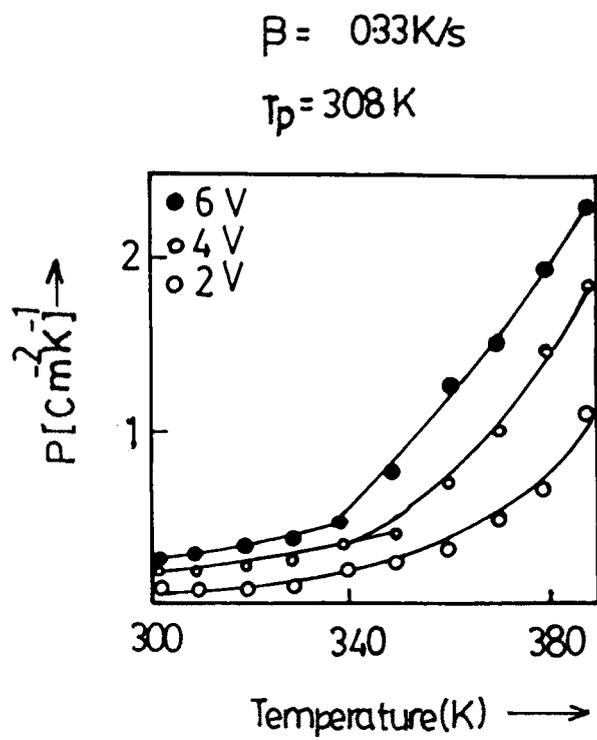   film polarised 333 K

$\beta = 033 K/s$

$T_p = 308 K$

Fig. 5.6(a) Pyroelectric coefficient versus temperature of acid doped Pani film   polarised   308 K

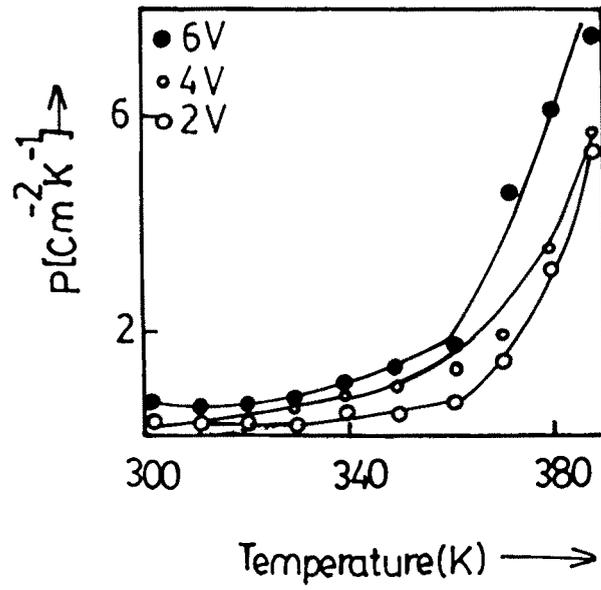$$\beta = \ 0.33 \, K/s$$

$$T_p = 333 \, K$$

Fig. 5.6(b) Pyroelectric coefficient versus temperature of acid doped Pani
film   polarised 333 K
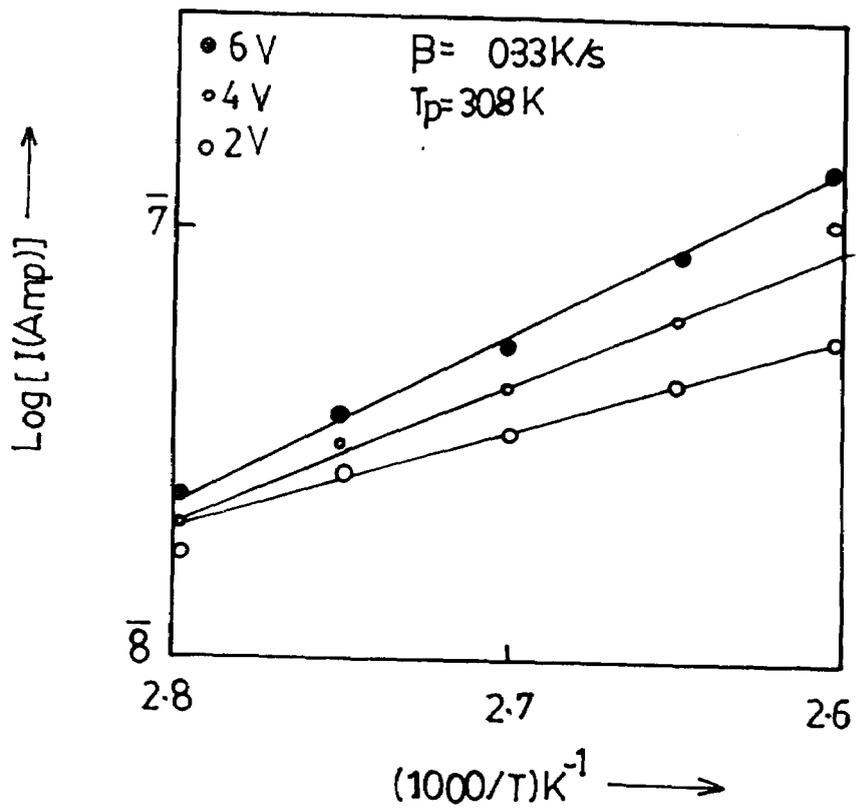
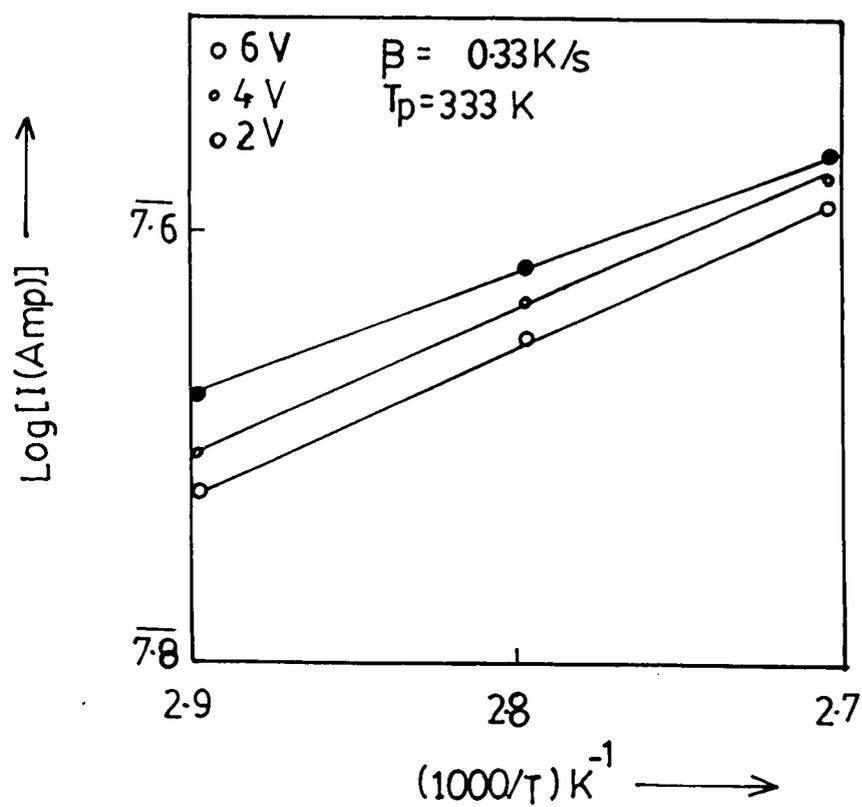Fig. 5.7(a) Log I versus 1000/T of Pani-EB film polarised at 308 K

Fig. 5.7(b) Log I versus 1000/T of Pani-EB film polarised at 333 K

graph,the activation energy values are calculated using plots from the initial rising portion of the individual peaks. Similarly the value of activation energy was calculated for acid doped Pani [Fig.5.8 (a & b)] films. The calculated values are presented in Table 5.1. The attempt-to-escape frequency and the capture cross-section were calculated from the values of activation energies using Grossweiner [9] equation. The calculated values are presented in Table 5.1.

The electric polarisation in a polymer may be due to dipole alignment, migration of ions within the material or charge injection from the electrodes. In the present study, the position of the peaks obtained varied only slightly with the polarising field. The activation energies also showed only slight variation with the polarising field. These factors support the dipolar orientation theory. The peaks observed at higher temperatures were more intense than the peaks at low temperatures. Only one peak was observed at 308 K. The absence of peaks at low temperatures may be attributed to the shallow trapping of mobile charges [13].

The pyroelectric activity in polyaniline-EB and acid doped polyaniline was studied by measuring the pyroelectric currents at polarising temperatures of 308 and 333 K and at different polarising fields. The experimental parameters employed were the same as that of TSDC measurements.
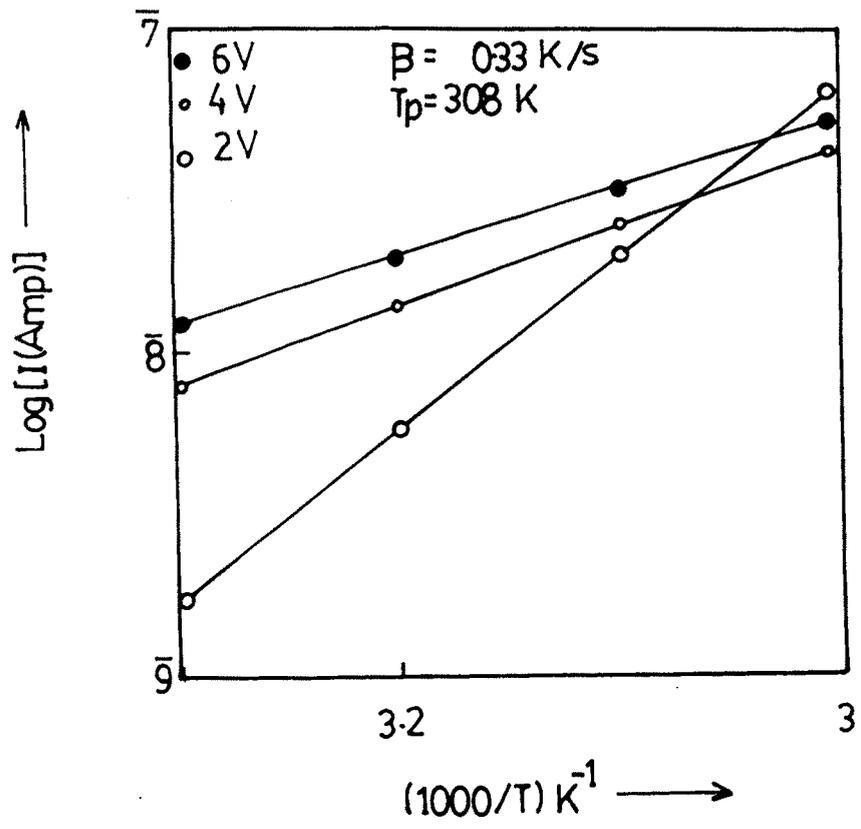
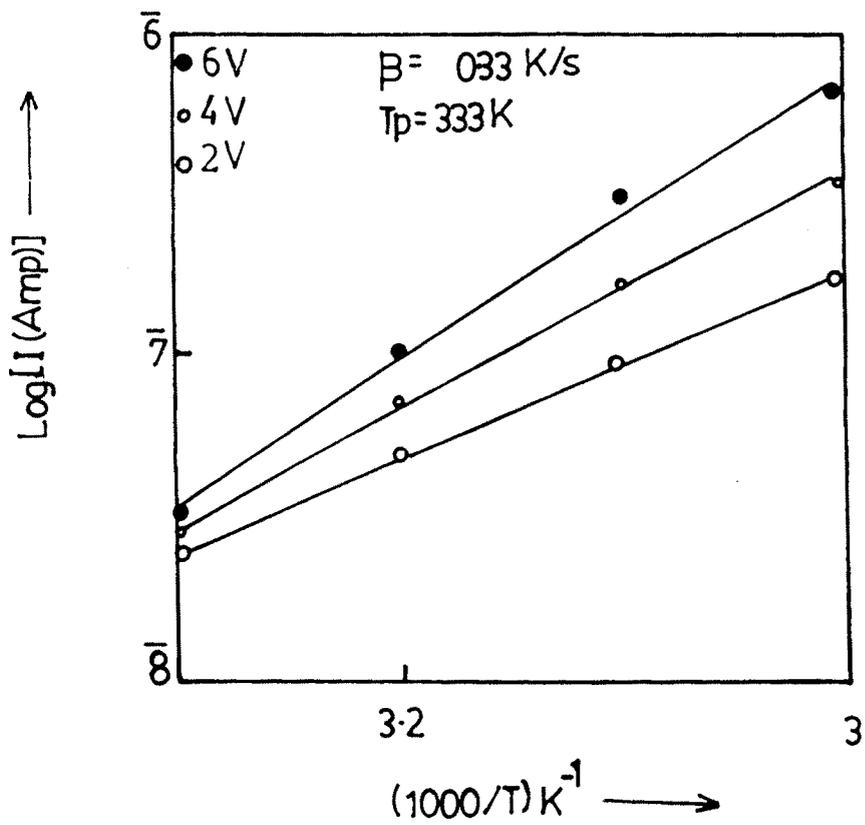**Fig. 5.8(a)** Log I versus 1000/T of acid doped Pani film polarised at 308 K

Fig. 5.8(b) Log I versus 1000/T of acid doped Pani film polarised
at 333 K

Pyroelectric activity is generally attributed to dipolar orientation which involves the rotation or motion of the permanent dipoles within the polymer upon the application of the field. Also the space charge polarisation, involving the displacement of ions or injection of charge carriers from the electrodes, contributes to the pyroelectric activity [14]. The peak observed in the low temperature range may be attributed to the dipolar orientation process. The peaks observed in the high temperature range could be attributed to charge injection process.

Table 5.1 Electrical parameters

Film Thickness (μm)	Polarizing Temperature (K)	Polarizing field 10^{5} (V/m)	Peak Temperature (K)	Capture cross-section(m^2)	Relaxation Parameter τ_0 (sec.) x 10^{-5}	Relaxation Parameter τ_m (sec.)
[Pani-EB]	308	4	375	5.32×10^{-31}	2.63	11.6
16		8	375	5.18×10^{-31}	2.46	10.7
		12	375	5.51×10^{-31}	5.35	24.3
	333	4	360	7.29×10^{-31}	8.02	35.9
		8	360	1.45×10^{-31}	7.41	33.3
		12	360	1.16×10^{-31}	6.80	30.6
[Acid Pani]	308	2.8	333	7.52×10^{-31}	2.51	11.9
15		5.7	333	7.69×10^{-31}	2.24	10.3
		8.6	333	8.37×10^{-31}	1.10	44.8
	333	2.8	378	3.93×10^{-31}	1.49	6.6
		5.7	380	2.93×10^{-31}	2.03	8.8
		8.6	380	4.22×10^{-31}	1.67	7.4

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