# Investigation of Traps density in Poly(9-vinylcarbazole) using Thermally Stimulated Discharge Current Technique

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**Abstract -** In this paper the results of thermally stimulated depolarization current (TSDC) for pure poly(9-vinylcarbazole) (PVK) and PVK doped with ferrocene, thermoelectrets are presented. The measurements of TSDC has been carried out in temperature range 30 to $170^0$ C with steps $5^0$ C in function of different polarizing fields at constant polling temperature. The TSDC spectra comprises two maxima, namely β and α peak with their respective location around $100^0$ C and $155^0$ C. β peak was attributed to the dipolar nature and α peak was assigned to a space charge trapping mechanism in the investigated material. The Trap energy is evaluated from the Garlick- Gibson plot of initial rise method. Similarly other parameters such as relaxation time, total charge release are evaluated. It is observed in present study that the value of the activation energy reduce according to the increasing the concentration of ferrocene molecules as dopant and it is found at poling temperature $100^0$ C and poling field 50 kV/cm for β peak of pure PVK, 0.73 eV and 2% ferrocene doped PVK, 0.24 eV.

**Keywords:** TSDC, PVK, activation energy, traps, total charge release, poling temperature, ferrocene

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## 1 Introduction

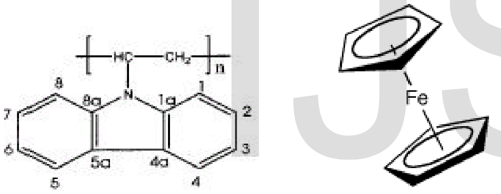
The most well known study of molecular motion is the study of relaxation processes, take place inside the polymers. In these studies almost two techniques are used, the first is dielectric spectroscopy (DS) and the other is the thermally stimulated depolarization current (TSDC). Thermally stimulated depolarization current is a most popular technique for investigation of charge storage and transport processes in high resistive materials **[1]**. A lot of work has been published on TSDC in polymeric materials during the past few decades **[2-4]**. Thermally stimulated current (TSC) one gets information concerning the trap structure of dielectric materials **[5]**. There are several methods to determine the properties of trap centers in polymeric materials and semiconductors. Among them, thermally stimulated depolarization current measurements are distinguished by the ease with which the experiments are performed and the detailed information provide on trap states **[6, 7]**. Various dielectric relaxation processes in polymers can be accurately described by applying the thermally stimulated depolarization current (TSDC) technique **[8]**. The TSDC technique essentially consists of two steps, in the first step, a thermoelectret state is formed in the investigated polymers and then in the second step, the depolarization current spectra at a constant heating rate are obtained. The main advantage of this technique is its high sensitivity, which makes it possible to detect very low dipolar or carrier concentrations.

Thermoelectrets effect was discovered in 1925, when Eguchi solidified a mixture of carnauba wax, resin and beeswax in presence of a high DC electric field **[9]**. The energy absorbed during the charging process resulted in space charge polarization by trapping of positive and negative charge at the interstitial sites **[10]**. However, the role of various polarization processes and their relative contribution to the electrets state of the polymers is not yet fully understood. Particularly, the space charge relaxation mechanism and the details of trap structure (including the trap distribution in energy and also over the volume of the polymer) are still to be well understood.

The purpose of the present work is to obtained further information concerning the deep and shallow defects in undoped PVK and doped PVK using well-established technique of TSDC measurements.

## 2 Materials and Methods

The material used in the present study was poly(9-vinylcarbazole) (PVK) supplied by Aldrich Chemical Co. USA, having a glass transition temperature ($T_g$) ~ $200^0$ C molecular weight average Mw ~ 1,100,000 product number 182605, CAS number 25067-59-8, refractive index 1.683 and density 1.2 g/ml at $25^0$ C was obtained. The structure of macromolecule of PVK and ferrocene are given as below figure (2.1).



(a) (b)

***Figure (2.1) (a) Chemical structure of PVK monomer (b) Chemical structure of Ferrocene molecule***

For the preparation of the thin film samples, polymer obtained was used as such without any further purification/recrystallization. Dopant ferrocene was used of Merk make. In present study, chloroform (AR-Grade) was used as a solvent for preparation of thin films. The thickness of the film varies was monitored as per selection of concentration of solution. Thin film samples obtained using solution casting technique was optically transparent.

For the preparation of polymer thermoelectrets in this study, thin film sample was sandwich between circular aluminum electrodes of the required size and mounted on spring loaded sample holder. The whole assembly was kept in a digitally temperature controlled electric oven for thermal and electrical treatment. After achieving thermal equilibrium at a predetermined polarizing temperature $T_P$ , a DC electric field i.e., polarizing field $E_{P,}$ was applied for polarizing time $t_{P,}$ 90 minute. The sample was the cooled down at room temperature under the presence of applied poling field. The field was then removed and sample short circuited for 15 minutes to remove stray charges. Now getting the TSDC spectra, according to experimental setup figure (2.2) connection plug $K_3$ and $K_4$ was closed and sandwiched thermoelectrets is heated at constant heating rate β.

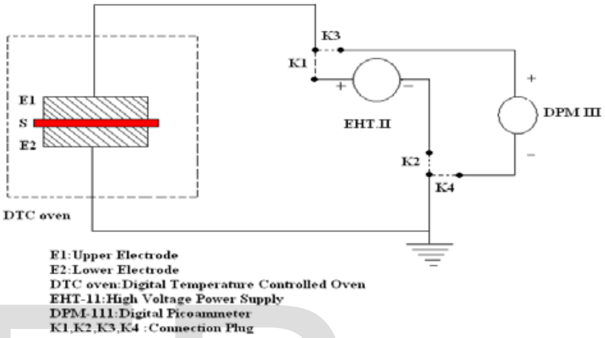


***Figure (2.2) Experimental setup of TSDC measurement***

The depolarization current is recorded as a function of temperature using DPM-III digital picoammeter with accuracy~$10^{-12}$ Ampere.

In this study TSDC spectra were obtained on poly(9-vinylcarbazole) and 2% ferrocene doped PVK of 55 μm thickness with experimental parmeters as follow: $T_P = 100^0$ C, $E_P$ = 50 kV/cm, $t_P$ = 90 min. $T_f = 30^0$ C and heating rate $\beta = 3^0$ C/min. The depolarization kinetic data i.e. activation energy, total charge release and relaxation time were calculated and listed in table 1 and 2. The activation energy was evaluated using the Arrhenius equation

$$I(T) = A\exp(-\frac{E_{ac}}{kT})$$

Where A is a constant, $E_{ac}$ is activation energy, T is the absolute temperature and k is the Boltzmann constant. By plotting $\ln I$ as a function of (1/T), one gets a straight line with the slope $(-\frac{E_{ac}}{k})$. The relaxation time was determined using the formula

$$\tau(T) = \frac{1}{\beta}\left(\frac{kT_m{}^2}{E_{ac}}\right)$$

Where $T_m$ is the temperature corresponding to the TSDC peak point. The relaxation time $\tau(T)$ of dipole is affected by the parameters of heating rate β, peak temperature $T_m$ and activation energy $E_{ac}$ .

The total charge release is obtained using the following relation

$$Q = S/\beta\int_{T_0}^{T} I(T)dT$$

Where S is the sample area and β is the heating rate. It gives the direct information about decay of stored charges. The charge released from these traps may be due to the thermal excitation and motion of molecular chain that causes the lowering of trap depth.

Experimentally value of total released charge (Q) is determined by Gaussian fit TSC peak and the total charge released in proportional to the area under the peak.

## 3. Results

The Thermally stimulated discharge current (TSDC) spectra of poly(9-vinylcarbazole) pure and doped with 2% ferrocene have been shown in figures 3.1(a) and 3.2(a) for different polarizing fields $E_P$ (25 kV, 50 kV, 100 kV) at fixed polarizing temperature $T_P$ =$100^0$ C. Two peaks are observed first β peak around temperature $90^0$ C to $110^0$ C and second $\alpha$ peak found between $150^0$ C to $160^0$ C. Figures 3.1(b) and 3.2(b) show the initial rise plot corresponding to TSD spectra of figures 3.1 (a) and 3.2(a) for pure and doped PVK thin films (thickness 55 μ m).

### 3.1. Effect of Polarizing Field $E_P$

**1.** Figure 3.1(a) shows the TSD thermograms for pure PVK at $T_P$ = $100^0$ C for three different fields (25 kV/cm, 50 kV/cm, 100 kV/cm). Two peaks (β and $\alpha$) are found for each polarizing field. The magnitudes of both peaks corresponding to each poling field increase by increasing the strength of poling fields. For initial poling field (25 and 50 kV/cm), β and $\alpha$ appear at nearly $105^0$ C and $155^0$ C respectively but at poling field 100 kV/cm the position of both peaks change and they appear at $100^0$ C and $150^0$ C respectively. Activation energies $E_{ac}$, associated with peaks of figure 3.2(a) are determined from the slopes LnI(T) versus 1000/T of corresponding to initial rise plots from figure 3.1(b). The others parameters like as relaxation time τ(T), total charge released Q are placed in table 1 and 2.

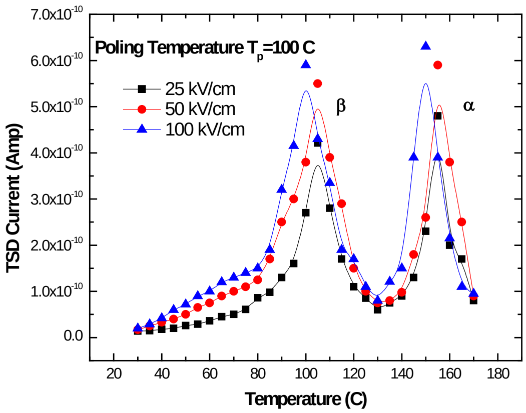


*Figure (3.1)(a) Variation of TSD Current versus Temperature with different poling field at poling temperature 100 C for pure PVK sample*

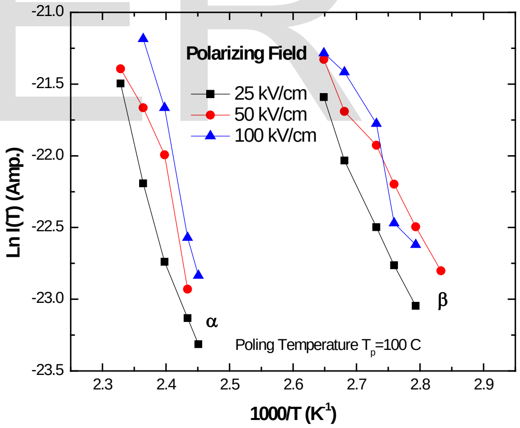


*Figure 3.1(b): Initial Rise Plots for different peaks of figure 3.1(a)*

**2.** Figure 3.2(a) represent the TSD thermograms for 2% ferrocene doped poly(9-vinylcarbazole) at poling temperature $T_P$ = $100^0$ C for polarizing fields (25 kV/cm , 50 kV/cm and 100 kV/cm) respectively. Plots of thermograms displayed similar nature but the magnitude and area under the peaks of β and $\alpha$ increase with increase in poling temperatures as well as poling field.

Figure 3.2(b) shows the initial rise plots for TSD spectra of figure 3.2(a) for each β and α peaks corresponding to poling fields 25 kV/cm, 50 kV /cm and 100 kV/cm at polarization temperature $T_P = 100^0$ C. The slopes of the curves determined the value of trap energy or activation energy, which are reducing almost with increasing poling fields.

Table 1.0, displays the values of evaluated depolarization parameters.

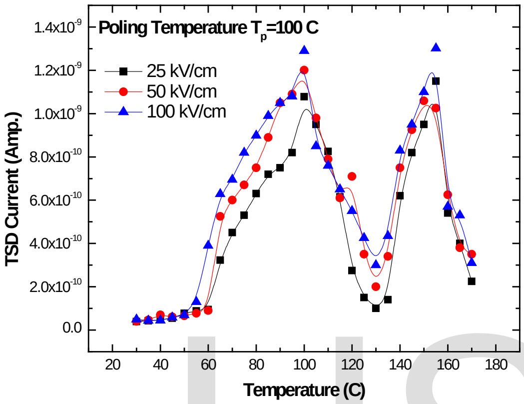


*Figure 3.2(a): Variation of TSD current versus Temperature with different Poling field, at poling temperature $100^0$ C for 2% ferrocene doped PVK sample.*

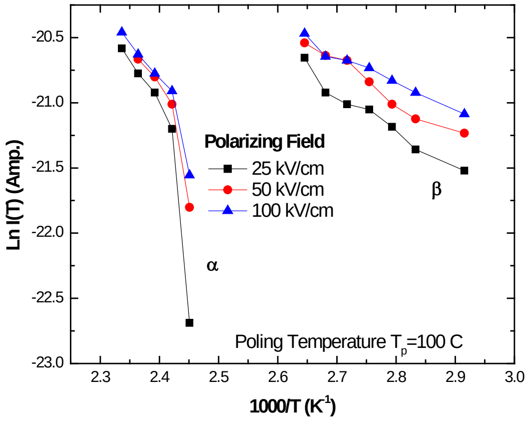


***Figure 3.2(b): Initial rise plots for different peaks of figure 3.2(a).***

## 4.0 Discussion

The thermograms of pure and ferrocene doped poly(9-vinylcarbazole) show regular behavior in their TSD spectra, showing uniform distribution of relaxation time. Generally polar polymer exhibit two or more relaxation peaks in their TSD spectra. Following parameters are affected the TSD spectra as seen in present study.

### 4.1 Affect of Poling Fields

Figures 3.1(a) and 3.2(a) represents the affect of poling fields on pure poly(9-vinylcarbazole) and 2% ferrocene doped PVK at different polarizing fields for fixed poling temperature, $100^0$ C. They show two relaxation peaks, first peak β appears at about temperature $100^0$ C and second peak α arises at temperature $155^0$ C i.e., around $T_g$ in all the cases and figures 3.1(b) and 3.2(b) show their initial rise plots. In each case, two peaks (β and α) are observed with their peak temperature ($T_m$) almost independent of $E_p$ but the peak current ($I_m$) increases with increase in poling fields. This increment in case of α peak is more pronounced than that in β peak.

One of the arguments advocated for distinguishing a dipolar polarization and space charge polarization is based on the field dependence of the TSDC properties, such as the peak current, peak temperature and charge released. The linear dependence of charge released and the peak current on polarization field strength is a characteristic of dipolar origin whereas in the case of space charge polarization, the peak current and charge released will show a non-linear variation with polarizing field strengths.

For a dipolar peak, the peak temperature will be independent of poling fields as well as poling temperature, whereas the peak temperature depends on the poling fields and temperature of the space charge polarization. The linear field dependence of peak current suggests that the TSDC spectra may be either due to dipolar origin or migration of charge carriers through microscopic distances with trapping. The increasing value of peak current with poling field and the observed activation energy values indicate that the peak may be contributed significantly by dipolar and ionic polarization.

### 4.2 Affect of Impurity

Earlier it has been discussed that PVK is a hole donating and ferrocene is an electron donor, therefore charge transfer complexes (CTCs) may be formed between them. Due to impregnation of ferrocene in PVK chains, creates conductive path ways for charge carriers and prevent their trapping at particular sites in the molecular chains. Some workers are also having same opinion of weaker trapping of carriers [11]. Ferrocene also enhances the conductivity of the polymer.

PVK doped with ferrocene exhibit pronounced field affect as compared to pure PVK. In doped system, the magnitude of peak current increases with field. For $T_P = 100^0$ C and $E_P = 100$ kV/cm peak current for β for pure PVK is found to be $5.9 \times 10^{-10}$ Ampere whereas it is $12.9 \times 10^{-10}$ Ampere for 2% ferrocene doped PVK. For α peak the corresponding values are $6.3 \times 10^{-10}$ (for pure PVK) and $13.0 \times 10^{-10}$ Ampere (for 2% ferrocene doped PVK). Increase in magnitude may be due to the increase in mobility of the carriers [12]. Inclusion of ferrocene in poly(9-vinylcarbazole) has developed, perhaps, a space charge cloud by filling all the traps present in the polymer matrix. At high temperature negative currents are found perhaps due to the contribution from net charges. It is also not improbable that up to these higher temperatures trapping sites would be destroyed and charges of only one sign give unidirectional current. High values of activation energies may be taken as standing proofs for this reason.

### 5.0 Conclusion

On the basis of preceding discussion, following conclusions may be derived.

**(1)** The dipolar relaxation process ($\beta$-relaxation) appears due to side chain of carbazole groups.

**(2)** $\alpha$-peaks occur due to the joint motion/deorientation of the back bone chain and side chains of PVK.

**(3)** As increase in poling fields helps in releasing and mobilizing the charges easily but the peak temperatures remain unaffected.

**(4)** Dipolar relaxations have been found mainly responsible mechanism in present case.

**(5)** Introduction of ferrocene in PVK forms strong complexes, prevents the trapping of charge

strong complexes, prevents the trapping of charge carriers, enhances the conductivity by increasing the mobility of the charge carriers.

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**TABLE 1.0 : TSDC parameters for 2% ferrocene doped Poly(9-vinylcarbazole) samples at $T_P$=100 C, with different Poling field.**

| Poling field $E_P$ (kV/cm) | Peak | Peak current (Amp) ….x $10^{-11}$ | Peak Temperature ($^0$C) | Activation energy (eV) | Relaxation time Sec. | Charge released ...x$10^{-11}$(Coul.) |
|---|---|---|---|---|---|---|
| 25 | β | 107 | 105 | 0.26 | $9.21 \times 10^2$ | 28.4 |
| | α | 115 | 155 | 0.60 | $5.17 \times 10^2$ | 9.51 |

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|---|---|---|---|---|---|---|
| 50 | β | 120 | 105 | 0.24 | $9.92 \times 10^2$ | 61.7 |
| | α | 105 | 155 | 0.51 | $5.93 \times 10^2$ | 8.82 |
| 100 | β | 129 | 105 | 0.16 | $8.92 \times 10^2$ | 41.8 |
| | α | 130 | 155 | 0.45 | $6.92 \times 10^2$ | 9.35 |

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