

Exploration of space charge behaviour of polyvinyl carbazole using measurement of thermally stimulated discharge current

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Abstract : Measurements of thermally stimulated depolarization currents (TSDC) have been employed to investigate the space charge behaviour and molecular motion in polyvinyl carbazole (PVK) foil samples at different poling fields and temperatures. One relaxation peak was observed around 70–110°C. It was found that with increasing applied electric field the order of peak current increases and peak shifts towards lower temperature side. The order of current for samples poled at 50°C was higher than the samples poled at 60°C. The activation energy decreases with the increase in poling field and temperature. The current maxima occurring above the polarizing temperature, have distributed relaxation times. The analysis of the results suggest that intense charge trapping in surface and bulk traps and of the injection of carriers from electrodes under strong field at near surface region created by heterocharge.

Keywords : Polyvinyl carbazole, thermally stimulated discharge currents, charge trapping, heterocharge.

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1. Introduction

Polymer films which are polarized in a strong electric field at an elevated temperature and are cooled with the field on, show semipermanent electric polarization which persists for years at room temperature; they are called polymer electrets [1]. Electrets formed by thermal methods are referred to thermoelectrets. The measurement of thermally stimulated current (TSC) which is caused by the thermal release of trapped charge carriers into either the conduction or valence band giving rise to TSC maximum, have been widely used to determine the density and energy distribution of charge carrier trapping centers in solids. A TSC peak arises in fundamentally different ways

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for band transport in the presence of traps and for thermally activated hopping. In the first case classical theories [2] assumes temperature controlled detrapping of charge carriers and either fast transport in the conduction band or recombinations in the bulk. The peak parameters allow one to obtain information about the depths, densities and possibly the distribution of traps which released the charge carriers. The second approach assumes that carriers hop from one localized state to another without ever moving in an extended state. These carriers are transported through the sample until they reach the electrode and the decrease of TSC is due to absorption of the carriers by the electrode. This approach allows one to derive information on the transport process [3]. The TSDC technique is a basic tool to identify and evaluate the dipole reorientation process, trapping and recombination levels in electrets and widely used to investigate the nature of various mechanisms in polymeric dielectrics.

Polyvinyl carbazole (PVK) displays a wide range of physical and chemical properties which are interesting as far as basic research and applications are concerned. The present paper reports the results of thermally stimulated discharge current measurement on solution grown polyvinyl carbazole samples to understand the mechanism of transport of the charge carriers during polarization.

2. Experimental details

The isothermal immersion technique was utilized for preparing polyvinyl carbazole (PVK) foil samples. The solution was prepared in a glass beaker by dissolving 5 gms PVK in 100 ml of chemically pure dimethyl formamide (DMF) at 40°C. The solution was kept for 24 hours to get a homogeneous and transparent solution. The solution thus prepared was then poured onto an optically plane cleaned glass plate floating on mercury. The solvent was allowed to evaporate in an oven at 50°C for 24 hours to yield the desired samples. This was followed by room temperature outgassing at 10^{-5} torr for a further period of 12 hours to remove any residual solvent. The plate was then drawn slowly out of the solution at a rate of 0.2 mm s^{-1} , leaving a uniform film on the plate. Samples thus obtained were uniformly smooth and could be easily peeled from the glass surface. The preconditioned samples were sandwiched between aluminized electrodes over a central circular area of 36 mm diameter. The thickness of the sample was of the order of $50 \mu\text{m}$, which was estimated by measuring the capacitance of the fabricated sandwiches. By using aluminium electrodes of 1.6, 2.6 and 3.6 cm in diameter it was observed that even the smallest currents measured were proportional to the electrode area. This indicates that the current flows through the bulk of the samples and not around the edges. Different steps for the preparation of a thermoelectret are as follows : (i) the sample is heated to the desired polarizing temperature T_p ; it is kept at T_p for some time (In the present case, 1 hour) to reach thermal equilibrium; (ii) then an electric field (E_p) is applied at T_p and kept on for a period of polarizing time (t_p), it is then cooled slowly under the field application to room temperature. The

field is then removed. The current was recorded with an electrometer (600B, Keithley) which was carefully shielded and grounded to avoid ground loops or extraneous electrical noise, as a function of applied field and temperature. The polarized samples were subsequently short-circuited for an arbitrary time of 10 min, so as to remove any frictional and stray charges present. The short circuit TSCs were then recorded by reheating the samples at a linear rate of 3°C/min [4–6].

3. Results

The experimental conditions under which the thermally stimulated discharge currents were measured are summarised below.

Polarizing field (E_p)	–	100–300 volts
Polarizing temperature (T_p)	–	40°, 50° and 60°C
Heating rate	–	3°C/min
Electrodes	–	Aluminium (both sides)

The thermally stimulated discharge current (TSDC) spectra for polyvinyl carbazole (PVK) films polarized with polarizing fields 100, 200 and 300 volts at temperatures 40°, 50° and 60°C are illustrated in Figures 1–6 for similar electrodes (*i.e.* Al-Al). The initial rise plots (*i.e.* $\log I$ vs. $1000/T$) for these figures are shown in Figures 7–12. The value of activation energy (Table 1) has been calculated from these initial rise plots. The points taken for the calculation of activation energy are in the initial rising part of the peak.

Table 1. Values of activation energy (eV) corresponding to polarizing fields.

Temp (°C)→	40		50		60	
	T_m °C	eV	T_m °C	eV	T_m °C	eV
Field (volts)↓,						
100	100	0.27	100	0.26	105	0.25
200	95	0.21	90	0.20	95	0.19
300	90	0.16	70	0.18	75	0.15

3.1. Field dependence :

The polarizing field dependence of TSDC thermograms was investigated by polarizing the PVK films with different fields 100, 200 and 300 volts at various fixed temperatures (40, 50 and 60°C).

The field dependent TSDC thermograms for PVK films are shown in Figures 1–3. The curves are generally characterized by one broad peak located in between 70–105°C. In general, the magnitude of TSD current increases with increase in the polarizing field, however the position of the peak maxima is found to be independent of E_p and shifts, towards lower temperature.

3.2. Temperature dependence :

The temperature dependence of TSDC thermograms was investigated by polarizing PVK

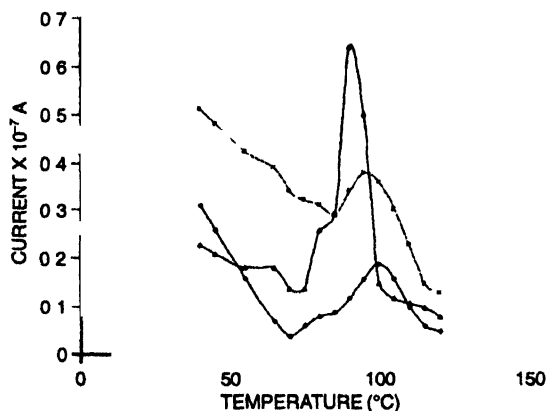


Figure 1. Thermally stimulated depolarization current of polyvinyl carbazole (PVK) sample poled at temperature 40°C with various fields : \blacklozenge - 100, \blacksquare - 200 and \blacktriangle - 300 volts

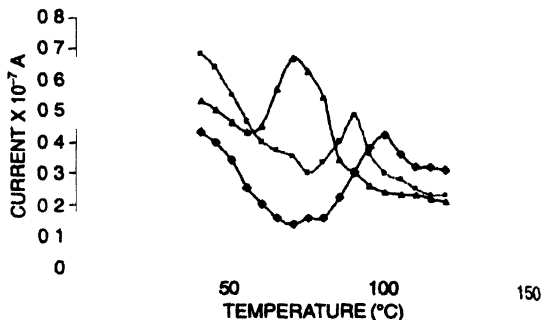


Figure 2. Thermally stimulated depolarization current of polyvinyl carbazole (PVK) sample poled at temperature 50°C with various fields \blacklozenge - 100, \blacksquare - 200 and \blacktriangle - 300 volts

film at different temperatures 40°, 50° and 60°C with various fixed polarizing field 100 200 and 300 volts.

The temperature dependence TSDC thermograms for PVK films are shown in Figures 4–6. The curves are characterized by a peak located between 70–100°C. The magnitude of the current increases with polarizing temperature. The TSDC peak shifts towards lower temperature side as the polarizing temperature increases.

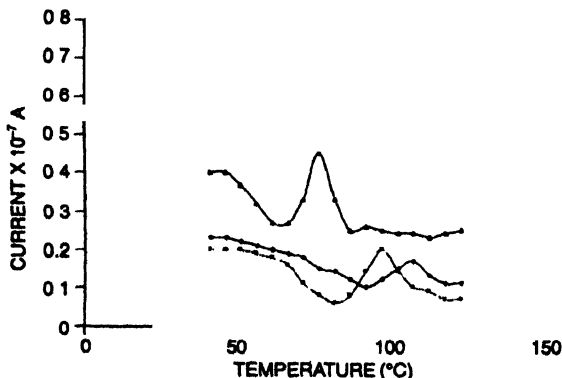


Figure 3. Thermally stimulated depolarization current of polyvinyl carbazole (PVK) sample poled at temperature 60°C with various fields : \blacklozenge - 100, \blacksquare - 200 and \blacktriangle - 300 volts.

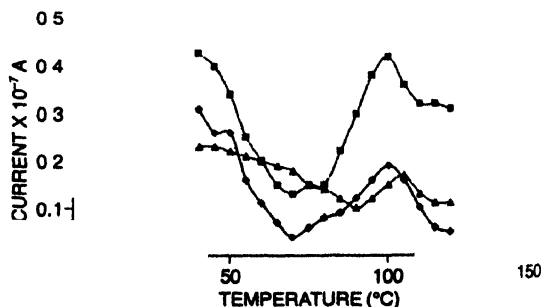


Figure 4. Thermally stimulated depolarization current of polyvinyl carbazole (PVK) sample with a field of 100 volts at various temperature : \blacklozenge - 40, \blacksquare - 50 and \blacktriangle - 60°C.

It is evident from all the observed TSDC thermograms (Figures 1–6) initially the current starts at higher order and gradually it decays upto a certain temperature and after that with the increase in polarizing field or temperature it increases and a broad peak appears. Current saturated at the end of thermograms. In all the thermograms the

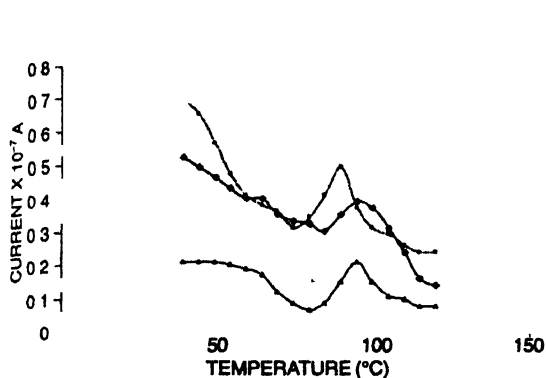


Figure 5. Thermally stimulated depolarization current of polyvinyl carbazole (PVK) sample with a field of 200 volts at various temperature : \blacklozenge - 40, \blacksquare - 50 and \blacktriangle - 60°C.

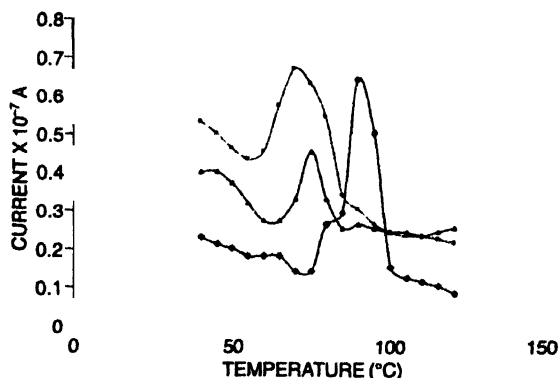


Figure 6. Thermally stimulated depolarization current of polyvinyl carbazole (PVK) sample with a field of 300 volts at various temperature : \blacklozenge - 40, \blacksquare - 50 and \blacktriangle - 60°C.

order of current for the samples poled at 60°C found lower than the samples poled at 50°C.

In order to clarify the nature of TSDC peak, the series of observations were taken at different field and temperature conditions. In the present paper only representative results are shown.

4. Discussion

When the polymer film is heated up to a temperature close to its glass transition temperature, the dipoles and the free charges present in the polymer are mobilized. Application of a field causes an alignment of dipoles and a drift of the free charges. After some time, when the sample is cooled to room temperature, the main chains of the polymer are immobilized and the free charges are frozen-in. When heating of the thermoelectret is started space charge of opposite polarity combined to give rise to the depolarization current. Then the current is contributed by the disorientation of dipoles and the release of ionic charges from the defects or dislocation. As the thermal treatment is continued the charge carriers are injected on the dielectric surface from the electrodes and due to the Maxwell-Wagner effect, also disappear and become the TSD current. Thermal activations at a constant rate causes the release of charges due to their mobilization giving a peak at the site of maximum release of charges [7].

The origin of TSD current can be attributed to the following mechanisms.

- (i) Polarization due to polar side group/dipole alignments;
- (ii) Ions trapped in defects on dislocation in crystalline region;
- (iii) Space charge build up due to the migration of ions over microscopic distances and
- (iv) The space charge injected from the electrode.

Polyvinyl carbazole (PVK) is a polar polymer, the major contribution to the polarization

may be due to alignment of the dipoles under the effect of the electric field at high temperature. In the present investigation, TSDC thermogram exhibits a broad peak (70°–105°C) and it represent presence of multiplicity of relaxation mechanism. The multiplicity of relaxation in PVK may be because of the presence of trapping levels of different depths. The appearance of the peak implies that the injection of ions may be significant in this polymer. It is also possible that PVK contains a high number of impurity molecules prior to field treatment and these molecules are dissociated in to various ionic species [8].

The discharge current available at the external circuit may be due to the rearrangement of ordered dipoles. From Table 1, it is evident that the activation energy varied between 0.16 to 0.27 eV *i.e.* charge carriers are trapped in levels distributed over a range of 0.11 eV, characterized by a continuous relaxation distribution. Further more, as the polarizing field increases the barrier height of the traps is lowered, accounting for the observed decrease of the activation energy with increasing polarizing field. The increasing trend of current is in conformity with increase of conductivity of PVK with field and this can be attributed to the increase in local conduction in the thermally generated defects in PVK. In the present case, various results obtained may be explained by stepwise superposition of various phenomena responsible for persistent polarization in electrets [9].

The broadness of the peak may be explained by assuming a distributed, or multiple, dielectric relaxation caused by a variation in activation energy, when the rotation of the dipoles does not proceed in the same environment. Alternatively, it may be due to a distribution in relaxation times, when the rotational masses of the dipoles are not equal. The broadness of the peak in the present case is, however, most likely to be a function of distribution in relaxation times, because the peak occurs near the T_g of the polymer, where the side groups move in unison with the main chain. Because the distribution of dipoles in the amorphous phase is most likely to be random, it may be expected that this is a complex process involving both distribution of the activation energy and relaxation times [10].

As the temperature is increased more charge is trapped in shallow traps. This larger amount of trapped charge on release gives a higher current and a higher sharp peak. With a further increase of temperature, due to increased mobility, carriers are shifted to deeper traps. Release from such deeper traps being difficult, the current show a decrease trend [11].

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_j ", and an attempt to escape frequency " ν_j ", the detrapping time constant for each trapping level can be assumed to be of the form

$$\tau_i = [\nu_i]^{-1} \exp(U_i/kT) \tag{1}$$

$i = 1, \dots, N_0$

where N_0 is the total number of trapping levels, τ_i the mean detrapping time for i -th trapping level, k is the Boltzmann constant and T is the temperature.

For a trapping level to contribute to the charge motion in the sample during charging, τ_i 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 higher temperature peak is expected to shift toward lower temperature with increase in poling temperature which is experimentally observed in the present case [12].

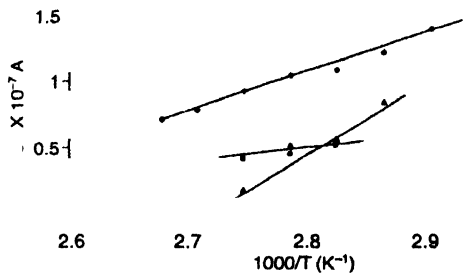


Figure 7. Log I vs. $1000/T$ (K^{-1}) for polyvinyl carbazole (PVK) sample poled at temperature $40^\circ C$ with various field \diamond - 100, \blacksquare - 200 and \blacktriangle - 300 volts.

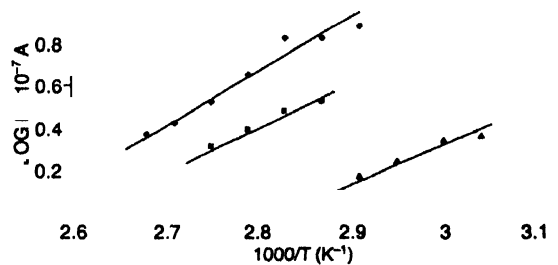


Figure 8. Log I vs. $1000/T$ (K^{-1}) for polyvinyl carbazole (PVK) sample poled at temperature $50^\circ C$ with various field \diamond - 100, \blacksquare - 200 and \blacktriangle - 300 volts.

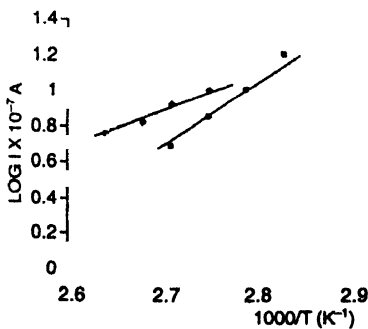


Figure 9. Log I vs. $1000/T$ (K^{-1}) for polyvinyl carbazole (PVK) sample poled at temperature $60^\circ C$ with various field \diamond - 100, \blacksquare - 200 and \blacktriangle - 300 volts.

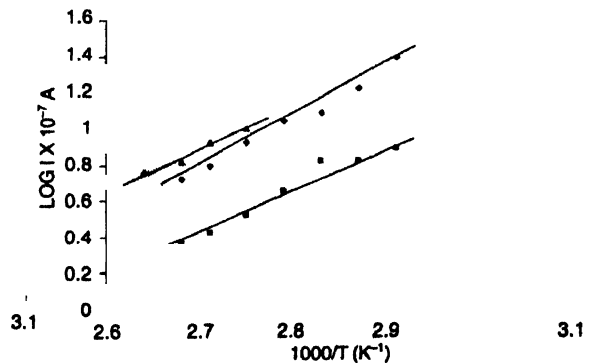


Figure 10. Log I vs. $1000/T$ (K^{-1}) for polyvinyl carbazole (PVK) sample poled with a field of 100 volts at different temperature : \diamond - 40, \blacksquare - 50 and \blacktriangle - $60^\circ C$.

The magnitude of peak increases with the increase in the field of polarization and this could be explained on the basis that under the influence of electric field detrapped excess charge carriers increases resulting in the corresponding increase in peak

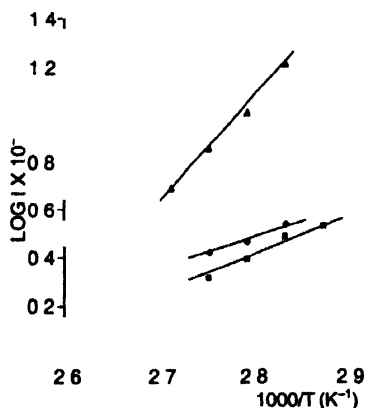


Figure 11. Log I vs $1000/T$ (K^{-1}) for polyvinyl carbazole (PVK) sample poled with a field of 200 volts at different temperature : \blacklozenge - 40, \blacksquare - 50 and \blacktriangle - 60°C

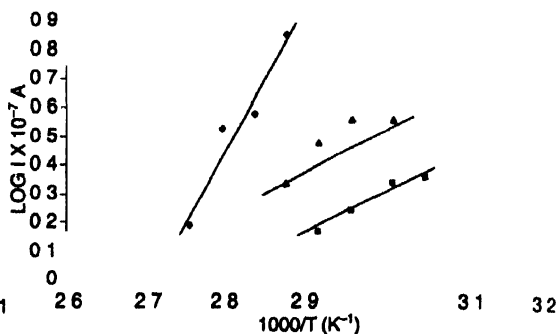


Figure 12. Log I vs. $1000/T$ (K^{-1}) for polyvinyl carbazole (PVK) sample poled with a field of 300 volts at different temperature : \blacklozenge - 40, \blacksquare - 50 and \blacktriangle - 60°C

current. The shift of the current maxima occurs because the excess charges are generally depleted or enhanced, creating a lower or higher deriving field and charges may get swept less or more quickly towards the electrodes.

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