CHAPTER IV

THERMALLY STIMULATED DISCHARGE CURRENT OF PURE AND IODINE DOPED PVP FILMS
4.1.1 General introduction about TSDC

Thermally stimulated discharge current (TSDC) technique is a powerful experimental method for explaining the morphology of a dielectric (polymer) and several other phenomena related to charge storage in dielectrics. In the last decade, TSDC has emerged out of forming wide scope of applications for studying dielectric relaxation process in pure and iodine doped polymers. In other words a more general review is presented of thermally stimulated discharge, a technique that has contributed significantly to current underlying of charge storage and charge decay process in electrets. This method of TSDC consists of measuring with a definite heating scheme, the current generated by the build-up or the release of a polarized state to an equilibrium state in a solid dielectric sandwiched between two electrodes.

The more general experimental procedure involves four steps for TSDC measurements:

1. The application of a d.c. bias $V_p$ at a particular $I_p$ for a polarizing time $t_p$;
2. Cooling under this bias voltage up to room temperature.
3. Removal of bias voltage from the sample and
4. Heating of a sample at a constant rate with the recording of current as a function of temperature.
By heating the polarized sample with a suitable heating rate up to or above the polarizing temperature, the release of charges speed up and gives rise to a current which first increases with increasing temperature and then decays when supply of charges is depleted. This technique also allows the determination of dipolar relaxation time and activation energy from the measurement of depolarization current. In TSDC thermograms (i.e., plot of current vs. temperature) peaks are observed during the thermally activated transition from the polarized state to an equilibrium state. Generally, current peaks are observed in higher temperatures where dipolar orientation, ionic migration or carrier release from traps are activated as a total polarization usually arises from a combination of several individual effects with various relaxation times. 3-7

4.1.2 TSD work on polymers and other materials

Faraday 8 theorized about electret properties due to application of external field, when he referred to a "dielectric which retains an electric moment after the externally applied field has been reduced to zero. The word "Electret" was first coined in 1892 by Heaviside.9 Equchi 10,11 formed electrets by the application of an external electric field to the cooling melt. The evidence for the presence of two different types of charges and identification of charges is observed in a series
of fundamental studies by Gross 12,13 in 1949(s). Apparently a large number of polymers and their various aspects have been investigated over the past few years and this trend is still continue in the field of polymers 3-9 because the use of TSD is expanding most rapidly and most successfully. Comprehensive studies on a large number of polymers and co-polymers have been conducted by van Turnhout, 1Vanderschuren 14,15 and other co-workers. 17

Turnhout and then Vanderschuren 14-17 systematically varied the temperature and duration of polling of PMMA samples and invented a new technique of fractional polarization for the samples. Their results have been observed in terms of distributed spectrum of depolarization, kinetic data and thus Vanderschuren with his co-workers 14-17 successfully explained the depolarization effect for dipoles with distributed activation energy under different polarizing conditions. Linken and Vanderschuren 17 confirmed that TSD is the only convenient method to measure the rubber-glass transition and a large amount of charge is released at Tg specially in the case of long chain polymers hence this method is more sensitive because it gives a peak due to release of charges near Tg. For the group of Tuclose Chatain 18,19 has focussed on polyamides (semi aromatic, aromatic and aliphatic) and polyglycience. The TSD measurements of these hydrophilic polymers 19-20 are found to depend strongly
on their water content. Lacabanne and Chatain 20 studied the TSD of two polynaphthoamides and critically reviewed the use of WLF equation. Several papers about these researches have appeared recently.3-7 There is a considerable interest in the TSD of polyethylene (PE) because of its use for high voltage cables in power transmission.23 The TSD of PE has been reported by Fischer et al.21,22 and Lacabanne et al.20 In the last decades, TSD work on polymers and polycarbonates has been reported by Vanderschuren et al.14 and Lilly et al.24 Recently the TSD studies of disordered polycarbonates and poly vinyl butyral have been reported by P.G. Mehadru and his co-workers.25 Some work on TSD of cellulosic materials has been observed by G.A. Baun.26 More recently the major work on cellulosic derivatives have been reported by Pillai et al.7,27 in polarized and unpolarized samples. Dielectric measurements on bio-materials have been reviewed by Schwarz 28 and Rosenberg et al.29 Mascarenhas 30,31 has indicated several possibilities for charge storage in bielectrets and also hinted that TSD might be useful for diagnosis of diseases. The piezo and pyroelectric properties of bio-materials are also of fundamental interest of life processes. Measurements of piezo electric coefficient Vs. temperature are made by Fukada et al. and his coworkers.31,32 Since 1974, the TSD work of polymers has been reported in the Annual conference on "Electrical insulation and
Dielectric phenomena. Stupp and Carr have observed the preferred orientation of polar side group in PAN (polyacrylonitrile) samples which possess the permanent dipoles. They have also observed the detrapping of charge carriers associated with high temperature peak (170°C) in TSD measurements of PAN samples. In the last few years, the TSD work is mainly concentrated on the impurity doped polymers and biopolymers because the doping of suitable impurities in polymers (or biopolymers) may form charge-transfer-complexes. The iodine doping in PVAc or PVByr have been observed as a charge-transfer-complex. The structural informations of a biopolymer can be determined by TSDC behaviours and these materials may form charge-transfer-complexes by ionic nature of suitable organic impurities. Recently, Gancheva and Dinev have observed the doping action of lead sulphate in PVC samples.

4.2.1 Present investigations of TSD

PVP is a growing polymer (also similar structure to biopolymer) in the field of pharmaceutical sciences hence it is necessary to introduce about the TSD work of PVP especially in the form of thin films (1 to 10 mum). The experimental studies of thermo electret and dielectric properties has been proposed for the present investigations. In the TSD study the vacuum evaporated electrodes of different metals have been used (i.e., Cu, Ag, Au or Al). The thin films of PVP are
made by isothermal immersion technique 41 as discussed in
Chapter II of Experimental Techniques. The different types of
electrode metal combinations have also been used here and these
TSD measurements of PVP must have a lot of information about the
dipolar polarization, dielectric relaxations, space charge
mechanisms and some structural modifications. The different
concentrations of iodine have been used for doping of PVP
samples and TSD measurement must have the informations about the
CTCs or other type of complex information.

4.3 Theory of Thermally Stimulated Discharge Current

Bucci and Fieschi 42 for the first time put forward a
theory of TSD method and now-a-days this theory has been
generalized by different workers with some modifications.1,43,44
In a simple case here, only one type of non-interacting dipoles
of moment \( \mathbf{p} \) and relaxation time \( \gamma \) are considered. The polymer is
heated to a temperature above its glass-rubber transition and a
polarizing field \( E_p \) is maintained up to a suitable time which
may be considered large as compared to the relaxation time of
dipoles at that polarizing temperature when the polymer is
quickly cooled with the applied field, then the polymer (main)
chain is immobilized and consequently most of the dipoles or
charges are "frozen in" condition. The polymer is cooled down
to such a low temperature that the relaxation time of the dipoles
at this temperature is of the order of several hours. The
polarized state of the dielectric is warmed with a constant heating rate (5°C per minute), the relaxation time decreases and a depolarization current \( I(t) \) may be detected when the dipoles/charges lose their preferred orientation. The depolarization current after some peaks drop to negligibly small value (zero). This current is called TSD current.

If the sample is polarized at temperature \( T_p \) by a field \( E_p \), the polarization will acquire an initial equilibrium \( P_0 \) is given by:

\[
\sqrt{P_0} = N \frac{\mu^2 E_p^2}{3 kT} \quad (4.1)
\]

where \( k \) is the Boltzmann constant, \( N \) is the dipole concentration, \( \mu \) is the dipole moment. The discharge current is simply the rate of polarization and can be given by:

\[
I = \frac{P_0}{\gamma} \exp \left[ -\int_0^t \frac{dt}{\gamma} \right] \quad (4.2)
\]

where \( \gamma \) is the relaxation time. The total charge released is given by:

\[
Q = \int_0^\infty I \, dt \quad (4.3)
\]

The relaxation caused due to local motion of polar side group can be written as:

\[
\gamma = \gamma_0 \exp \left( -\frac{J}{kT} \right) \quad (4.4)
\]
where \( \gamma_0 \) is a constant, \( J \) is the activation energy, \( k \) represents the Boltzmann constant and \( T \) is the temperature. For a uniform heating rate, one can say:

\[
T = A + Bt
\]

(4.5)

where \( A \) and \( B \) are constants.

Combining Equations 4.2, 4.4 and 4.5, expression for \( I(t) \) can be written as:

\[
I(t) = \frac{p_0}{\gamma_0} \exp \left[ -\frac{J}{kT} - \frac{1}{\beta \gamma_0} \int_t^T \exp \left( -\frac{J}{kT} \right) \right] dt
\]

(4.5)

Under limited conditions, the discharge current due to the release of charge carriers from traps, has the same form as given in Equation (4.5) but with different constant in front of exponential. By differentiating Equation (4.5) and equating \( \frac{dT}{d\gamma} = 0 \), the temperature \( T_m \) can be written as

\[
\gamma_0 = \frac{k T_m^2}{B \gamma_j \exp \left( -\frac{J}{k T_m} \right)}
\]

(4.7)

Thus \( T_m \) is independent of \( T_p \) and \( E_p \) conditions. The low temperature of glow peak curve from Equation (4.5) can be written as:

\[
\ln I(t) = C - \frac{J}{kT}
\]

(4.8)

where \( C \) is a constant. From this method the activation energy \( J \) can be determined by plotting a semilog of \( I(t) \) Vs. \( 1/T \). This
method is known as initial rise method of Garlick and Gibson. Grossweiner has extended this technique to other dielectrics and also used to find the capture cross-section and attempt-to-escape frequency. The straight line obtained as Bucci-Fleshi-Guidi (BFG) plot has a slope equal to E/k and like the initial rise method, this procedure does not require a strictly linear heating rate.

4.4 Experimental Arrangements

4.4.1 Preparation of Sample:

Commercial grade PVP (mol. weight 40,000) used was supplied by Loba-Chemie, Bombay. Films of pure and iodine doped are made from solution of PVP in chloroform (AR grade). The films are made by isothermal immersion technique as described in Chapter II of Experimental procedure. The known impurities of iodine are also soluble in chloroform and thus the different quantities of iodine are added in PVP solution. The different iodine concentrations used for PVP samples are 0.5, 0.10, 0.50, 0.75 and 1.0% by weight.

4.4.2 Electrode Systems:

Vacuum evaporated aluminium, copper, silver and gold are used as lower electrodes for M₁ - PVP - M₂ structure. The similar electrodes of copper or aluminium are used for Cu - PVP - Cu
or Al – PVP – Al configurations. The dissimilar electrode materials are also used for TSDC measurements: Ag – PVP – Al, Cu – PVP – Al, and Au – PVP – Al.

4.4.3 Experimental arrangement for TSDC measurements

To form the electrets of PVP a suitable polarizing time has been chosen at a certain desired temperature. This is known as polarizing temperature (Tp). For the polarizing field an arrangement is made with the help of DC batteries of different values. A calibrated variac with a suitable arrangements has been used to control the constant temperature of the shielded chamber. After giving sufficient time for polarizing field to the sample, the chamber was cooled immediately within the limited time with field still maintained to the sample used. In the last of TSDC measurements, the sample was heated with a uniform heating rate with the help of calibrated heater and other attached arrangements. The heating rates tested with higher accuracy by plotting the graphs between time in minutes and corresponding temperatures of the chamber.

4.4.4 Ep, Tp and tp conditions of PVP samples:

The samples were polarized by different fields at certain temperatures (Tp) i.e., 70°C, 85°C, 95°C, 125°C, 145°C and 175°C maintained for 1 hour duration (3.6 x 10³ sec.). The polarizing field varied from 0.5 x 10⁵ to 3.5 x 10⁵ V cm⁻¹.
4.5 Results of T3DC measurements:

(A) Al - PVP - Al System - Variation of \( t_p \)

At first the depolarized current has been observed in PVP samples (\( \approx 1 \) \( \mu \)m) as a function of polarizing time \( t_p \). Here the samples are polarized with identical conditions of \( E_p \) (2.7 \( \times \) 10\(^5\) V cm\(^{-1}\)) and \( t_p \) (30\(^\circ\)C) but different polarizing times are chosen. The \( t_p \) is varied from 0.9 \( \times \) 10\(^3\) to 7.2 \( \times \) 10\(^3\) sec. The different curves A, B, C and D in Fig. 4.11 correspond to different polarizing times of 0.9\( \times \)10\(^3\), 1.8\( \times \)10\(^3\), 3.6\( \times \)10\(^3\) and 7.2\( \times \)10\(^3\) sec. respectively. The discharge curve 'A' exhibits only a single peak at 77\(^\circ\)C, whereas all the other curves C, D and E exhibit two peaks in distinct regions of temperatures. The lower temperature peak (peak I \( \approx 830 \pm 4 \)\(^\circ\)C) has been observed for all the discharge curves with a peak magnitude of 10\(^{-9}\)A. The second peak has been observed for B, C and D in the vicinity of higher temperature of discharge current with a higher order of peak magnitude. The position of peak I has been observed with a regular shifting towards higher temperature region for increasing \( t_p \) conditions and in the case of peak II a shifting in position has been observed in a opposite direction (i.e., lower temperature region) for B, C and D curves (10\(^{-9}\)A). The values of activation energies related to peak I and II (\( E_1 \) and \( E_2 \)) are found to be 0.62 \( \pm \) 0.02 and 1.13 \( \pm \) 0.2 eV respectively. These values are also in good agreement with Bucci's method \(^{47}\) (Table 4.1).
4.5.1 Temperature Variation

Five different polarizing temperatures are selected for the polarization of samples on the basis of peak temperatures as already observed (Fig. 4.11). The TSD results of PVP films polarized at 55°, 95°, 125°, 145° and 175°C temperature conditions (Tp) are shown in a set of Figs. 4.12, 4.13, 4.14, 4.15 and 4.16 respectively. In every polarizing condition of Tp, the field is varied from 0.6x10^3 to 3.5x10^5 V cm⁻¹. Somewhere much higher polarizing fields are not used to the samples at higher Tp conditions. Some discharge curves have also been omitted from the thermograms due to similar nature of TSD current.

For both the peaks, the activation energies and relaxation times are evaluated by initial rise method and these values are listed in Table 4.11 (Figs. 4.18 and 4.19).

In all the thermograms, the two well resolved peaks have been observed for all the fields. The lower temperature peak has been observed with a widely distributed temperature range in TSD thermogram, while peak II has a limited distribution in its peak temperature range (frequency also, Table 4.11). At the polarizing conditions of 145°C and 175°C of Tp, the order of peak currents for both the peaks have been found the same (i.e., 10⁻² A). The different discharge curves A, B, C, D and E (Fig. 4.17) correspond to different polarizing temperatures of 55°C, 95°C, 125°C, 145°C and 175°C. In thermogram (Fig. 4.17) the position of peak I
TSD curves of PVPyr thin films polarized at 30°C with \( E_p = 2.7 \times 10^5 \text{ Vcm}^{-1} \) for different polarizing times (S);
Curve A, \( t_p = 0.9 \times 10^3 \); Curve B, \( t_p = 1.8 \times 10^3 \); Curve C, \( t_p = 3.6 \times 10^3 \);
Curve D, \( t_p = 7.2 \times 10^3 \).
TSD curves of PVPyr thin films polarized at 65°C with different polarizing fields (V/cm):
Curves A, $0.6 \times 10^5$; Curve B, $0.9 \times 10^5$; Curve E, $1.8 \times 10^5$; Curve F, $2.7 \times 10^5$; Curve G, $3.6 \times 10^5$.

Fig 4.12
TSO curves of PVPyr thin films polarized for $3.6 \times 10^3$ S at 95°C with different polarizing fields (V/cm);
Curve A, Ep $0.6 \times 10^5$; Curve B, Ep $0.9 \times 10^5$; Curve C, Ep $1.2 \times 10^5$;
Curve D, Ep $1.5 \times 10^5$; Curve E, Ep $1.8 \times 10^5$; Curve F, Ep $2.7 \times 10^5$.

Fig 4.13
TSD curves of PVPy thin films polarized for $3.6 \times 10^3$ S at 125°C with different polarizing fields ($V/cm$),
Curve A, $E_p 0.6 \times 10^5$; Curve B, $E_p 0.9 \times 10^5$; Curve C, $E_p 1.2 \times 10^5$,
Curve D, $E_p 1.5 \times 10^5$; Curve E, $E_p 1.8 \times 10^5$. 

Fig 4.14
TSD curves of PVPyr thin films polarized for $3.6 \times 10^3$ (S) at 145°C with different polarizing fields (V/cm):
Curve A, $0.6 \times 10^5$; Curve B, $0.9 \times 10^5$; Curve C, $1.2 \times 10^5$; Curve E, $1.8 \times 10^5$.

Fig 4.15
TSD curves of PVPyr thin films polarized for $3.6 \times 10^3$ (S) at 175°C with different polarizing fields (VCm$^{-1}$):
Curve A, $0.6 \times 10^5$; Curve B, $0.9 \times 10^5$; Curve C, $1.2 \times 10^5$; Curve E, $1.8 \times 10^5$. 

Fig 4.16
TSD curves of PVPyr thin films polarized for $3.6 \times 10^3$ S with $2.7 \times 10^5$ V/cm at different polarizing temperatures (°C):

- Curve A, Tp 65
- Curve B, Tp 95
- Curve C, Tp 115
- Curve D, Tp 145
- Curve E, Tp 175

Fig 4.17
Initial rise method for low temperature peak (Al - PVP$_{yt}$ - Al)
Initial rise method for higher temperature peak (\text{Al-PVPy-Al})

Fig 4.19
has been found continuously shifting towards higher temperature region with increasing Tp conditions with two exceptional cases of discharge behaviours. These exceptional behaviours at temperatures 65° and 175°C for polarization are found with some special interest due to moisture effect and a temperature which is greater than Tq with space charge effects (detailed discussion in 4.5.3).

4.6 Discussions

4.6.1 General discussions:

The origin of TSD current can be attributed to the following mechanisms.\textsuperscript{48,49}

(i) Polarization due to polar side group/dipole alignments.
(ii) Ions trapped in defects or dislocations in crystalline regions.
(iii) Space charge build-up by the migration of ions over microscopic distances and
(iv) The space charges injected from the electrodes. The first two processes give a uniform volume polarization\textsuperscript{23} with hetero-charge and the third process gives non-uniform homocharge or heterocharge depending upon the electrode-dielectric workfunctions while the fourth process is related to non-uniform homocharge only due to injected electrodes from metal.\textsuperscript{3} The long chain PVP seems to be disordered material in its discharge behaviour and the different behaviour can be explained in terms of disorientation of polar side groups or the phase transition behaviour which correspond
to a large amount of released charge. Many biopolymers such as proteins, gelatins and other materials contain some different groups of oxygen, nitrogen, carbon and hydrogen atoms in their structures as side or main chains. In the polymerization of these monomers the unshared electron pair may behave as the "free radical" (solid) especially in case of carbonyl group of double bond coupled with amide bond structures. These structures are also observed in PVP, PVCz (polyvinyl carbozole) and other polymers. The process of "free radical" behaviour of a structure may possess some different types of charges/ions such as proton and hydroxyl ion or the pair of electrons and holes especially in the presence of some water molecules in the structure. In PVP structure the carbonyl group of double bond possesses in the side chain position while the nitrogen atom is also attached to the main and side chain with amide bonds. The different possibilities for explaining the discharge behaviour of polarized samples are in favour of different types of charge carriers/ions which may originate due to the presence of different active groups. This may also be possible in the presence of moisture in the PVP samples (Chap.III). As discussed in SCE measurements that the polar moiety of the long chain structure in pyrrolidone ring which itself possesses a net dipole moment of 1.9 D. This polar group of PVP can be oriented in the field direction in the presence of polarizing field and the disorientation of these polar groups attributed to peak I in
TSDC results. On the other side electrons of carbonyl group and a proton and electron as a charge pair (opposite charges) near these active groups of PVP may be in favour of some ionic separation in two different compartments due to "free radical" (solid)\textsuperscript{51,52} behaviour. A large amount of charge is associated with peak II due to its complete phase transition behaviour along with ionic dipoles due to solid free radical behaviour. In this phase transition behaviour all types of different carriers/ions must be associated with this process and a large amount of released charge may form a peak in higher temperature region of TSD current. One of the aspects of electret research in biophysics concerning biopolymers is that water absorbed to these materials as a so called structured form. The absorbed water in PVP may also influence the electret state of the polarized sample. The TSDC of protein,\textsuperscript{57} collagen and gelsatin\textsuperscript{28-32} in the dry state are explained in terms of electrical energy storage in two different compartments of ionic charges. One is thus led to suspect that dipoles of water absorbed in biopolymers in a structured way to macromolecules could have energy levels for dipole rotation in the local field of the biopolymer macromolecules.\textsuperscript{58} According to Tan et al,\textsuperscript{55} PVP is known to be a highly hygroscopic material and the equilibrium water content varies with relative humidity. According to them\textsuperscript{55} the absorbed water in PVP has a marked effect in lowering the value of $T_m$, and the correct value of it is $171^\circ\pm 1^\circ C$ for zero water content. The absorbed water may also act
as a dipole and the electret state of PVP may be influenced by water traces. The absorbed water may also be dissociated in the form of different carriers/ions such as:

\[
\text{HOH} \rightleftharpoons H^+ + OH^- \tag{4.9}
\]

as discussed in discussion of SCE, the water may have probably a weak hydrogen binding with PVP (weak complex formation).

\[
> N - |\overset{\text{C}}{\overset{\text{O}}{\text{O}}} + \overset{\text{H}}{\text{O}}| \text{H} \rightleftharpoons > N - \text{COOH} + H^+ + e^- \tag{4.10}
\]

Hence there may be a possibility of weak internal field within the polymer due to ionic separations and these separated ionic charges may either oppose the external field or in some favourable conditions there may be the joined polarizing effects in some other direction. In this manner the internal field is assisted by the external field and this may lead to some inconsistencies in TSD results because the origin of polarization is related to ionic separation of charges and desorption of absorbed water molecules at Tg or other lower temperatures.

4.5.2 Lower Temperature Peak (TSDC)

If the polarization field is applied to the sample then it is possible that all types of dipoles/polar side groups may be oriented in the field direction. Thus a polarized state could result in the sample when the polarized sample is heated, the polarization due to dipolar orientation and ionic separation of charge carriers at Tg will manifest in the form of different peaks (peaks I and II). Peak I is attributed to disorientation of polar
side groups and a rise in discharge current may be possible in lower temperature region than the rubber-glass transition. The presence of water molecules may also be possible in PVP films due to its hydroscopic nature. The dipolar nature of this peak has been observed from the amount of charge released (Q) and corresponding polarizing fields (Fig. 4.19). The activation energy associated with this peak (Ea = 0.62 ± 0.02 eV) is quite appreciable for a dipolar nature of peak which must be related to disorientation of polar groups of PVP. Some contribution towards this may also be possible due to water as a dipole as suggested in hydroscopic biopolymer materials. Several workers have observed such type of dipolar peak in T&D measurements due to heavy adjacent groups, especially in polar polymers such as PVAc, PEO, PAN, etc. A peak may also be attributed to the disorientation of aligned dipoles of permanent nature. Throughout 1 and Vanderschuren have observed the similar nature of dipolar peak in polar polymers which is due to disorientation of polar side groups. According to Vanderschuren the peak position of dipolar peak very much depends upon the polarizing conditions such as field and temperature etc. A distributed temperature region of this type of peak in different conditions can be observed and this may also be in favour of disorientation of some polar moiety with a distributed spectrum of energies. Here the pyrrolidone group may have different possible orientations/rotations with respect to main chain of the polymer and thus a distributed energy may be
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B | 448 | 0.9 | 3.6 | 448 | 1.26 | 4.92x10⁻¹³ | 1.61x10³  | 2.32x10⁹ |
C | 448 | 1.2 | 3.6 | 447 | 1.26 | 1.62x10⁻¹² | 1.65x10³  | 1.3x10⁹ |
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<th>Dτ(°K)</th>
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**Peak II**

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### Table 4.14 - Depolarization Kinetic Data for Iodine Doped Samples

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<th>U(eV)</th>
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<th>T(_m)(s)</th>
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### Peak II

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associated with TSD results. The dionic polymer 27 (such as PVP) can be polarized even at room temperature and this may also suggest the disorientation of some adjacent group with respect to backbone position. The activation energy $E_a$ related to peak I seems to be slightly higher in comparison to the energy related to disorientation of other polar moieties in polymers. 41,54,55 This may be probably due to presence of adjacent heavy polar group of PVP. The adjacent heavy polar group may be associated with much amount of energy for orientations in possible directions with respect to main chain because the carbonyl group and nitrogen atoms in the side groups are in active positions for polarisation behaviours. 53,54 These facts of TSD results are also in favour of a higher band gap for PVP material which may be needed for higher amount of energy for orientation of pyrroolidone ring. The freedom of adjacent group for rotation is many time restricted because it is allowed for orientation at the two points of the long chain. The restriction in possible orientations of side group is based on the structure of PVP itself. 55 The polar moiety is in the side chain and it possesses double bond but this is also attached to nitrogen atom of the amide group with amide bond and thus the nitrogen atom is attached at two different points of the chain (backbone). Thus the different freedom of rotations about the carbon-oxygen bond or nitrogen-carbon bond is severely restricted 5,54 and it may certainly require a slightly higher amount of energy for
orientation of polar side groups. When the polarized sample is heated with a uniform heating rate then the polarized state of the polar side group has a equilibrium position in certain temperature ranges. The current magnitude being of the lower value for peak I in comparison to Im of second peak, this may suggest the possibility of distributed relaxation process in the temperature range of 80°-120°C. The distributed relaxation with distributed frequency of TSD cycle must be associated to a process of secondary nature in the presence of water molecules as a dipole. The distributed peak temperatures in different cases of Ip and Ep of TSDC may be a adjoining polarization effects of PVP and water molecules. The higher order of current corresponds to 45°C can be explained with the help of moisture effect in comparison to other case of 95°C of polarization with lower amount of Im (TSD current) may suggest the possibility of disorientation of absorbed water molecules along with polar groups. Thus the current associated with this peak is thermally assisted randomisation of polar groups probably in the presence of absorbed water molecules in the temperature range of 80°C and at this condition the segments of main chain are in frozen conditions.¹ From the thermograms (Figs. 4.12 to 4.14) it can be easily seen that the best resolution of both the peaks has been observed in three different conditions i.e., when the sample is polarized at room temperature or at 145°C or at 175°C (Ip) conditions. The other conditions of Ip are not found
suitable for the polarization of PVP samples. From different TSD results, two different types of relaxations have been observed i.e., one in the lower temperature range of 80°C–120°C and the other in the higher temperature range of 171°C ± 5°C. The lower temperature peak is found as a distributed one while the higher temperature peak has been found with a limited distribution of frequencies. For the TSD results in different cases, Vanderschuren 51,52 has suggested different types of relaxation processes for the limited and distributed frequencies. The peak I is certainly a dipolar peak and it is attributed to disorientation of polar side group of PVP and peak II is associated with the primary relaxation process which occurred in the temperature range of rubber-glass transition of PVP (Tg). The non-appearance of this peak in second heating run is also in favour of secondary relaxation process which has already attended a equilibrium position in the first heating run of TSD measurement.3

4.5.3 Peak II

The activation energy associated with higher temperature peak (peak II, \( E_2 \)) is found of the order of 1.23 ± 0.2 eV which may be supposed to be much higher in comparison to peak I, \( E_1 \) and this value of \( E_2 \) suggests the possibility of some ionic process 51,53,55 rather than electronic charge carriers and this must be related to charge carriers of ionic nature as electrons and protons, hydrogen and hydroxyl ions. These different
carriers/ions may have different types of opposite nature of charges such as proton and electron (pair), hole and electron (pair) or H$^+$ and CH$^-$ etc. The behaviour of these opposite pair of charges can be observed similar to a large dipole in polarization of the samples. These created dipoles can be oriented in the field direction in the presence of some external field as suggested by Gastra and Serra (1971). PVP also exhibits the properties of solid free radical probably at the temperature of phase transition hence the ionic and other electronic charges may certainly be present during the polarization of the sample associated with peak II. The discharge behaviour of peak II may be considered in terms of a solid polyelectrolyte behaviour containing different types of carriers/ions. The structure of different compartments in different regions which contain different types of charges/ions as also considered in measurements of proteins or other like structures. In PVP the portions of different charges/ions are due to presence of different active groups. According to Chaterjee et al. the active groups are (1) carbonyl (C=O) and (ii) nitrogen atom with carbon and oxygen; PVP possesses the presence of nitrogen and oxygen in asymmetric positions, hence the asymmetric distribution of electronic charges may be possible due to different bond lengths and different types of atoms. The specific binding tendencies of different ions are very important in explaining the poly electrolyte behaviour of PVP and other
polymers and it is to these glosy state transitions owe their efficiency as exchange of ions. Another possibility of many structural defects may seem to be possible such as chain irregularities or broken chains in long chain network along with dissolved molecules of water. Thus all types of dissociated ions may be possible including opposite charge pairs at Tc and in a long chain structure, different types of conformational rearrangements of main chain may be possible at Tc. In this manner a possibility of releasing the carriers/ions from the polarized state seems to be possible in the above cited temperature of TSD range (Tc). Here the structure also gets loosened to some extent and according to Linkens and Vanderschuren a large amount of charge may release in such a complete phase transition of the polymer. In this way all types of carriers/ions may release and a peak in higher temperature region (1750 ± 70°C) has been observed in discharge behaviour of polarized samples. Created dipoles may orient in certain possible directions and these may be liberated as a pair of opposite nature of charges in TSD measurements. The main chemical process (as a internal field) in complicated networks of structures such as poly-4 vinyl pyridine, protein or gelatin are directly connected with the transfer of energy and electrons, protons as well as ions thus produced cannot be explained within the framework of classical physics. A deficiency of ideas about purely chemical mechanism is found on considering the ion-exchange
mechanism at Tg and a complex network of conjugated chemical reactions may be possible by exchanging of electrons/ions. As discussed in SCE measurements (Chap. III) the transfer of electrons with hydrogen atom may be possible at electrode-dielectric interfaces in the presence of absorbed water and at the same moment the attention may be given for exchange of H⁺ and OH⁻ ions in the process of oxidation at Tg of PVP. This process may be possible only when PVP is impermeable to H⁺ and OH⁻ ions which may accumulate on different sides of the sample. The reduction of oxygen is also accompanied with the liberation of OH⁻ ions and thus PVP may have free charge carriers/ions (e⁻, H⁺ or CH⁻) at Tg. The complete phase transition behaviour of PVP is similar to a solid poly-electrolyte behaviour of a biopolymer 32,58 in which the active group has an additional property of self ionization.30,31 PVP films thus may undergo a sterio change in its structure above a certain higher temperature (≥ 170°C) and due to carbonyl hroup of PVP its structure may have suffered a ketoenol-tantomerism mechanism (sterio change).

The PVP can be polarized even at room temperature and from this fact a conclusion can be drawn that it must be a dipolar polymer in nature because dipolar polymer can be polarized at such a low temperature.2 In Fig. 4.11 the tp is varied from 0.9x10³ to 7.2x10³ sec. for PVP samples and the resolved peaks have been observed for 3.5x10³ sec. condition of tp. The discharge curve
A suggests incomplete polarization effect for insufficient time and thus a single peak has been observed in this condition. At the highest \( t_p \) condition of \( 7.2 \times 10^3 \) sec., the discharge current has been observed with a reduced peak magnitude which suggests the possibility of TSD current after a saturated effect of polarization condition (\( E_P = 7.2 \times 10^5 V \ cm^{-1} \)). The single peak in curve A corresponds to dipolar disorientation of polar side group while peak II is attributed to different types of carriers/ions released in primary relaxation process of PVP films. In Fig. 4.12, the sample is polarized with different \( E_P \) conditions but at \( T_p \) of 65\(^\circ\)C both the peaks are resolved but the order of currents for these found to be \( 10^{-9} \) to \( 10^{-8} \) A for different fields. This condition is not suitable for electret formation of PVP samples. Figs. 4.13 and 4.14 correspond to the discharge behaviour of PVP samples which are polarized at 95\(^\circ\) and 125\(^\circ\)C with different polarizing fields. At \( T_p \) condition of 95\(^\circ\)C the moisture effect has been greatly reduced and thus peak I has been observed with a lower (Im) peak magnitude. These conditions are not more suitable for electret formation of PVP films. The polarization is saturated at 145\(^\circ\) and 175\(^\circ\)C of temperature and all the curves exhibit two well resolved peaks in the thermograms, 4.15 and 4.16 with the same order of TSD current. A exceptional case of less depolarization current has also been observed due to some space charge mechanism.
as a shoulder of TSDC in high temperature range (220°C) when the sample is polarized at the temperature of 175°C. The mechanism of space charge as a peak is not fully grown in PVP samples but the TSD results of other type of PVP samples such as Cu-PVP-Cu, Ag-PVP-Al, Au-PVP-Al and Cu-PVP-Al space charge peak at much higher temperature range has been observed.

4.7.1 and 4.7.2 Results and Discussions

(Different electrode systems)

Cu-PVP-Cu, Ag-PVP-Al, Au-PVP-Al, Cu-PVP-Al.

The TSD thermoqram 4.21 exhibits the discharge behaviour of Cu-PVP-Cu system polarized at 145°C and the different discharge curves A, B and C correspond to different polarizing fields of 0.9x10⁵, 1.2x10⁵ and 1.5x10⁵ V cm⁻¹ (tp = 3.5x10³ sec.), two usual peaks have been observed in different ranges and these are attributed to disorientation of polar side groups (for peak I) and peak II is associated to the charge released at Tq (phase transition behaviour). In addition to these two peaks, a new peak (peak III) or 0 peak has been observed at much higher temperature range of TSDC measurements. The current magnitudes of Peaks II and III have been observed of the same order (10⁻⁹A) in Cu-PVP-Cu samples. The discharge behaviour of Ag-PVP-Al and Au-PVP-Al configurations (systems) are shown in Fig. 4.22.
Curves of Cu-PVPyr-Cu thin films polarized at 175°C with different polarizing fields (V cm⁻¹).

Curve B, 0.9 X 10⁵ ; Curve C, 1.2 X 10⁵ ; Curve D, 1.5 X 10⁵
TSD current spectra of PVPyr with structures of $A_2$ - PVPyr - Al and Au - PVPyr - Al polarized for $3.6 \times 10^5$ (S) at 125°C with different polarizing fields (V/cm).

$A_2$ - PVPyr - Al: Curve A, Ep 0.9 x 10^5; Curve B, Ep 1.5 x 10^5; Curve C, Ep 1.8 x 10^5.

Au - PVPyr - Al: Curve D, Ep 0.9 x 10^5; Curve E, Ep 1.8 x 10^5.

Fig 4.22
TSD spectra of PVPyr with structures of Cu-PVPyr-Al polarized for \(3.6 \times 10^3\) s with \(E_p = 0.9 \times 10^5\) V cm\(^{-1}\) at different polarizing temperatures (°C).

Curve A, Tp 65
Curve B, Tp 110
Curve C, Tp 125
Curve D, Tp 145

Fig 4.23
These samples are polarized under the identical conditions of $T_p$ and $t_p$ ($t_p = 3.5 \times 10^3$ sec.). The full curves A, B and C correspond to different polarizing fields $0.9 \times 10^5$, $1.5 \times 10^5$ and $1.8 \times 10^5$ V cm$^{-1}$ for Au-PVP-Al samples and the dotted curves D and E correspond to the polarizing fields of $0.9 \times 10^5$ and $1.8 \times 10^5$ V cm$^{-1}$ for Au-PVP-Al systems. In all the different curves A, B, C, D and E in Fig. 4.22, two well resolved peaks have been observed in the positive direction of current as per convention of heterocharge whereas peak III has been found in the temperature range of $214^\circ \pm 2^\circ$C ($10^{-7}$ to $10^{-6}$ Amp) in a direction which is opposite to both the peaks (i.e., negative).

The samples of Cu-PVP-Al system are polarized at different temperatures but with identical conditions of $E_D$ and $t_D$ ($t_p = 3.5 \times 10^3$ sec., Fig. 4.23). The discharge curves A, B, C and D correspond to different polarizing temperatures of $65^\circ$, $110^\circ$, $125^\circ$ and $145^\circ$C respectively. The activation energies for all the peaks are evaluated by initial rise method $^{45}$ and they are found as $0.61 \pm 0.05$, $1.13 \pm 0.1$ and $1.65 \pm 0.1$ eV for first, second and third peak respectively for Cu-PVP-Cu samples. The study of the influence of electrode material is undoubtedly one of the most reliable ways for distinguishing between dipolar ionic and injected charge carriers in TSCC results because the various materials used as connecting electrodes in independent experiments do not obviously affect the dipolar polarization but they may lead to release the excess charge of external origin.
owing to the net difference of work functions of the materials and their injecting factors. 69, 70 The different configurations of different metals have been used for detail analysis to differentiate the dipolar/ionic and space charge due to injected space charge carriers. 70, 71 The peak I is attributed to disorientation of polar dipoles, while peak II is contributed by a large number of charge carriers/ions. The ionic nature of this peak is similar as described in previous case of TSC results of Al-PVP-Al. Primary relaxation process of PVP is associated in the same temperature range in asymmetric electrode metal systems although this is also influenced by the work function 69 of different materials. The slightly different peak positions (peak II) in different cases have been observed in different electrode metal combinations and these results suggest that the liberated opposite pair of ions and carriers may be slightly affected by the work function differences of the different combinations as also described in SCE of PVP samples (Chap. III). This may be due to the different work functions of different electrode metals and in these results a possibility seems to be present that the internal field of PVP may get modified by different work functions of different electrode materials. The high value of activation energy of 1.75 eV is associated with peak III and it suggests the possibility of space charge mechanism produced by injected charge carriers from the electrodes. This value of $V_{III}$ is also in favour of self motion
of charge carriers/injected charge carriers (or ions) to some atomic distances $^2$ towards composite electrodes. Alternatively, there is also a possibility of homocharges due to air breakdown between dielectric and electrode interfaces as suggested by Gross $^1$ but it can be ruled out in this case since the vacuum deposited electrodes are used during studies. These charges of external origin are injected from the injecting nature of electrodes (metal) and some of these may get trapped in different trap levels hence another possibility of detrapping $^3, ^{59, 71}$ of trapped charged carriers may also be present. As suggested in previous discussions that PVP may have two different types of trap distributions due to its carbonyl groups and also due to difference of energy levels in different phases of amorphous and crystalline regions.$^3, ^{59}$ Space charge may also be affected by the neutralization process of charge carriers/ions near the electrode-dielectric interfaces. This phenomena of neutralization of charge carriers/ions is the usual phenomena at higher temperatures of the polymer films.$^{71}$ In PVP the segmental mobility may increased after the complete phase transition and thus the possibility of injection of charge carriers near the electrodes consequently seem and their drift to be possible by self motion of charge carriers/ions above the Tg range ($>$ $175^\circ$C). Above Tg of the polymer a sudden change in its volume (densification) may occur and due to this structural rearrangement of chains (segments) may be possible due to sufficient mobility of segments.$^1, ^2$
A marked electrode effect has been observed for the third peak and the direction and magnitude of current are very much dependent upon the choice of electrode materials and in this manner the injecting or ohmic contacts of the different electrode metals also depend upon the differences of work functions of metal used along with the work function of the polymer. The injection of charge carriers from electrodes have suggested by different workers when the electrode-dielectric contacts or ohmic or injecting. In this condition and also suggested in other polymers the work function of the polymer is in matching condition or greater than the work functions of the electrode materials \( \psi_1, \psi_{m1}, \psi_{m2} \) where \( \psi_1, \psi_{m1}, \psi_{m2} \) are the workfunctions of PVP and upper/lower electrode metals. From the results of space charge peak in different cases, a conclusion can be drawn that a higher order of workfunction may be possible for PVP and this must be related to the injection mechanism along with \( \psi_{m1} \) or \( \psi_{m2} \) of the electrode materials. The higher value of the workfunction of PVP must be related to the bio-chemical nature of oxygen-nitrogen with hydrogen and carbon which suggests the possibility of direct injection with some detrapping of carriers after the densification of the polymer and due to higher mobility of segments. Some of these injected charge carriers/ions which are opposite in nature may neutralize within the material or near the electrode-dielectric interfaces. Vanderschuren has observed the similar nature of space charge peak in polarized PMMA.
samples. In polycarbonate this space charge peak has been observed due to injected charge carriers from the electrode metals in dissimilar electrode systems. The contribution from detrapping of charge carriers is also found towards this peak III. The detrapping mechanism at such a higher temperature may also be possible in PVP films and thus after moving through some atomic distances of these carriers, they may get trapped to some deeper trap levels which are available for trapping due to presence of C = O in the structure. In this manner the injection mechanism is possible with subsequent trapping of charge carriers in deeper trap levels ($\approx 1$ eV). The superimposed of these "external and internal fields" may also interpreted in terms of TSD results of Cu-PVP-Al samples. The different types of informative results have been obtained in TSD measurements of Cu-PVP-Al samples which are polarized at different temperatures such as 55°, 110°, 125° and 145°C (Fig. 1, 23). These results can be interpreted in terms of "narrow window of polarization" of samples at different Tp conditions. Vanderschuren 51, 52 has observed similar type of results in polar polymers and then he introduced this term in explaining the TSD results. The discharge curve A in TSD results (Tp = 55°C) has been found with a single peak with a reduced peak current magnitude, while the other curves B, C and D (correspond to different Tp conditions of 110°, 125° and 145°C) have been found with two well resolved peaks along with a new peak (peak III) in opposite directions as per convention.73
Vanderschuren has proposed the similar nature of TSD results from the lower Tp conditions and these are supposed to be the fractional polarization effects of PVP samples. In this way the lower Tp conditions are not suitable or less effective for electret formation. In thermogram 4.23 a continuous shifting of peak position has been observed for peak II when the sample is polarized under appropriate conditions of increasing Tp conditions otherwise a lacking in polarization effects have been observed for lower Tp conditions of TSD results. The interaction between the external and internal applied field of PVP can also be treated as an important fact for the reversal effect of current magnitude after a certain limited conditions. Stupp and Carr have also suggested a similar behaviour of internal and external fields in polarized and unpolarized samples of PAN and a reversal of TSD current has been observed in polarized samples. From the above results a conclusion can be drawn that two different relaxation processes are involved in TSD of PVP samples along with a mechanism of space charge formation and thus the higher amount of energy must be needed in primary relaxation process due to conformational rearrangements of long chain (segments) or in the injection mechanism of charge carriers from the injecting electrodes.

4.8.1 and 4.8.2 Results and Discussions

(ISD of Iodine doped PVP Samples)

The discharge curves A, B, C and D in Fig. 4.31 correspond
to different concentrations of iodine 0.05, 0.10, 0.75 and 1.0 % by weight respectively and these samples are polarized under the identical conditions of temperature, field and time (Tp = 95°C, Ep = 2.7x10^5 V cm^-1). The peak magnitudes for second peak lies in between 0.35x10^-10 to 0.3x10^-9 A for A, B and C discharge curves of three different concentrations of iodine doped PVP films. A abrupt change (0.12x10^-9 A) in peak magnitude for the peak II has been observed in TSD measurements of 1.0% iodine doped PVP sample. The effect of polarizing fields on the fixed concentration of iodine doped (0.75%) PVP samples have also been observed and the samples are polarized under the identical conditions of Tp and tp (Tp = 95°C, tp = 3.6x10^-3 sec.). In Fig. 4.32 the different curves A, B and C correspond to different polarizing fields of 0.2x10^5, 1.8x10^5 and 2.4x10^5 V cm^-1 of iodine (0.75%) doped PVP samples.

**Discussions**

The polymer can be doped with different concentrations of iodine and there may be a possibility of complex formation between the dopant and dielectric as explained in case of spontaneous current emission of iodine doped PVP samples. Several workers have suggested a possibility of complex formation and in the present investigations the results can be interpreted in terms of CTCs between polymer and dopant.
TSD current spectra of iodine doped PVPy film polarized under identical conditions of $E_p = 2.7 \times 10^5 \text{ V cm}^{-1}$, $T_p = 95^\circ\text{C}$ and $t_p = 3.6 \times 10^3 \text{ s}$; Curves A, B, C and D correspond to different iodine concentrations 0.05, 0.10, 0.50 and 1.0 % by weight respectively.
TSD current spectra of iodine doped (0.50 % by weight) PVPyr polarized at 95°C with different polarizing fields (V cm⁻¹). Curve A, 0.9 × 10⁵, Curve B, 1.8 × 10⁵, Curve C, 2.4 × 10⁵, Curve D, 2.7 × 10⁵.
Initial rise method [Iodine doped PVP].
It has been proposed by Creswell\textsuperscript{23} that the total charge stored in a polymer electret and different mechanisms such as doping is very sensitive to the structure of the forming of polymer itself. This phenomena in PVP films is because of different active groups ($\text{\textgreek{N}} - \text{\textgreek{C}} = \text{\textgreek{O}}$) of polymer in molecular chains and the iodine doping may have the property of complex formation with different groups of PVP. A depolarization resulting from orientation of dipoles is only one which can be expected to be relatively less affected by iodine doping.\textsuperscript{74-75} In iodine doped PVP samples, the created dipoles (pair of opposite charges, H\textsuperscript{+} and CH\textsuperscript{-} or H\textsuperscript{+} and e\textsuperscript{-}) are related to peak II may also be influenced by iodine doping in different manner and the iodine doping may decrease the effective number of ionic dipoles which is related to primary relaxation of PVP films. A regular shifting of peak I has been observed towards higher temperature region for all the different iodine doped PVP samples, whereas peak II has been found shifting towards lower temperature region for a certain limit of concentration of iodine doped PVP samples (0.75\%) and reverse trend has been observed for the highest concentration doped in PVP films (curve D, 1.0\%). The doping effects of iodine in PVByr films\textsuperscript{4} have been found similar for peak magnitudes with different concentrations. The doping effects in polymer can determine the different mechanisms of dipolar and ionic polarization and the iodination of PVP may affect the ionic dipoles by forming the charge transfer complexes.
between them. The iodine–PVP complexes are found in the literature and thus a possibility of strong adsorption of iodine has suggested by the research workers. Several other complexes of PVP have also been reported with other materials such as phenols, congo red and with other polymers. Chaterjee et al. have suggested the complexing properties of PVP with other materials and these complexes are formed due to its active groups. Bublevski et al. have also suggested the complex formation between carbonyl group of PVP and OH group of polyphenol. According to Chaterjee these active groups of PVP are carbonyl group and tertiary nitrogen atom for complexing with organic materials may have also in a reactive position in certain higher temperature region and in this manner PVP may have the electrons to donate to iodine molecules:

\[ D^+ + A^- \rightarrow DA \]

The easier the iodination, the easier for the polymer to play the role of electron donor. The higher electronegativity of different atoms such as oxygen or nitrogen of PVP may also suggest the formation of CTCs with iodine in two different active positions. The side group of PVP ( electrons) may form CTCs by donating the electrons to iodine, or the nitrogen may also be involved in CTCs formation at certain higher temperature conditions after the side group rotation of PVP.
As observed in earlier experiments that the complexing between PVP and iodine is so strong that no apparent vapour pressure of iodine has been observed even in heating up to a higher temperature. In the present investigations of TSD of polarized samples (even unpolarized) of iodine doped PVP, a systematic increasing peak magnitudes have been observed with a regular shifting of peak positions. These results may have in this way informations about the nature of CTCs between PVP and different iodine concentrations. In these complexes the iodine may get absorbed as a whole of aggregates in the structure near the different active positions of PVP. The first peak in TSD measurements is associated with lower amount of energy, hence this must be attributed to CTC formation by polar side group with iodine and the disorientation of these polar groups may give rise to a peak. The higher amount of energy must be associated with the segmental motion of main chain and hence the CTC may involve in peak II.

The active group of PVP at higher temperature is the tertiary nitrogen atom attached to the main chain hence the iodine may transfer from the side chain to the main chain and this may be associated with higher amount of energy (≈ 1 eV). The two usual peaks have been observed in the discharge behaviour of iodine doped samples. The CTCs formations between PVP and iodine suggest the saturation tendency of the polymer structure by absorbing the iodine concentrations in different active positions.
peaks. The UV study of PVP and polyphenols have been studied by Bublevski et al. and they suggested the complex formation of PVP between carbonyl group and tertiary nitrogen atom.

The CTCs formed between PVP and iodine is more useful even than iodine due to its reduced germinal properties. The toxicity of iodine is thus reduced with PVP and for the same properties it is more useful in pharmaceutical sciences and with the help of present investigations of TSD results, the toxicity of PVP-iodine can be examined at much higher temperatures also. The reduction of activation energies of both the peaks are also in favour of CTCs formation. The strong absorption of iodine by the two different groups of PVP may also reduce the asymmetric distribution of charges by making CTCs and thus the "internal field" may reduce and the external applied field is more useful in electret forming properties. In this manner the iodine concentration is more useful with PVP structures and thus the toxicity of iodine is more reduced due to charge transfer complexes between them.
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