Field-induced thermally stimulated currents in poly (p-phenylene sulphide)

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Thermally stimulated polarization currents (TSPC) have been investigated in poly p-phenylene sulphide (PPS) in temperature region 30-250 °C under various polarization fields, ranging from 3 to 18 kV/cm and with different heating rates. The effect of high temperature annealing on TSPC behaviour has also been investigated. The TSPC spectra show the presence of a single peak (I_p) around 110 °C. This peak has been attributed to a weak polar nature of C-S linkage. A phenomenal rise of several order of magnitudes in the current dominated by conduction current is observed above 170 °C. During the successive cooling the current retains its positive polarity and in the 2nd TSPC cycle the peak P1 disappears due to temperature dependence of saturation polarization confirming the polar nature of this peak. The kinks observed in the TSPC spectra of annealed samples and with slow heating rates around 170 °C are due to the dipolar relaxation process associated with other linkage, a cross-linked structure formed due to high temperature annealing. The thermal variation in dielectric constant, deduced from TSPC spectra is in good agreement at low temperature, with the result obtained by other method.

1. Introduction

Owing to its possible application as conducting polymer, p-phenylene sulphide (PPS), a well-known high temperature polymer has drawn considerable attention in recent years. A detailed understanding of its various dielectric relaxation processes and transport mechanism becomes essential for their further progress in practical applications of PPS as conducting polymers. The Field-Induced Thermally Stimulated Current (FTTSC) technique is acknowledged to be a precise and powerful tool for such studies. It involves two mutually inverse processes: (i) the thermally activated transition from neutrality to polarized state, i.e. build-up of polarization and (ii) the thermally activated transition from polarized state to equilibrium state, i.e. dissipation of polarization, known as thermally stimulated polarization current (TSPC) and thermally stimulated depolarization current (TSDC) technique, respectively. Though the authors already carried out extensive TSDC studies in PPS, the relevance of the corresponding TSPC investigations are imperative because the comparison between the currents generated during construction and destruction of internal polarization furnishes some crucial clues not available from either of these. In fact, the TSPC technique is considered a comparatively more efficient diagnostic tool than TSDC in many respects. For example, it avoids the overheating of the test piece and eliminates the search for optimum poling temperature. Apart from this, the TSPC measurements give an idea of the temperature at which ohmic conduction becomes significant. This is necessary because after the onset of conduction the stored charges in a high-resistivity solid get quickly neutralized preventing the subsequent TSDC or TSPC from its proper functioning.

The present paper is primarily concerned with elucidating the dielectric relaxation behaviour of poly (p-phenylene sulphide) by measuring TSP current under various test conditions, like different bias voltage, heating rates, successive heating, cooling/TSDC cycles. The effect of thickness and annealing has also been studied on the pattern of TSP-current behaviour.

2 Theoretical Considerations

While measuring the thermally stimulated current under a bias field (E_b), the total conductivity (σ) of the sample at any instant comprises two components, viz. one resulting from orientation of
dipoles ($\sigma_0$) and the other from residual ionic conductivity ($\sigma_i$). This ($\sigma_i$) could be assumed to be negligible in view of the assumption that the specimen is thoroughly uncharged, i.e. $P(t)=0$ at $t=0$ and the operating temperature is not too high.

In case of an ideal dielectric consisting of free rotating dipoles with single relaxation mode, the built-up polarization and the corresponding displacement current density are given by:

$$P(t) = \exp\left(-\frac{t}{\tau}\right) \left(\frac{P_0}{\tau}\right) \exp\left(\frac{t}{\tau}\right)$$

and

$$J_{\mu}(T) = \frac{P_0(T)}{\tau_0} \exp\left(-\frac{E_a}{kT}\right) \left(-\frac{1}{\beta \tau_0}\right) \exp\left(-\frac{E_a}{kT}\right) \left(-\frac{E_a}{kT}\right)$$

where $\tau_0^{-1}$ is the frequency factor, $E_a$ the activation energy, $\beta$ uniform heating rate, and $P_0(T)$ the saturation polarization given by the Langevin formulae:

$$P_0(T) = \frac{N_0 \mu^2 d}{3kT}$$

where $N_0$ is the dipole concentration, $\mu$ the dipole moment and $k$ the Boltzmann’s constant.

Eq. (2) can be re-written in a more simplified form as:

$$J_{\mu}(T) = \frac{N_0 \mu^2 E_a}{3kT \tau_0} \exp\left(-\frac{E_a}{kT}\right)$$

The integral term in Eq. (4) is negligible over the initial part of curve following Garlick and Gibson’s assumptions. The activation energy ($E_a$) could be calculated from the slope of low temperature curve of the $\ln(J(T))$ versus $T^{-1}$ plot.

Now, if the temperature dependence of $P_o$ is ignored Eq. (4) gives the condition for a maximum ($T_m$) in the TSPC thermogram as:

$$\exp\left(-\frac{E_a}{kT_m}\right) = \frac{kT_m^2}{\beta E_a \tau_0}$$

and the slope of the initial part of the $\ln(J(T))$ against $T^{-1}$ plot should come out to be $(-E_a/k)$.

- Interestingly, the above mentioned TSPC Eq. (4) possesses the same form as that for the TSDC derived by Bucci et al. as well as for TSDC due to disorientation of dipoles by Shindo except the opposite sign. This is plausible, as the concept of the phenomena of built-up and destruction of polarization as established and they are analogous. Therefore, from the theoretical point of view, a TSPC peak should have the same position, shape and activation energy as its TSDC counterpart.

- Another source of TSPC is number of ions, which gradually jump from their equilibrium troughs due to rise in temperature, and which migrate under the influence of the applied field. But this is least significant for practical purposes, because the corresponding peak being at higher temperature is generally occurred due to intense ohmic currents.

- In general, the conduction currents accompany the actual charging currents; so it would be more appropriate to express the observed TSP current in the form:

$$i(T) = \frac{dP(T)}{dT} + g(T) E_a$$

where $g(T)$ is the ohmic conductivity. Also, the thermally generated polarization in a polymer could be represented in terms of its dielectric constant ($\varepsilon$) as

$$P = (\varepsilon - 1) E_a$$

Further, the thermal variation of dielectric constant ($\varepsilon$) with reference temperature ($T_0$) might be calculated through the TSPC spectra by using the relation:

$$
\text{(7)}
$$
\[ \Delta \varepsilon(T) = \varepsilon(T) - \varepsilon(T_0) = \frac{1}{\varepsilon_0 E_p A} \int \left[ \frac{1}{I(T) - I_0(T)} \right] dT \]

where \( A \) is the sample area, \( I \) and \( I_0 \) are the values of the first TSPC at temperature \( T \) with and without the electric field \( (E_p) \), respectively.

3 Experimental Details

The poly p-phenylene sulphide (PPS) pellets were prepared from the powder (Poly Science, USA) by using a pellet formation machine. A constant weight of 5 ton was applied. The pellets of size 1.3 cm diameter and 1 mm thickness were prepared until stated otherwise. The samples were metallized on both sides by vacuum evaporation of Al for electric contacts. The sample holder was placed inside a properly grounded metallic chamber. As the transient current at room temperature became almost negligible, a linear thermal program \((2{^\circ}C/min \) unless stated otherwise) was run with simultaneous application of a constant dc field \( E_p \) \((from 3 to 18 \text{ kV/cm})\) across the sample in series with a sensitive electrometer (Keithlay 610 C) to measure the TSP current. The slow heating rate \((2{^\circ}C/min)\) was maintained in order to prevent temperature gradient within the sample; temperature lag between sample and surroundings, as well as in obtaining a fine resolution in the current-temperature spectrum. McKeever and Hughes described the initial cooling of the sample to very low temperature, e.g. 77 K (so as to freeze the dipoles in their random positions) prior to the start of heating in the presence of dc field. However, the initial cooling may be done up to relatively higher temperature also, as reported by other workers. It may altogether be eliminated if the sample is short-circulated for a sufficient time and spurious polarization is allowed to decay. This has been successfully employed by the authors.

While performing repeated TSPC cycles, between two successive repeated TSPC cycles the sample was allowed to cool from the highest temperature \( T_2 \) to room temperature \( (T_1) \) under ambient conditions and was maintained at \( T_1 \) for about half an hour to allow almost all the relaxation modes to become saturated at that point. The activation energy \( (E_1) \) of the TSPC peak has been evaluated (Table 1) via the Bucci-plot method.

4 Results and Discussion

The typical TSPC spectra of PPS samples for various polarizing field (ranging from 3 to 18 kV/cm) has been illustrated in Fig. 1. A single peak
(P1) around 110 °C is appearing in each current-temperature (I-T) curve. After completion of the peak a steady rise in current in high temperature region beyond 170 °C is observed. These observations are in conformity with the non-isothermal charging mechanism of a dielectric as outlined in theory, where the polarizing current (I0) is supposed to consist of two components behaving differently as a function of temperature. The dipole orientation as a transient process gives rise to a peak, whereas the conduction current that derives from the motion of equilibrium charge carrier increases continuously with temperature. The PPS structure consists of zig-zag chain of sulphur atoms and benzene rings adjacent to each other as shown below:

\[
\begin{array}{c}
\text{S} \\
\text{H}
\end{array}
\]

Though the PPS does not contain any major polar group, the sulphur atom in PPS being sp3 hybridized there will be some deviation from the linearity between C-S and S-C linkage. Under this condition the C-S linkage in PPS may be associated to a weak dipolar relaxation. As the polymer is heated in the presence of a biasing field, the dipolar relaxation time decreases and they are progressively oriented. The larger the polarizing field, the stronger is the polarization. This is corroborated by the fact that an almost linear relationship is obtained notably in the high field range between the field strength, E0, and peak amplitude, I0 (Inset Fig. 1). This also implies the occurrence of uniform bulk polarization. The dipolar origin of peak P1 is also confirmed by the fact that (i) its location is very close to that of dipolar peak (β-peak) appearing in the TSDC spectra of PPS thermoelectret, (ii) the average activation energy (0.4 eV) corresponding to this relaxation though is more than the theoretical predicted value (0.24 eV) for this peak, is justified in the sense because the later is for side group orientation whereas C-S linkage is in main chain. Emergence of this peak is also consistent with the dielectrics loss maxima observed near 110 °C by Huo and Cech.¹⁷

- Once the dipolar relaxation is over, the TSPC spectra seem to be dominated by conduction current. In an attempt to separate the contributions from the dipolar motion and ohmic conduction after the first TSPC cycle is over, the sample is cooled down to original room temperature (T1) with field (E0) retained and under identical conditions a 2nd TSPC cycle is carried out. It is observed from Fig. 2(a) that the peak vanishes in 2nd TSPC cycle and current possesses positive polarity in the entire temperature region with decreased magnitude in low temperature region and eventually shows a fast increase at high temperature. Since during the repeated polarizing cycle no more dipoles are there to orient and the saturation polarization (P0) that has already been saturated at the lowest temperature (T1) begins to decay as per Eq. (3), the displacement current in principle should remain throughout negative. But this displacement current gradually becomes insignificant in comparison to the conduction current with increase in operating temperature and it is mainly the later component, which is observed. Similarly, the instantaneous polarization increases according to the increase in P0 with descending temperature maintain current positive under the bias through the cooling step (Fig. 2). A small kink around 170 °C in second TSPC cycle is very interesting and associated to a cross-linked product to be discussed later.

- An attempt was also made for isolating the conduction current from the actual polarizing current adopting different heating rates during the TSPC process as it affects the characteristics of the later component but not that of former one. Analogous to the case of TSDC, the TSPC maxima shifts towards higher temperature (Fig. 3) with increasing heating rate. However, the peak current decreases with heating rate, which is somewhat unusual. The I-T curves for peaks with low heating rate (1 °C/min) show a kink at higher temperature side around 170 °C similar to the kink in 2nd TSPC cycle curve (Fig. 2).

The dipolar nature of peak P1 is also supported by the fact that its location is unaffected by sample thickness (Fig. 4). The increase in total polarization (area under the curve) with sample thickness indicates an overall dominance of uniform volume polarization. A shoulder appearing around 85 °C in thinner sample may be due to a sub T2 -weak relaxation process.¹⁸
The two major differences in our experimental findings and the theoretical model for FITSC proposed by Vanderscherin et al.\textsuperscript{7} or the model calculations for pure displacement current by Shindo\textsuperscript{6} are (i) absence of any current reversal following the dipolar peak (Fig. 1) and (ii) the large magnitude of TSPC current than that of corresponding TSDC current (Fig. 2(b)). However, these deviations can be accounted for in the light of the fact that the assumptions made in the aforementioned models are too simplified and rarely valid in actual practice. Further, the charging currents inherently superimposed onto the dc conduction current. Another pre-requisite viz. the existence of a single relaxation mode could also not be satisfied even when the ohmic conduction is negligible.

\square The quantitative discrepancy in TSP and TSD (Fig. 2(a), 2(b)) current can be understood owing to the following facts: (i) the monitored value of TSPC
includes an additional contribution from conduction phenomena and (ii) the monitored value of TSDC is smaller because of the incomplete discharge of an electret in the very first TSDC cycle and due to the build up of an ionic space heterocharge during the polarization step, which reduces the internal electric field, consequently causing reduction in the dipolar relaxation. The TSDC peak appearing around 190 °C (Fig. 2b) and attributed to the space charge relaxation is not observed in the TSPC characteristics. This is not surprising, since during the polarization cycle sufficient time is not available for space charge trapping and also to the fact that the high temperature region is dominated by conduction current.

Some interesting observations are observed in the TSPC of high temperature annealed samples (Fig. 5). Not only there is a shift in the peak position towards higher temperature (=120 °C), but also the peak magnitude is nearly 20 times more than the corresponding TSPC of pristine sample at respective temperatures.

![Figure 3](image1.png)

**Fig. 3** — The TSPC spectra of PPS samples using different heating rates (1) 1 (2) 2 (3) 3 (4) 4 °C/min. ($E_p=18$ kV/cm)

![Figure 4](image2.png)

**Fig. 4** — The TSPC spectra of PPS samples of different thickness (1) 0.7 (2) 1.00 (3) 1.2 mm. ($E_p=5$ kV/cm)
fields. High temperature annealing of PPS in presence of oxygen leads to the formation of cross-linked structure with new ether linkage as:

\[ \text{Similarly the TSPC at very slow heating rate (1 °C/min) will give some annealing like effects in high temperature region, resulting in the formation of some ether linkage, responsible for the kinks appearing around 170 °C (Fig. 3).} \]

Table 2 — The temperature variation of dielectric constant of PPS samples with respect to the reference temperature \( T_0 = 30 °C \) (\( \Delta \varepsilon \), deduced from TSPC spectra, and \( \Delta \varepsilon ' \) from direct measurements)

<table>
<thead>
<tr>
<th>( T (°C) )</th>
<th>( \Delta \varepsilon )</th>
<th>( \Delta \varepsilon ' )</th>
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<tbody>
<tr>
<td>( E_\varepsilon = 3 ) kV/cm</td>
<td>( E_\varepsilon = 5 ) kV/cm</td>
<td>( E_\varepsilon = 10 ) kV/cm</td>
</tr>
<tr>
<td>30</td>
<td>3.42</td>
<td>5.16</td>
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<tr>
<td>120</td>
<td>2.48</td>
<td>41.20</td>
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Table 2 gives the variation of dielectric constant (\( \Delta \varepsilon \)) from the room temperature value of PPS as a function of temperature as deduced from their respective TSPC curve along with those measured \( \Delta \varepsilon ' \) independently using precision LCZ meter. At low temperature, \( \Delta \varepsilon \) and \( \Delta \varepsilon ' \) exhibit a slight agreement but deviation becomes more pronounced at high temperature with the onset of ohmic conduction. It is very likely in the present case that the dipolar peak \( (P_1) \) may include some contributions from charge trapping as well, because the unsaturated phenyl group acts as traps for charge carriers. This is also supported from the activation energy values for this peak (Table 1) which are somewhat larger than those recognized for pure dipole.

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Fig. (5) — The TSPC spectra of annealed PPS samples (annealed at 280 °C for 1 hr) under different polarizing fields (1) 3 (2) 5 (3) 10 kV/cm

References