Thermally stimulated depolarization current
Investigations of copolyesteramide (Vectra B 950)
polymer liquid crystal

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Thermally stimulated depolarization current (TSDC) characteristics of copolyesteramide (Vectra B950), a polymer liquid crystal having a monomeric composition of 60/20/20 mol % of 6-hydroxy-2-naphthoic acid (HNA), terethalic acid (TA) and 4-aminophenol (AP) were investigated in the temperature range 20–250 °C in function of polarizing temperature (80–190 °C), polarizing field (2.77–13.88 kV/cm), polarization time (0.5–2 h) and storage time (1 – 100 h). The TSDC spectra in general comprise four maxima, namely \( \beta' \), \( \beta \), \( \alpha \), and \( \delta \) with their respective locations around 30°C, 110 °C, 160 °C and 220 °C. The \( \beta \) peak was attributed to the dipolar nature of the carbonyl group (\( > C = O \)) present in HNA and TA non liquid crystalline phase of Vectra B, whereas the \( \beta' \) peak is due to the dipolar nature of the ester group. The \( \alpha \) peak was assigned to a space charge trapping mechanism. A major contribution towards \( \alpha \) relaxation comes from interfacial polarization arising from liquid crystalline phase in Vectra B. A high temperature of the \( \delta \) relaxation is associated with the onset of melting due to the movement of large segmental groups of liquid crystalline phase.

Keywords: Vectra B; polymer liquid crystal; thermally stimulated depolarization current

1. Introduction

Polymer liquid crystals, i.e. polymers exhibiting liquid crystalline behaviour, were first reported in the mid 1970s [1–3]. These polymers consist of polar groups in anisotropic distribution and non polar groups in the side chains that determine characteristic properties of the liquid crystal. Polymer liquid crystals are demonstrably superior than most widely used engineering thermoplastics with regard to chemical resistance, low inflammability, low melt viscosity, high mechanical and thermal properties, applicability at elevated temperatures, and low isobaric expansivity [3–11]. However, polymer liquid crystals exhibit more complex behaviour than flexible ones. Despite

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their potential for many applications, the molecular dynamics of various dielectric relaxation processes in polymer liquid crystals are still not well understood, however it is essential before they can be exploited in practical applications. Various dielectric relaxation processes in polymers can be accurately described by applying the thermally stimulated discharge current (TSDC) technique [12]. The TSDC technique essentially consists of two steps: in the first step, a thermoelectret state is formed in the polymers, and then in the second step, the depolarization current spectra at a constant heating rate are obtained. The main advantage of this technique is its high sensitivity, which makes it possible to detect very low dipolar or carrier concentrations. In addition, its very low equivalent frequency allows multicomponent peaks to be resolved accurately. Various current maxima appearing in the TSDC spectra provide deep insight into the molecular origin of dipolar, space charge and other relaxations.

The paper presents our interpretations, based on TSDC analysis, regarding various dielectric relaxation processes occurring in aromatic copolyesteramide polymer liquid crystal, commercially known as Vectra B. Boersma et al. [13] also obtained TSDC data on Vectra B, but only for one polarization parameter $T_P$ (polarization temperature) ranging from 200–280 °C. In the present study, the TSDC spectra of thermoelectret formed under various polarization conditions such as field strength, temperature, time and storage time. In addition, the Cole–Cole distribution was also obtained for the dipolar relaxation process.

2. Theoretical considerations

The decay of polarization after removal of the external field when a polarized polymer is heated uniformly is given as [12]:

$$\tau \left[ \exp \left( -\int_0^t \frac{dt}{\tau} \right) \right]$$

where $\tau$ is the dipolar relaxation time and $P_e$ is the steady state polarization given by the Langevin formula [12]

$$P_e = \frac{N \mu^2 E_p}{3kT_p}$$

where $N$ is the dipole concentration, $\mu$ – the dipole moment, $E_p$ – applied electric field, $k$ – the Boltzmann constant and $T_p$ – the polarizing temperature.

Furthermore, the temperature dependence of $\tau$ for a single relaxation mechanism is given by the Arrhenius equation

$$\tau(T) = \tau_0 \exp \left( \frac{U}{kT} \right)$$
where the pre-exponential factor $\tau_0$ is the relaxation time at infinite temperature, and $U$ is the activation energy. Based on Eqs. (1) and (3), the depolarization current density is given as the rate of change of polarization

$$i(t) = -\frac{dP(t)}{dt} = \frac{P(t)}{\tau}$$  \hspace{1cm} (4)

Furthermore, in TSDC experiments since time and temperature both vary simultaneously, a new variable $T$ can be introduced by assuming a simple temperature program, so that

$$T = T_0 + ht$$  \hspace{1cm} (5)

where $T_0$ is the initial temperature and $h = \frac{dT}{dt}$ is the heating rate.

From Equations (1)–(5), the TSD current density $i(t)$ at a particular time $t$ can be given as:

$$i(t) = \frac{N \mu^2 E_p}{3kT_p\tau_0} \exp \left[ \frac{-U}{kT} - \frac{1}{h\tau_0} \int_0^\tau \exp \left( \frac{-U}{kT} \frac{1}{hT} \right) dT \right]$$  \hspace{1cm} (6)

The relaxation time $\tau$ at any temperature $T$ can be estimated by the ratio of two quantities: (i) the area under the TSDC curve between the reference temperature $T$ and $T = \infty$, and (ii) the value of the TSDC at the reference temperature $T$.

From Equation (3) we have

$$\ln \tau = \ln \tau_0 + \frac{U}{kT}$$  \hspace{1cm} (7)

The activation energy $U$ can be calculated from the slope of the straight line of the $\ln \tau(T)$ versus $1/T$ plot, using the Bucci plot method [12].

3. Materials and methods

The material used in the present study was liquid crystal of aromatic copolyesteramide polymer procured by the Good Fellow (UK). The polymer is commercially known as Vectra B950, with a composition of 60 mol % of 6-hydroxy-2-naphthoic acid (HNA), 20 mol % of terethalic acid (TA) and 20 mol % 4-aminophenol (AP) [14]. Henceforth we will refer to this polymer liquid crystal as Vectra B. The Vectra B samples in the form of pallets of thickness 1.8mm and diameter 19mm were metalised on both sides by vacuum evaporation of aluminum, to form electrical contacts. The sample holder designed for this purpose was suspended in a specially prepared tem-
perature-controlled furnace, shielded against stray pickups. The furnace could be heated at an arbitrary, but constant, rate from room temperature to 250 °C.

The samples were polarized by subjecting them to the desired field $E_p$ at constant temperature $T_P$ for the polarization time $t_p$, following the usual method [13]. The TSDC data were obtained at a constant heating rate $h$ in the temperature range 20–250 °C using the Keithley electrometer (610C). For studying the aging (storage time) effect, the polarized samples were stored for a specified period $t_s$. For all the measurements, the heating rate, polarization time and storage time were 2 °C/min, 60 min and 10 min respectively, unless specified otherwise. The activation energies $U$ for various relaxation modes were calculated.

4. Results

Figures 1–4 illustrate the TSDC spectra of Vectra B samples in the temperature range 20–250 °C for various polarization and storage conditions. The number of peaks in the spectra, their location, height and sharpness are found to be governed by the polarization and depolarization parameter as well as the storage time. The TSDC spectra show current peaks at around 30 °C, 110–130 °C, 160–170 °C and 220 °C, and are denoted as $\beta'$, $\beta$, $\alpha$ and $\delta$ peaks, respectively. The values of the activation energy ($U$) and the pre-exponential factors $\tau_0$ for the $\beta'$, $\beta$ and $\alpha$ peaks with $E_p$ are given in Tables 1, 2 and 3, respectively. The activation energy of the $\delta$ peak, which appears only for a high polarization time ($t_p = 120$ min), comes out to be 0.90 eV.

4.1. Polarization field dependence

Figure 1 illustrates the effect of the polarization field $E_p$ ranging from 2.77 kV/cm to 13.88 kV/cm on TSDC spectra of Vectra B samples polarized at $T_P = 100$ °C and 190 °C, respectively. We observe a well defined $\alpha$ peak around 160–170 °C (Fig. 1b). The peak temperature $T_m$ is almost independent of $E_p$ but the peak current $I_m$ increases upon increasing polarization field and it exhibits a linear dependence on $E_p^{1/2}$ (inset of Fig. 1b). In addition, a $\beta'$ peak also appears around 30 °C. The $\beta$ peak located around 110–130 °C, is pronounced only for $T_P = 100$ °C (Fig. 1a). The peak height $I_m$ for this peak shows a linear dependence on $E_p$ (inset of Fig. 1a).

4.2. Polarization temperature dependence

The effect of the polarization temperature on TSDC spectra of Vectra B samples ($E_p = 5.55$ kV/cm) is shown in Fig. 2. The presence of the $\beta$ peak is clearly evident in Fig. 1a. A shift in the $\beta$ peak is observed for samples poled at $T_P > 110$ °C. This temperature is also the glass transition temperature $T_g$ of Vectra B. The $\alpha$ peak appears only in the spectra of samples poled at high $T_P$. A shift in the $\alpha$ peak location is also
observed towards higher temperatures as $T_P$ increases. A significant enhancement in the height of the $\alpha$ peak is observed in high $T_P$ poled samples. Interestingly, the $\beta'$ peak (around 30 °C) is well defined in all the cases, and is observed to increase as $T_P$ increases.

4.3. Effect of storage time ($t_s$)

The TSDC spectra of Vectra B samples, polarized and discharged under identical conditions but stored for different times (electret aging), are shown in Fig. 3. An increase in $t_s$ suppresses the entire TSDC spectra. The heights of the $\beta'$, $\beta$, and $\alpha$ peaks reduce gradually. However, the $\beta'$ and $\beta$ peaks vanish completely at high storage times. Further, the $\alpha$ peak shifts towards higher temperatures and becomes broader as $t_s$ increases.
4.4. Effect of polarization time

The effect of polarization time on the TSDC spectra of Vectra B samples is shown in Fig. 4. Upon the increasing polarization time the $\beta'$ peak gradually decreases. The $\beta$ peak at a short polarization time remains unaffected, but at a long polarization time it disappears completely. A significant increase in the height of the $\alpha$ peak is observed at high $t_p$, and the peak also becomes broader.
Fig. 4. The TSDC spectra of Vectra B samples polarized for various polarization times:
   a) 30 min, b) 60 min, c) 120 min; $E_p = 5.55$ kV/cm, $T_p = 190$ °C

5. Discussion

The dielectric relaxation processes in liquid crystal polymers are quite complex in nature and presumably result from several different competitive mechanisms involving various physical states associated with crystalline and amorphous phase. The chemical structure of Vectra B is shown below [15]:

The monomeric composition of Vectra B is 60/20/20 mol % of 6-hydroxy-2-naphthoic acid (HNA), terethalic acid (TA) and 4-aminophenol (AP). A benzene ring associated with the aminophenol molecule provides the liquid crystalline phase to the Vectra B, whereas the amide and the ester group act as bridging groups. The dipolar nature of Vectra B arises from the presence of carbonyl [\(\text{C} = \text{O}\)] groups in HNA
as well as in TA. A dielectric relaxation process associated with the dipolar nature of 
>C = O groups in various polymeric materials (termed as β relaxation) has been dis-
cussed by many groups [12, 16, 17].

<table>
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<tr>
<th>$E_P$ [kV/cm]</th>
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<th>$U$ [eV]</th>
<th>$\tau_0$ [s]</th>
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Table 2. Activation energies and pre-exponential factors for β relaxation of Vectra B

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Table 3. Activation energies and pre-exponential factors for α relaxation of Vectra B

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In the present TSDC analysis, the current maximum (β peak) appearing around 110–130 °C (Figs. 1a, 2) has been attributed to the dipolar nature of >C = O groups present in Vectra B structure. The dipolar nature of this relaxation can be judged from certain characteristics observed for this peak, such as: (i) its height varies linearly with the polarizing field (inset of Fig. 1a) which is also an indication of uniform induced bulk polarization [18]; (ii) the activation energy associated with this peak (Table 2) is of the same order of magnitude as that predicted theoretically for the side group orientation in polymers [19]; (iii) a shift in the peak temperature occurs as \( T_p \) increases. The broad nature of this peak shows a large distribution in the relaxation times. This is due to the fact that various >C = O groups present in Vectra B monomer units are situated at different locations; one >C = O group is present in ester linkage of HNA and AP and other >C = O is present in amide linkage of TA and AP.

For a certain relaxation process in a polymer, the peak temperature is given as [12, 20, 21]:

\[
T_m = hU \frac{\tau_{r_m}}{k}
\]

(8)

where \( \tau_{r_m} \) is the relaxation time at temperature \( T \) and \( k \) is the Boltzmann constant. The above dependence shows that for a single relaxation time (single energy of activation) and for a given rate of heating \( h \), \( T_m \) should be independent of \( T_p \) and \( t_p \). At low values of \( T_p \) (or \( t_p \)) only fast sub-polarizations could be operative but as \( T_p \) (or \( t_p \)) is increased, more and more sub-polarizations with longer relaxation times would be activated [22, 23], thereby shifting the peaks towards higher temperatures and also enhancing their heights. In Vectra B, the distribution of the polarization may appear due to non-identical environment around different >C = O groups. Vectra B, being a longitudinal polymer liquid crystal, has 4-aminophenol particles as liquid crystalline phase sandwiched between HNA and TA being non-liquid crystalline flexible spacers [24]. Lenz [25] has shown that flexible spacers are particularly important for thermotropic longitudinal polymer liquid crystals. The type and length of the spacers can determine whether a nematic, cholesteric or smectic phase is formed. At elevated temperatures, under the influence of a field, reduction in the length of the spacer results in an increase in the rigidity of molecules there, by shifting \( T_m \) to higher temperatures.

The TSDC maximum appearing around 160–170 °C (α peak, Fig. 1b) has been assigned to a space charge trapping mechanism. In polymer liquid crystals, the charge trapping is possible owing to the presence of crystalline phase, which is responsible for space charge formation via interfacial polarization (Maxwell, Wagner–Sillars effects) [26]. In addition, unsaturated amide and carbonyl groups (due to conjugation) can act as traps for charge carriers contributing to their transport and trapping. The charge trapping may also take place at aromatic carbon, but the probability is much lower compared with the probability of charge trapping at carbonyl carbon. It is due to the delocalization of \( \pi \) electron in the aromatic ring. The space charge origin of this
peak is also confirmed by the following facts: (i) its peak current $I_m$ depends linearly on $E_p^{1/2}$ (inset of Fig. 1b), which also shows the occurrence of an overall non-uniform bulk polarization; (ii) during the electret storage, the peak vanishes almost completely during long storage time (Fig. 3), and; (iii) the corresponding activation energy values for this peak (Table 3) are in the same range as that reported for $\alpha$ relaxation. Furthermore, it is an established fact that viscoelastic and dielectric properties of polymers are directly related to each other. The dynamic mechanical analysis (DMA) of Vectra B samples show a maximum in the loss modulus versus temperature curve, at around 160–170 °C [27]. This is in conformity with the occurrence of $\alpha$ relaxation around this temperature.

A significant enhancement in the $\alpha$ relaxation observed for high $t_P$ (Fig. 4c) is also in conformity with the enhancement in the crystallinity resulting from increased annealing time [28, 29]. The broad nature of the $\alpha$ relaxation for high $t_P$ further shows the merger of multiple transition processes (with large distribution in relaxation time) in the vicinity of $\alpha$ relaxation

An enhancement in the crystallinity with increasing temperature in polymer and also in liquid crystalline polymers particularly above glass transition temperature has been reported by several authors [29, 32]. Increase in crystallinity in polymers result in an increase in $\alpha$ relaxation and lowering of the dipolar relaxation. This is in agreement with the TSDC analysis for this study, namely increases in the $\alpha$ peak intensity correspond to increases in $T_P$ (Fig. 2). A higher poling temperature or poling time means more intense annealing and this explains a weaker $\beta$ relaxation process in high $T_P$ poled samples.

The TSDC maximum appearing at high temperature is generally considered to be due to the charge injection into the polymer from the electrodes directly and/or through interfacial layers, i.e. the Townsend breakdown [12, 20]. However, in the present case, the current maximum appearing around 220 °C ($\delta$ peak, Fig. 4c) in high $t_P$ polarized samples cannot be attributed to the charge injection phenomenon, as the polarization fields used are not sufficiently high to cause the Townsend breakdown. Furthermore, the possibility of charge injection can also be ruled out because of the vacuum deposited electrodes. Brostow et al. [33] have shown a high temperature transition in PET/x.PHB polymer liquid crystal due to melting, i.e. movement of large segmental groups in liquid crystalline phase. This transition has also been observed by Quamara et al. [32] in the TSDC analysis of PET/x.PHB polymer liquid crystal. Although the melting temperature of Vectra B has been reported to be around 280 °C [14], the onset of such a melting process should take place at much lower temperature than the actual melting point itself. Hence the $\delta$ relaxations can be attributed to melting, i.e. to the movement of large segmental groups in liquid crystalline phase. The onset of this melting process, at around 220 °C, in Vectra B is also evident from an abrupt decrease in its tensile moduli for the same temperature range [27]. The occurrence of $\delta$ relaxations in Vectra B is also confirmed from our thermally stimulated
polarized current investigations [34] where we observed a saturation in the polariza-
tion current at around 220 °C.

The β’ peak around 30–35 °C cannot be associated with any known transition in
Vectra B. Though Dreher et al. [11] have shown a dielectric loss peak around 77 °C
but this temperature is almost 45 °C above the β’ peak temperature, thus we are not
sure whether the β’ peak can have any relationship with this tanδ peak. Interestingly,
in the case of Vectra A and Vectra E, transitions are observed to occur around 35 °C,
based on analysis of the temperature versus loss modulus characteristics [27]. Since
the β’ peak also lies in the same temperature range, it appears that some common mo-
lecular dynamics in these polymer should govern this relaxation process. From the
structural analysis of Vectra series polymer liquid crystals (A, B and E), we observe
that the ester linkage is common amongst them. This indicates that the dipolar nature
of ester linkage may be the cause of β’ relaxation. The activation energy associated
with this peak (Table 1) is also in agreement with its dipolar character.

6. Cole–Cole distributions

A distribution function is a measure of the distribution of relaxation times associ-
ated with different relaxation processes in a polymer. As we have discussed above,
there appears to be a broad distribution in the relaxation times for the β relaxation
process in Vectra B. A number of independent causes may be responsible for this dis-
tribution. Though there are several forms of distribution functions suggested by many
authors [35–38], the most suitable one for describing the distribution of relaxation
times $\tau_m$ for TSDC is given by the Cole–Cole distribution function [35]. We have ob-
tained the Cole–Cole distribution function of the β peak for Vectra B samples for dif-
ferent polarizing parameters, using following equation [35]

$$f'(u) = \frac{\sin(\beta \pi)}{2\pi} \left[ \frac{\cosh(\beta u) + \cos(\beta \pi)}{\cosh(\beta u) + \cos(\beta \pi)} \right]$$

(9)

where $\infty < \tau < \infty$, $0 < \beta \leq 1$ and $u = \ln(\tau / \tau_m)$. The values of $\tau$ and $\tau_m$ are evaluated
using Eq. (3).

The Cole–Cole distribution curves in the form of $f'(u)$ versus $u$ for Vectra B
samples polarized at various $E_p$ ($T_p = 100$ °C) are shown in Fig. 5. These curves show
the distribution of $\tau$ becomes wider as $E_p$ increases. This is corroborated by the fact
that with an increase in the polarizing field, there should be an enhancement in the
spectrum of dipolar relaxation times. The shifting of β peaks towards higher tempera-
tures as $T_p$ increases suggests that the distribution function is temperature dependent.
In Vectra B, the spectrum of relaxation times is attributable to the presence of differ-
ent $>C = O$ groups in its monomer units at various locations. In addition, the anisot-
ropy of the internal field in which the dipoles realign may also contribute to the re-
laxation spectrum, as in case of other polymers [38].
Fig. 5. Cole–Cole spectra of Vectra B samples

7. Conclusions

The TSDC spectra of Vectra B samples polarized under various polarization conditions confirm the occurrence of multiple relaxation processes, denoted $\beta'$, $\beta$, $\alpha$, and $\delta$ in ascending order of temperature of occurrence in the polymer liquid crystals. The presence of carbonyl groups in the structure of Vectra B is responsible for the occurrence of $\beta$ relaxation, whereas the $\alpha$ relaxation is due to space charge trapping mechanism via interfacial polarization arising from liquid crystalline phase. The activation energy, as computed using the from Bucci plot method, confirms different types of the relaxations. The $\beta'$ relaxation has been associated to ester linkage and $\delta$ relaxation is due to the movement of large segmental groups in a liquid crystalline phase.

Acknowledgements

The authors are grateful to DRDO New Delhi for providing funds for the present work.
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Received 9 January 2010
Revised 6 August 2010