

Research Article

Study of Dielectric Relaxation Behavior of Liquid Crystal Copolyester Vectra-A by Thermally Stimulated Discharge Current Technique

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The dielectric relaxation behavior of thermotropic liquid crystal copolyester of 73% of p-hydroxy-benzoic acid (HBA) and 27% of 2-hydroxy-6-naphthoic acid (HNA) (Vectra-A) at poling temperature 80°C has been studied using thermally stimulated depolarization current (TSDC) technique in the temperature range from 15°C to 250°C. The TSD currents were obtained for different polarizing fields ranging from 3.8 kV/cm to 19.2 kV/cm. TSD current spectra in the temperature range from 15°C to 250°C show three current maxima around 25°C, 110°C, and 220°C. The maxima around 25°C and 110°C correspond to characteristic dipolar relaxations β and α , respectively. The peak around 220°C is due to space charge effects named as δ -relaxation. The various relaxation parameters like activation energy (U), relaxation strength ($\Delta\epsilon$), preexponential factor (τ_0), the quantity of charge released (Q) and concentration of trap (N_t) for β - and α -relaxations at polarizing temperature 80°C for different polarizing fields were evaluated using Bucci-Fieschi fit. The linear variation between activation energy and natural logarithm of preexponential factor indicates the presence of compensation effect for dipolar relaxations of Vectra-A under present poling conditions.

1. Introduction

Liquid crystal copolymers of hydroxybenzoic and hydroxynaphthoic acids have received much interest due to their high chemical resistant which makes them suitable for making surgical instruments; their easily molded sheets have very good dimensional accuracy and strength and stiffness, and high strength-to-weight ratio makes them suitable for metal replacement applications. The dielectric and electrical properties of liquid crystal polymer (LCP) are strongly influenced by the molecular order and orientation. Thermally stimulated discharge current (TSDC) is a powerful tool for determining the characteristics of dielectric relaxation behavior of polymeric materials [1–4]. The advantage of this technique is its high sensitivity. In the present work, TSDC technique has been used to investigate the dielectric relaxation behavior of liquid crystal copolyester of 73% of p-hydroxybenzoic acid (HBA) and 27% of 2-hydroxy-6-naphthoic acid (HNA) commercially known as Vectra-A in the temperature range from 15°C to 250°C at poling temperature 80°C. The TSD

currents were obtained as a function of temperature for polarizing fields ranging from 3.8 kV/cm to 19.2 kV/cm. The TSDC spectra were analyzed using Bucci-Fieschi-Guidi analysis [5]. The relaxation parameters activation energy, relaxation strength, preexponential factor, charge released, and concentration of trap density were determined from BFG plots. The effect of poling field on TSDC spectra and relaxation parameters is also discussed in the present paper. The linear variation of activation energy with natural logarithm of preexponential factor indicates the presence of compensation effect for dipolar relaxations of Vectra-A under present polarizing conditions.

2. Theory

The stored polarization's $P(t)$, decay rate $dP(t)/dt$, and dipolar relaxation time $\tau(T)$ are expressed by

$$\frac{dP(t)}{dt} = -\frac{P(t)}{\tau(T)}. \quad (1)$$

The uniform decay rate of dielectric is a function of time and temperature. The solution of (1) is

$$P(t) = P_0 \exp\left(-\int_0^t \frac{dt}{\tau(T)}\right). \quad (2)$$

In case of freely rotating dipoles, the dielectric is polarized by application of an electric field (E_p) and temperature (T_p). Then,

$$P_0 = \frac{N\mu^2 E_p}{3kT_p}, \quad (3)$$

where N is the concentration of dipoles, k is Boltzmann's constant, and μ is the dipole moment.

The rate at which polarization changes or in other words depolarization current density is given by

$$J(T) = -\frac{dP(t)}{dt} = \frac{P_0}{\tau} \exp\left(-\int_0^t \frac{dt}{\tau(T)}\right). \quad (4)$$

From (1) and (4), we obtain

$$P(t) = -\int_0^t J(T) dt, \quad (5)$$

$$J(T) = \frac{-P(t)}{\tau(T)}.$$

Therefore,

$$J(T) = \frac{\int_0^t J(T) dt}{\tau(T)}. \quad (6)$$

In order to obtain the current density produced by the progressive decrease in polarization in the course of TSDC experiment where time and temperature are simultaneously varied, the differentiation must be done by taking T as a new variable. The parameter T is linearly increasing from a temperature T_0 according to the following relation:

$$T = T_0 + ht. \quad (7)$$

Here, T_0 is initial temperature and h is the heating rate, that is, $h = dT/dt$.

By making the use of (6), we get

$$\tau(T) = \frac{\int_T^\infty J(T) dT}{hJ(T)}. \quad (8)$$

Thus, the relaxation time $\tau(T)$ at any temperature can be calculated as follows:

$$\tau(T) = \frac{\text{Area under the TSDC curve between } T \text{ and } T_\infty}{\text{Value of TSD current at temperature } T}. \quad (9)$$

The Arrhenius equation for the variation of τ with temperature is given as follows:

$$\tau(T) = \tau_0 \exp\left(\frac{U}{kT}\right), \quad (10)$$

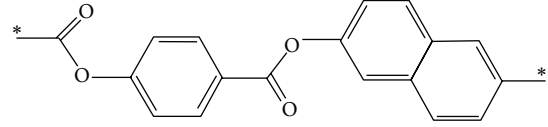


FIGURE 1: Structure of Vectra-A.

where τ_0 is the natural relaxation time and U is the activation energy needed to disorient a dipole. The energy U can be seen as a potential barrier which the dipole has to surmount before it can readjust its direction

$$\ln \tau(T) = \ln \tau_0 + \frac{U}{kT}. \quad (11)$$

Thus, the graph between $\ln \tau(T)$ and $1/T$ is a straight line (BFG plot) whose slope gives the value of activation energy [5, 6].

The quantity of charge released (Q) is calculated from TSDC curve [7]. The concentration of the traps has been estimated using the following relation:

$$N_t = \frac{Q}{(SLeG)}. \quad (12)$$

Here, S and L are the area and thickness of the sample, respectively, e is the electronic charge, and G is the photo-conductivity gain, which is equal to the number of electrons passing through the sample for each absorbed photon. The value of G is taken unity for the calculation of concentration of the traps [8].

3. Material and Method

The liquid crystal copolyester commercially known as Vectra-A is a random copolyester of hydroxybenzoic acid (HBA) and hydroxynaphthoic acid (HNA), composed of 27% of HNA and 73% of HBA. Vectra-A consists of rigid rods like molecules that are ordered in the melt phase to form liquid crystal structures [9]. It has operating temperature up to 300°C, very low-melt viscosity, excellent dimensional stability, very high tensile strength, and very high impact resistance [10]. The rigid rod-like macromolecules of Vectra-A are aligned in the melt state to produce its structure, as shown in Figure 1.

The Vectra-A, ivory in color, is procured in the form of rod having a diameter of 18 millimeters and a length of one meter from Goodfellow Cambridge limited Ermine Business Park, Huntingdon PE296WR, UK. The Samples were prepared by cutting the rod in the form of pellets of 1.3 millimeter thickness. The samples were metalized on both surfaces with aluminum by vacuum evaporation. The TSDC technique used to study the dielectric relaxation behavior of Vectra-A is shown in Figure 2.

The procedure for preparing thermoelectrets for the measurement of TSDC spectra is as follows.

- (1) Samples of Vectra-A were heated up to 80°C in the specially designed temperature controlled furnace.

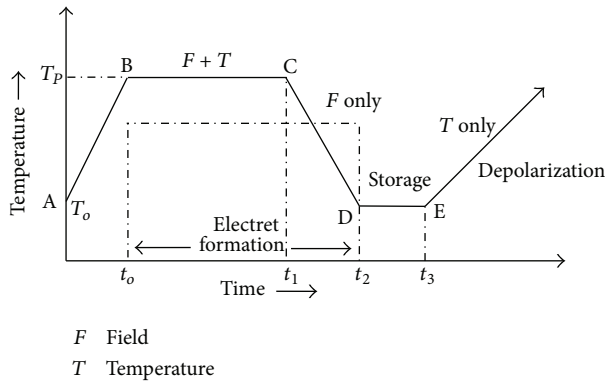


FIGURE 2: The TSDC technique.

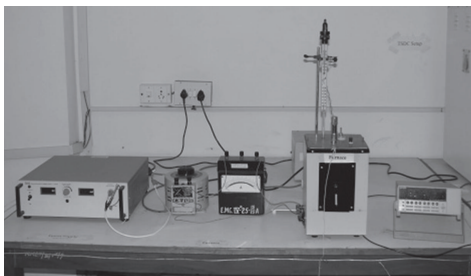
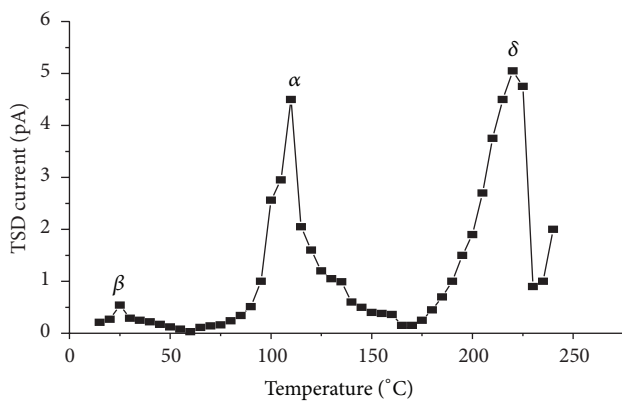
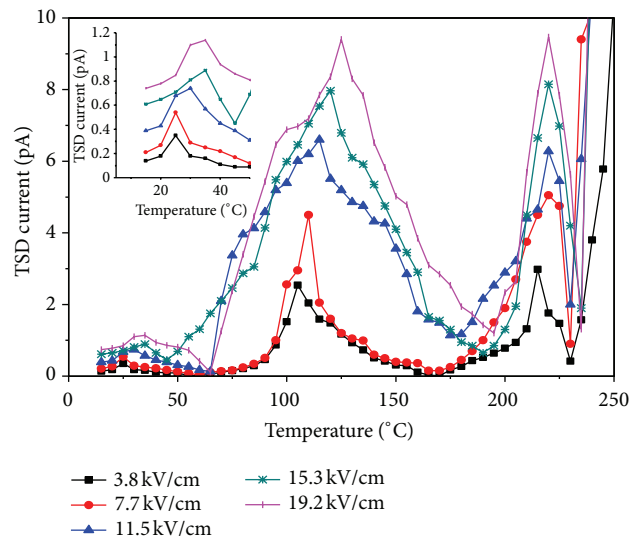


FIGURE 3: Experimental setup for TSDC.

FIGURE 4: TSDC plot for polarizing field 7.7 kV/cm at polarizing temperature $T_p = 80^\circ\text{C}$.

- (2) The thermoelectrets at $T_p = 80^\circ\text{C}$ were prepared by subjecting them to dc fields E_p (from 3.8 kV/cm to 19.2 kV/cm).
- (3) The polarizing voltage was supplied using high voltage Aplab power supply for 1 hour.
- (4) The samples were cooled to room temperature in the presence of electric field.

After this, both of the electrodes were short circuited for 24 hours. The sample is then reheated at constant rate of $2^\circ\text{C}/\text{minute}$. The depolarization current was measured with sensitive Keithley Electrometer 6514 procured from Keithley

FIGURE 5: The TSDC spectra of Vectra-A samples at different electric fields ($T_p = 80^\circ\text{C}$).

Instruments, Inc., Cleveland, OH, USA. The experimental setup for the present investigations is shown in Figure 3.

4. Results and Discussion

The TSD current spectra of Vectra-A at polarizing field 7.7 kV/cm in the temperature range from 15°C to 250°C is shown in Figure 4. The TSDC spectrum reveals three maxima, around 25°C , 110°C , and 220°C which are termed as β -relaxation, α -relaxation, and δ -relaxation, respectively. The β -relaxation located at low temperature is related to the local motion of HNA groups as this motion is accompanied by reduced conformational constraints. Also, at low temperature due to steric hindrance, only naphthalene with their ester groups will rotate as a single unit [11]. The peak observed at high temperatures around 110°C , namely, α -relaxation is associated with the glass transition [1, 2]. The glass transition is attributed to the cooperative rotation of main chain segments. Lukacs [12] also reported β - and α -relaxations around 25°C and 110°C , respectively, by studying the temperature-dependent time resolve fluorescence spectra of Vectra-A. The δ -relaxation is known as a space charge relaxation. The space charges are frozen at low temperatures, but with the increase in temperature, they gain their mobility and contribute to space charge relaxation.

In order to study the effect of polarizing field, the TSD spectra at different polarizing fields ranging from 3.8 kV/cm to 19.2 kV/cm are plotted as a function of temperature shown in Figure 5. From the figure, it is clear that there is significant effect of polarizing field on the magnitude as well as on the positions of β - and α -relaxations. The position of β -relaxation changes in the range from 25°C to 35°C and that of α -relaxation in the range from 105°C – 125°C with an increasing polarizing field in the range from 3.8 kV/cm to 19.2 kV/cm. This shift with the increase in the polarizing field may be attributed to the fact that in liquid crystal

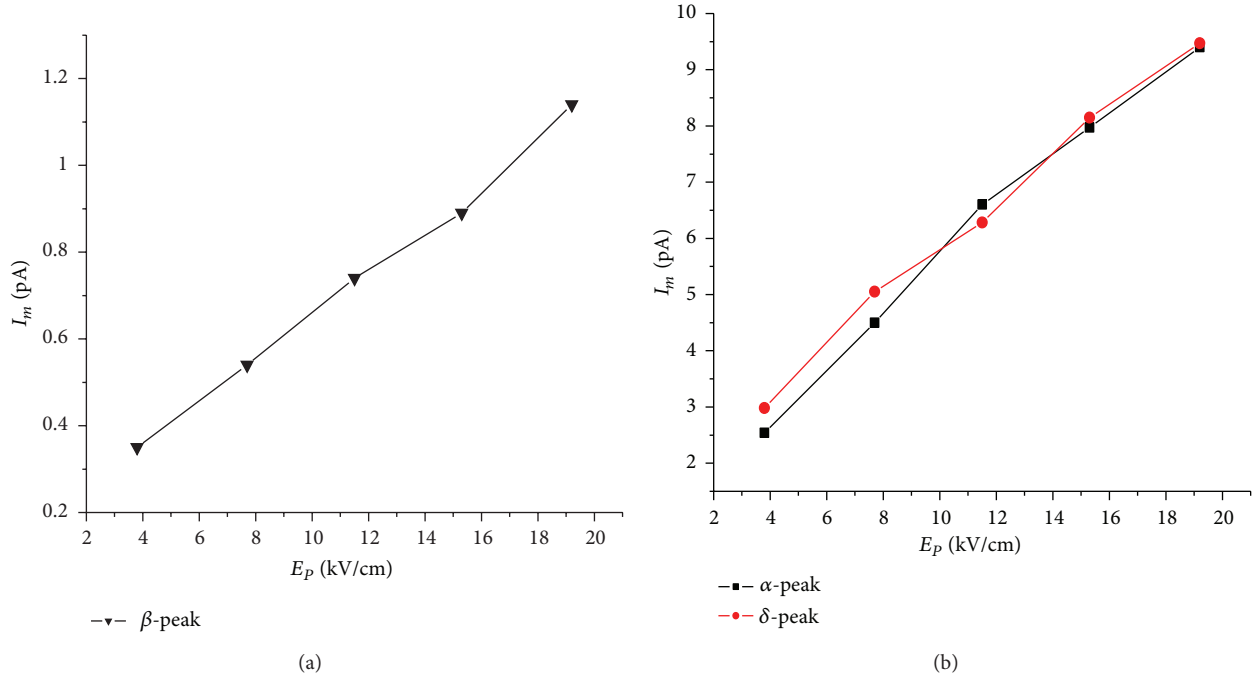


FIGURE 6: (a) Field dependence of maximum current (I_m) for β -peak. (b) Field dependence of maximum current (I_m) for α and δ -peaks.

TABLE 1: Values of activation energy (U), dipolar relaxation strength $\Delta\epsilon$, preexponential factor (τ_0), charge released (Q), and concentration of traps (N_t) for β -relaxation at poling temperature $T_p = 80^\circ\text{C}$ for various polarizing fields.

Poling fields (kV/cm)	β -relaxation				
	U (eV)	$\Delta\epsilon$	τ_0 (Sec)	Q (C)	N_t (m^{-3})
3.8	0.51	0.27	1.74×10^{-6}	2.27×10^{-10}	6.19×10^{11}
7.7	0.49	0.27	3.54×10^{-6}	4.65×10^{-10}	12.65×10^{11}
11.5	0.42	0.32	6.83×10^{-5}	8.30×10^{-10}	22.59×10^{11}
15.3	0.38	0.34	2.04×10^{-4}	11.56×10^{-10}	31.47×10^{11}
19.2	0.32	0.34	3.39×10^{-3}	14.85×10^{-10}	40.42×10^{11}

polymers, the length of spacer shrinks, and the results in increasing the rigidity of the molecules hence shift the peak to a higher temperature [13]. The position of δ -relaxation is nearly independent of a polarizing field.

The magnitude of maximum current (I_m) for β -, α -, and δ -relaxations are plotted with polarizing electric fields and shown in Figures 6(a) and 6(b). The plot shows that maximum current (I_m) depends on the strength of polarizing field for a given poling temperature. The maximum current (I_m) increases linearly with the polarizing fields. The linear increase of I_m with the increase in the applied field for α - and β -relaxations is confirming the presence of uniform bulk polarization and hence dipolar nature of these relaxations [14]. An increase in current maxima of δ -peak, that is, located at higher temperature is attributed to the space charge effects that are the increasing with increasing polarizing field [1].

It is clear from Figure 5 that the glass transition of this aromatic copolyester is broadened, at higher polarizing fields. The broad glass transition in the liquid crystal polymers may be attributed to structural heterogeneities of the chains [15]. Various studies such as calorimetric [16] and TSC [15] have shown that the glass transition width is significantly broad in LCP's as compared to amorphous polymers and even high crystalline materials.

The TSDC spectra were analyzed using Bucci-Fieschi-Guidi analysis. Table 1 gives the relaxation parameters activation energy, relaxation strength, preexponential factor, charge released, and concentration of traps for β -relaxation, at various polarizing fields evaluated using BFG plots. Similarly, the values of various relaxation parameters for α -relaxation are listed in Table 2. The relaxation parameters, activation energy, dielectric strength, and preexponential factor were calculated by taking the linear part of BFG plot. It is observed from Tables 1 and 2 that with the increase in polarizing field, activation energy decreases, while preexponential factor and relaxation strength increase. Also, the charge released and concentration of traps increase with the increase in polarizing field. The natural logarithm of preexponential factor is plotted as a function of activation energy for β - and α -relaxations as shown in Figures 7 and 8, respectively. The linear variation between the $\ln \tau_0$ and activation energy indicates the presence of compensation effect for dipolar relaxations of thermotropic liquid crystal copolyester Vectra-A under present polarizing conditions, that is, at $T_p = 80^\circ\text{C}$ and for poling fields in the range of 3.8 kV/cm–19.2 kV/cm. The compensation effect in thin films of Vectra-A and Vectra-E was also reported by Collins and Long [2]. Compensation in terms of the linear dependence of E and $\log \tau_0$ or in

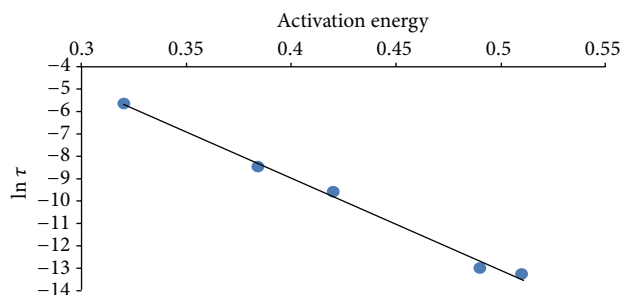


FIGURE 7: Variation of natural logarithm of preexponential factor with activation energy for β -relaxation.

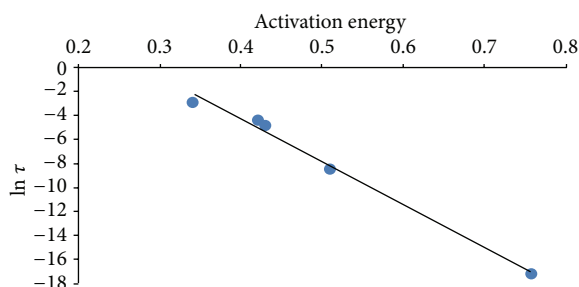


FIGURE 8: Variation of natural logarithm of preexponential factor with activation energy for α -relaxation.

TABLE 2: Values of activation energy (U), dipolar relaxation strength $\Delta\epsilon$, preexponential factor (τ_0), charge released (Q), and concentration of traps (N_t) for α -relaxation at poling temperature $T_p = 80^\circ\text{C}$ for various polarizing fields.

Poling fields (kV/cm)	α -relaxation				
	U (eV)	$\Delta\epsilon$	τ_0 (Sec)	Q (C)	N_t (m^{-3})
3.8	0.76	2.8	3.75×10^{-8}	24×10^{-10}	6.53×10^{12}
7.7	0.51	3.3	1.98×10^{-4}	58.80×10^{-10}	16×10^{12}
11.5	0.43	4.6	7.48×10^{-3}	120×10^{-10}	16×10^{12}
15.3	0.42	4.73	1.25×10^{-2}	162.87×10^{-10}	44.33×10^{12}
19.2	0.34	4.99	5.60×10^{-2}	216.09×10^{-10}	58.82×10^{12}

algebraically similar forms in terms of ΔH and ΔS is discussed in the literature [17, 18]. The activated phenomena like solid-state diffusion in crystals and polymers, dielectric relaxation, conduction and thermally stimulated processes in polymers, and electronic conduction in amorphous semiconductors show the presence of compensation behavior [19, 20].

5. Conclusions

The TSDC investigations of liquid crystal copolyester Vectra-A reveals two dipolar relaxations, namely, β -, α - and a space charge δ -relaxation in the temperature range from 15°C to 250°C . The β -relaxation around 25°C is due to rotation of HNA groups, and the α -relaxation around 110°C is associated with glass transition. The δ relaxation around 220°C is due to space charge trapping. The present studies

indicate that positions and maximum currents of dipolar β - and α -relaxation are dependent on polarizing fields. The maximum current of β -, α -, and δ -relaxations increases with the increasing polarizing fields. There is also a shift in maximum current of β - and α -relaxations towards high temperature with the increase in polarizing field which is the characteristics of dipolar peaks. The linear variation between the activation energy and natural logarithm of preexponential factor indicates the presence of compensation effect for dipolar relaxations of thermotropic liquid crystal copolyester Vectra-A.

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