

## **THERMALLY STIMULATED PROCESSES IN A LIQUID CRYSTAL POLYMER**

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### **Abstract**

Measurement of voltage-induced thermal depolarization current and calculation of the rate of depolarization as well as the parameters of drift mobility and conductivity of charge carriers for melt-extruded neat unreinforced grade A950 VECTRA<sup>®</sup> resin – a wholly aromatic copolyester – strongly suggest that an irreversible minor transition centered around 65°C is the primary thermal process related to molecular realignment. Changes in capacitance values with temperature also show this to be the most active temperature region. A major depolarization peak at 100°C having the characteristics of a  $T_g$  cannot be justified as due to glass transition but likely to result from molecular motions involving long range intermolecular order. The interpretation for both transitions can be supported by the mechanical response of this polymer. An important outcome of this work is the assertion that contrary to current thinking, it is the number of charge carriers and not viscosity alone that will have to be considered in future development of fast response liquid crystal displays along with the development of newer liquid crystal polymer structures.

**Keywords:** charge carriers, depolarization rate, liquid crystalline polyester, molecular realignment, thermal depolarization current, viscosity

### **Introduction**

Liquid crystal polymers (LCP's) are dielectric materials comprising both polar groups in anisotropic distribution and non-polar side chains that impart the characteristic liquid crystal properties. Applicable liquid crystal parameters include viscosity, elasticity, dielectric constant and optical birefringence. Temperature is an important controlling factor for these variables in the use of LCP's which requires application of a voltage. The applied voltage causes molecular realignment and internal polarization associated with a certain amount of charge accumulation in the polymer domains. Depolarization and current discharge can only be effected by thermal stimulation. The discharge current is entirely characteristic of the charging process.

LCP's typically contain rigid rod-like molecules in parallel configuration. Multifaceted orientations in liquid crystal polymer molecules and dipolar entities have been and continue to be studied for applications in opto-electronics and display technologies [1]. Primary requirements for these applications are fast molecular realignment and an effectively low viscosity when a voltage is applied. These two parameters have been examined in this paper.

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Temperature plays an important role since response time for electro-optical effects is temperature dependent, even though LCP's must be liquid crystalline at ambient temperature for practical applications.

A large variety of liquid crystal mixtures with different molecular structures are used in a given application. Voltage-induced thermally activated processes can be complex and difficult to study for such mixtures. It was therefore thought desirable to establish a correlation between these processes and the functional characteristics of a typical liquid crystal polymer.

### Experimental

Samples in the form of films (7 mil/0.017 cm) from melt extruded pellets of neat unreinforced grade A950 VECTRA<sup>®</sup> resin – a wholly aromatic copolyester – based partly on 2,6-naphthalene dicarboxylic acid and *p*-hydroxybenzoic acid manufactured by Hoechst-Celanese Corporation [2] were used in this work. The films, as produced, contain highly uni-directional linear molecules and are colored brownish-yellow.

The test specimens were readily susceptible to static charging, an example of which is shown in Fig. 1 which was obtained according to test protocol EIA-541 [3], using a Spellman High Voltage DC power supply (Spellman High Voltage Electronic Corporation, Plainview, N. Y. ) and a Faraday cup test fixture. It shows this material to be capable of considerable charge accumulation and slow discharge over sufficiently long period of time. The charging voltage was 5 KV DC. The test samples were short-circuited for all subsequent work in a pair of Balsbaugh stainless steel electrodes (Balsbaugh Laboratories, Hingham, Mass.) at 50°C for one hour to dissipate any inherent or residual charge prior to testing. The actual magnitude and variability of intrinsic thermal discharge current for a test specimen without prior voltage application is shown in Fig. 2.

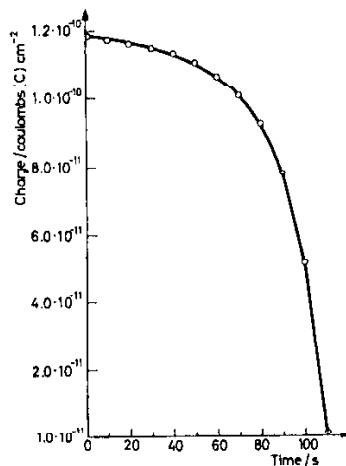


Fig. 1 Time-dependent charge dissipation for VECTRA<sup>®</sup>

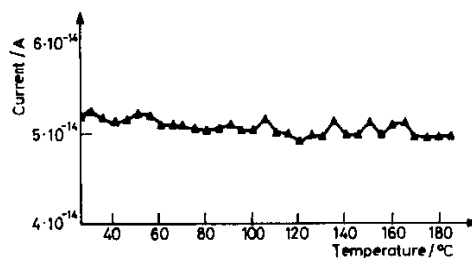


Fig. 2 Thermal discharge current without prior voltage application

Complete description of experimental details for voltage-induced polarization and thermal discharge procedures can be found in [4]. In this work, samples were poled at 100°C with 500, 1000 and 1500 V DC, annealed at 185°C for 2 h and air-cooled to room temperature under constant voltage. The heating rate was 5°C min<sup>-1</sup> for both polarization and discharge. A Delta temperature-programmable test chamber, model 1060S (Delta Design Engineers, San Diego, CA) in conjunction with a pair of Balsbaugh electrodes (total electrode area=31.669 cm<sup>2</sup>) and a Spellman DC Power Supply were used for the experimental set-up. A Keithley 617 programmable electrometer (Keithley, Cleveland, OH) was used for data collection and retrieval. Graphical figures were computer-drawn from this data.

## Results and discussion

Figure 3 shows two depolarization current vs. temperature curves obtained at poling fields of 500 and 1500 V. Each curve shows two prominent transitions – one centered around 65 and the other at 100°C. Both curves have the same relative current dispersion but show higher intensity at the higher voltage. The data at 1000 V has the same characteristics but omitted here to maintain clarity in Fig. 3.

Molecular alignment and orientational aspects are important parts of liquid crystal properties in functional applications. The large peak at 100°C and its shoulder at 65°C are thus manifestations of molecular mobility.

In keeping with the fact that VECTRA<sup>®</sup> exhibits strong energy-absorbing (damping) characteristics in the general temperature region of 50 to 80°C [5], the broad 65°C peak typifies elastic realignment of molecules from the initial isotropic orientation i.e. from (rigid) crystals to liquid crystals. It was also observed that the test sample does not produce the 65°C peak on repeat polarization. The loss of elastic transformation is thought to be due to high temperature annealing.

Since this material does not have a demonstrable  $T_g$  either by DSC or DMA, the prominent relaxation peak at 100°C is not due to glass transition but demonstrates long range intermolecular order which is a unique feature of liquid crystals. It has been claimed that future developments in high information content liquid crystal display devices will rely heavily on this singular attribute [1]. The intensity of this peak can be explained by the fact that creep resistance of this polymer in this temperature range is significantly lower than at ambient temperature [5].

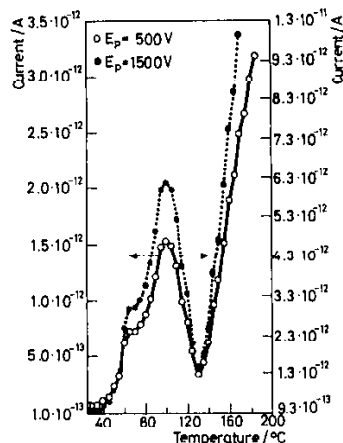


Fig. 3 Depolarization curve at 500 and 1500 V

The steady increase in current beyond 130°C is due to ohmic conduction which arises from external charging [6, 7] or Townsend breakdown [8] in the surrounding atmosphere.

The data for the above essential liquid crystal processes connected with the two transitions were further examined by their actual rate of depolarization. An equation, given below, was developed by the author earlier [9] for calculation of temperature dependent depolarization rate (in  $\text{A V}^{-1} \text{s}^{-1}$ ) from discharge current values:

$$\text{Depolarization rate} = [4\pi di(T)] / [\alpha(T)VA]$$

where  $d$  is the sample thickness in cm,  $i(T)$  is the discharge current as a function of temperature,  $\alpha(T)$  is the temperature dependent transport frequency (reciprocal of relaxation time),  $V$  is voltage drop across sample,  $A$  is the surface area of sample in contact with the electrodes.

Figure 4 shows the depolarization rate vs. temperature plots for the curves of Fig. 3. From these data, relaxation time ( $\tau$ ) at each temperature ( $K$ ) was calculated by using the equation:  $\tau = KT^2 / [H_r \Delta H_{a \text{ exp}} \Delta H_a / KT]$  where  $H_r$  is the heating rate ( $\text{K s}^{-1}$ ),  $\Delta H_a$  is the activation energy determined from an Arrhenius plot of  $\ln i$  vs.  $1/T$ ,  $K$  is Boltzmann constant (in  $\text{eV K}^{-1}$ ).

The use and calculation of all of the above parameters including those for drift mobility and conductivity of charge carriers have been described previously [10]. Additionally, voltage drop, required for the calculation of depolarization rate, was obtained by multiplying the measured current by sample resistance,  $R$ :

$$R = \rho(d/A)$$

$$\rho = 1/\text{conductivity}$$

where  $d$  is the sample thickness and  $A$  is the surface area of sample.

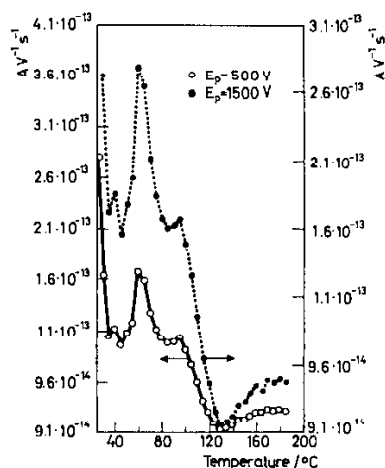


Fig. 4 Depolarization rates at 500 and 1500 V

As seen in Fig. 4, a major change in the rate of depolarization passes through a peak between 45 and 85°C which is the temperature region for the essential molecular realignment. The peak at 100°C appears only as a minor transition. The rate process clearly establishes the primary requirement of molecular realignment at the lower temperature to be the controlling parameter in liquid crystal properties.

It is known that liquid crystals exhibit dielectric anisotropy i.e. dielectric properties differ in different molecular orientation depending on the degree of freedom of dipole rotation. The effect of temperature on this property in VECTRA<sup>®</sup> was determined by measuring static capacitance values (directly related to dielectric constant) at 1 KHz over the temperature range of ambient to 110°C. Figure 5 shows a plot of capacitance vs. temperature for a sample specimen of VECTRA<sup>®</sup>. The measurements were made using a modular setup of a General Radio 716-C Capacitance bridge, a Hewlett-Packard 650A Oscillator, a pair of Rutherford Research (Rutherford, NJ) 1592-2T high temperature electrodes and a Tektronix 5103N Analog Oscilloscope. The graph clearly shows an initial rise in capacitance and a large drop in values occurring roughly in the general temperature region of 35 to 80°C before resuming the normal tendency of capacitance to increase with increasing temperature. This again lends support to the correlation that the main thermally stimulated process in the representative liquid crystal polymer occurs in this active temperature region.

Finally, numerical values of drift mobility,  $\mu_D = (J NeE)$ , where  $J$  is the current density in  $A cm^{-2}$ ,  $N$  is number of charge carriers in  $cm^3$ ,  $e$  is the magnitude of charge on the electron,  $E$  is the field strength in  $V cm^{-1}$  and conductivity of charge carriers,  $\sigma$  (in  $ohm^{-1} cm^{-1}$ ) or Siemens (S)  $cm^{-1}$ :

$$\sigma = Ne\mu_D$$

were calculated for the two depolarization curves of Fig. 3

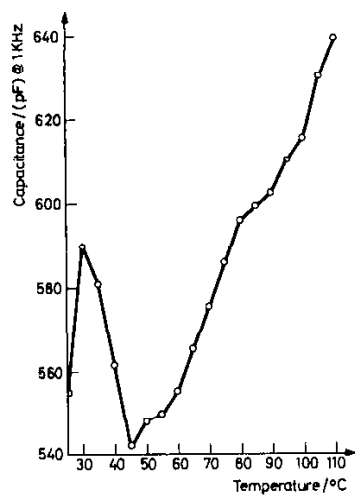


Fig. 5 Capacitance at 1 KHz vs. temperature for VECTRA®

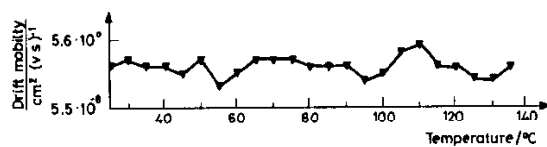


Fig. 6 Drift mobility vs. temperature at 500 V

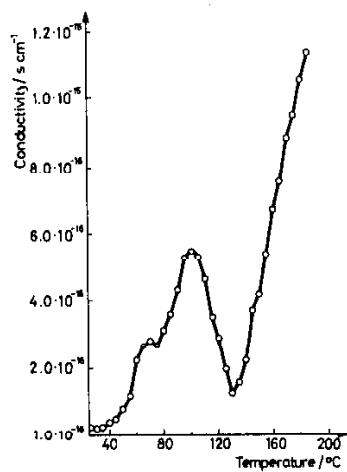


Fig. 7 Conductivity vs. temperature at 500 V

Conductivity in polymers is usually attributed almost exclusively to the diffusion of ionic charge carriers which is dependent on the viscosity of the transport medium. In the case of VECTRA<sup>®</sup>, the ratio of the calculated values of current density to the number of charge carriers were found to remain practically constant over the entire temperature range studied. Consequently, drift mobility does not vary much with temperature, as shown for example, in Fig. 6 for the poling field of 500 V DC. Conductivity (Fig. 7), on the other hand, parallels the thermal depolarization pattern which arises from variations in the number of charge carriers with temperature. Changes in viscosity alone would cause drift mobility to change accordingly. It is therefore concluded that it is the volume of charge carriers and not viscosity alone that will have to be considered in future developments for producing fast response in liquid crystal applications.

## Conclusions

Measurement of voltage-induced thermal depolarization current and calculation of the rate of depolarization as well as the parameters of drift mobility and conductivity of charge carriers for VECTRA<sup>®</sup> – a liquid crystalline polyester – clearly indicate that an apparent minor transition in the temperature range of approx. 50 to 80°C is the primary thermal process related to molecular realignment. Changes in capacitance values with temperature also show this to be the most active temperature region. A major depolarization peak at 100°C is not due to glass transition but may result from molecular motions involving long range intermolecular order. Additionally, it is concluded that it is the number of charge carriers and not viscosity alone that will have to be considered in future development of fast response liquid crystal displays along with the development of newer LCP structures .

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