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Dielectric Relaxation Investigations in Copolyesteramide (Vectra B950) Polymer Liquid Crystal: Thermally Stimulated Polarization Current Technique

J. K. Quamara[a]; S. K. Mahna[a]; Sanjeev Garg[a]

[a] Department of Physics, National Institute of Technology, Kurukshetra, India

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DIELECTRIC RELAXATION INVESTIGATIONS IN COPOLYESTERAMIDE (VECTRA B950) POLYMER LIQUID CRYSTAL: THERMALLY STIMULATED POLARIZATION CURRENT TECHNIQUE

J. K. Quamara, S. K. Mahna, and Sanjeev Garg

Department of Physics, National Institute of Technology, Kurukshetra, India

Thermally stimulated polarization currents (TSPC) in copolyesteramide (Vectra B950) polymer liquid crystal have been investigated in the temperature region 20°–250°C under different polarizing fields ranging from 0.7 to 7 kV/cm and with different heating rates. The low temperature region of the TSP current spectra shows a pronounced peak (P_1) around 30°C. This peak has been attributed to the dipolar relaxation process associated with ester group. The peak (P_2) observed around 140°C has been attributed to a combination of two relaxation processes, the dipolar and space charge relaxation processes. A steady rise in the TSP currents by several orders of magnitude is observed above 150°C. Saturation in the TSP current around 220°C reveals the presence of a relaxation process owing to the movement of large segmental groups in LC phase.

INTRODUCTION

The aromatic copolyesteramide polymer liquid crystal (plc) commercially known as Vectra B950 has drawn much attention owing to its unique rheological behavior and outstanding mechanical, chemical, and thermal properties.[1–3] Although considerable work has been reported on mechanical and thermal properties of Vectra B950 plc, only a few reports are available on its dielectric and electrical properties. Dielectric relaxation investigations in particular will not only be helpful in understanding the molecular dynamics of different segmental groups in the plc but will also determine its suitability for various practical applications. The field-induced thermally stimulated current (FITSC) technique is acknowledged to be a precise and powerful tool for studying the different dielectric relaxation processes in polymers. It comprises two mutually inverse processes, namely, thermally stimulated polarized current (currents generated in construction of polarization, TSPC) and thermally

stimulated depolarized current (currents generated in destruction of polarization, TSDC).[4–10]

Though a few TSDC results of Vectra B950 have been reported by Boersma et al.,[11] the relevance of the corresponding TSPC in addition to TSDC investigations is essential because comparison between the currents obtained during construction and destruction of internal polarization provides some valuable information regarding the molecular dynamics not available from either alone. In fact, TSPC is a more efficient diagnostic tool than TSDC in many respects, as it avoids overheating of the sample and also eliminates the search for optimum poling parameters. TSPC measurements also give an idea of the temperature at which ohmic conduction becomes significant.[5] This is necessary because after the onset of conduction, the frozen-in polarization in polymers gets quickly neutralized, thereby preventing subsequent TSDC or TSPC from its proper functioning. Apart from this, TSPC offers an attractive alternative to the conventional bridge methods for dielectric spectroscopy analysis. In the present article we report the dielectric relaxation behavior of Vectra B950 by investigating the TSP currents obtained under various biasing fields (E_p) and successive heating-cooling cycles with and without applying electric fields.

In the case of an ideal dielectric with free rotating dipoles with single relaxation mode the corresponding polarization current density is given as[4]

$$I_p(T) = \frac{N_d E_p \mu_0^2}{3kT\tau_0} \exp\left[\frac{-U}{kT} - \frac{1}{h\tau_0}\int_{T_1}^{T} \exp\left(\frac{-U}{kT'}\right)dT'\right] \tag{1}$$

where τ_0^{-1}, U, h, P_0, N_d, and μ_0 are the characteristic frequency factor, activation energy, uniform heating rate, saturation polarization, dipole concentration, and dipole moment respectively.

Since actual charging currents are, in general, accompanied by conduction currents, it would be more appropriate to express the observed TSP current in the form

$$i_P(T) = \frac{dP(T)}{dT} + g(T)E_P \tag{2}$$

where $g(T)$ is the ohmic conductivity. Further, the thermally generated polarization in the polymer can also be represented in terms of its dielectric constant (ε) as follows:

$$P = (\varepsilon - 1)\varepsilon_0 E_P \tag{3}$$

The thermal variation of dielectric constant (ε) with respect to its value at definite reference temperature (T_0) may be given as:[4,10]

$$\Delta\varepsilon(T) = \varepsilon(T) - \varepsilon(T_0) = \frac{1}{\varepsilon_0 E_P A h}\int_{T_0}^{T} I(T) - I_0(T)dT \tag{4}$$

where A is the sample area, h is heating rate, and I and I_0 are the values of first TSPC at temperature T with and without biasing field (E_P) respectively.

MATERIALS AND METHODS

The Vectra B950 used in the present investigations is a numetic thermotropic liquid crystal polymer with a composition of 60 mol% of 6-hydroxy-2-naphthoic acid (HNA), 20 mol% of terethalic acid (TA), and 20 mol% of 4-aminophenol (AP). The material was procured from Good Fellow (UK). The Vectra B950 samples in the form of pellets of thickness 1.4 mm and diameter 19 mm were metallized on both sides by vacuum evaporation of aluminum to form electrical contacts. The sample holder designed for this purpose was suspended inside a properly earthed metallic chamber. After the transient current was reduced to almost negligible value at room temperature, a linear thermal program (2°C/min) was run with simultaneous application of constant dc electric field E_P across the sample in series with a sensitive electrometer (Keithley 610C) to measure the TSP currents.

The slow heating rate is essential in order to prevent temperature gradient within the sample as well as in obtaining a fine resolution in the current temperature spectra. McKeever and Hughes[12] have described the initial cooling of the samples to very low temperature (around 77 K) so as to freeze the dipoles in their random positions prior to the start of the heating in the presence of dc field. However, the initial cooling may also be done up to relatively higher temperatures, as reported by other workers.[13,14] If the sample is short-circuited for a sufficient time and spurious polarization is allowed to decay, it may be eliminated altogether. We have successfully applied this in the present work while carrying out 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 kept at (T_1) for about 30 min to allow all the relaxation modes to become almost saturated at that point. The activation energy of the TSPC peaks has been obtained using the Bucci plot method.

RESULTS AND DISCUSSIONS

Typical TSPC spectra of Vectra B950 samples for various polarizing fields ranging from 0.7 to 7 kV/cm are depicted in Figure 1. A well-defined current peak (P_1) around 30°C and a current peak (P_2) around 140°C, which is not as pronounced as peak (P_1), appear in each current temperature characteristic. After completion of peak (P_2), we observe a steady rise in the TSP current in the high temperature region above 150°C. These observations are in conformity with the non-isothermal charging mechanism of a dielectric as mentioned in the theory, where the polarization current I_P is supposed to consist of two components behaving differently as a function of temperature; the dipolar orientation as a transient process gives rise to a current peak, whereas the conduction current that originates from the motion of the equilibrium charge carriers increases continuously with temperature.

Boersma et al.[11] have discussed the occurrence of a relaxation process (termed β-relaxation) in Vectra B950 in the low temperature region owing to the rotation of HNA units around 15°C, which is almost 15°C below peak (P_1). This shows that there may not be a significant contribution of β-relaxation towards peak (P_1). Interestingly, in the case of Vectra-A and Vectra-E, a transition has been shown around 35°C in temperature versus loss modulus curves.[15] Since peak (P_1) lies in
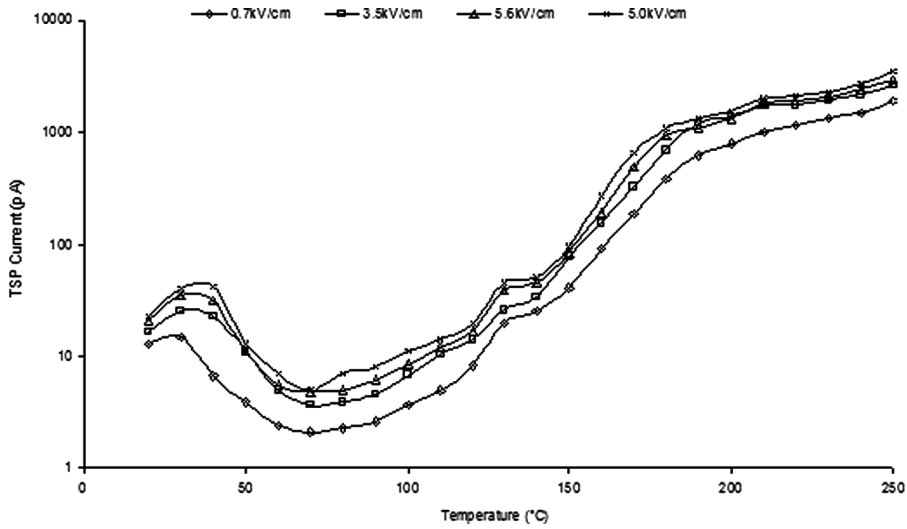
Figure 1. TSPC spectra of Vectra B samples under different polarizing fields.

the same temperature region, it appears that there should be some common molecular dynamics in these plcs governing this relaxation process.

From the structural analysis of Vectra series plcs (A, B, and E), it is observed that ester linkage is common among them. It is therefore very likely that the dipolar nature of ester linkage (we term it β'-relaxation) may be the cause of peak (P_1). An increase in peak current with increasing polarizing field implies the occurrence of uniform bulk polarization. The vanishing of this peak in the second TSPC cycle (Figure 2) further supports the dipolar nature of peak (P_1).

Figure 2. Repeated heating-cooling-reheating cycles for $E_P = 3.5\,kV/cm$.

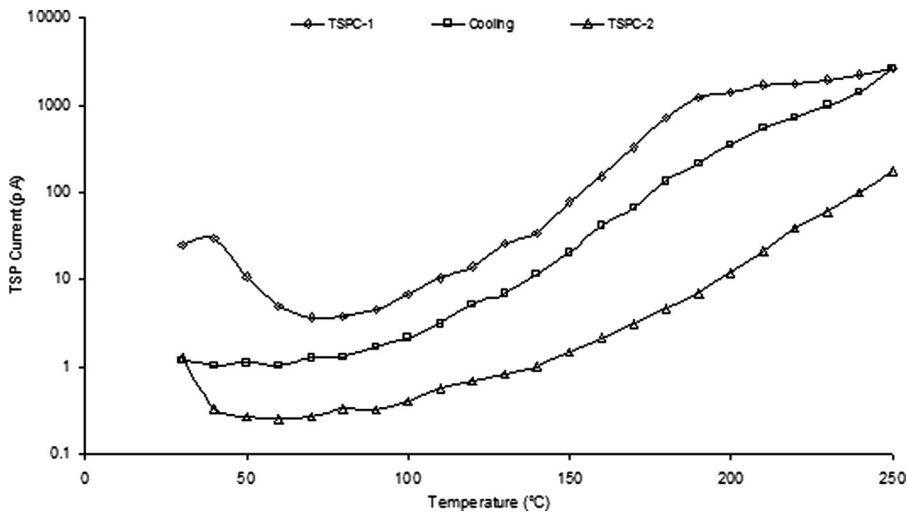This is owing to the fact that during the repeated polarization cycle no more dipoles are there to orient, and the saturation polarization has already been completed and would not result in the formation of any current maxima.

The origin of peak (P_2) can be associated with a composite relaxation process occurring in Vectra B. Boersma et al.[11] and Jawad et al.[16] have discussed the presence of a relaxation process (termed α-relaxation) around $144°C$. They have ascribed this relaxation to the cooperative rotation of the main chain segment related to the glass transition temperature. The activation energy for this peak (P_2) computed from the present TSPC data comes in the order of $0.38\,eV$. This value is very close to activation energy of a dipolar relaxation process owing to carbonyl groups.[14] We observe the presence of a large number of carbonyl groups in Vectra B structure linked with HNA as well as TA units. It is therefore very likely that the segmental rotation discussed by Jawad et al.[16] is nothing else than the dipolar orientation relaxation process associated with carbonyl group $[>C=O]$ as also observed in other plcs.[17] Interestingly, we do not observe a proportional relationship between the peak magnitude and polarizing field E_P for this peak, a major aspect of a dipolar relaxation process. Therefore it will be reasonable to relate peak (P_2) with a hybrid character arising from the combination of dipolar relaxation and a space charge relaxation process.

The space charge relaxation process in polymers (we term it α-relaxation) usually arises from the space charge trapping mechanism. In polymer liquid crystals, charge trapping is possible owing to the presence of the crystalline phase responsible for space charge formation via interfacial polarization (Maxwell-Wagner-Sillars effect).[18] In addition, the unsaturated amide and carbonyl groups, which are due to conjugation, can act as traps for charge carriers, contributing to their transport and trapping. Charge trapping may also take place at aromatic carbon but the probability is much lower than that of charge trapping at carbonyl carbon. This is due to the delocalization of π-electron in the aromatic ring.

In the light of the above, it will be more reasonable to associate peak (P_2) to a relaxation process governed jointly by dipolar and space charge relaxation. The combination of these relaxation processes is usually termed the $\alpha\beta$-relaxation laxation process.[19,20] This happens when the characteristic relaxation time for the β-relaxation process reaches an order of magnitude similar to that of primary α-relaxation. Though the occurrence of such $\alpha\beta$-relaxation process is not quite common in amorphous polymers, in the case of liquid crystal polymers owing to their biphasic character there is ample possibility of such a relaxation process. It is also not difficult to understand why $\alpha\beta$-relaxation does not result in a well-defined or fully developed current peak. Since α-relaxation, which is primarily a space charge relaxation process, is more sensitive to the migration of charge carriers, it is very likely that during the TSPC process the $\alpha\beta$-relaxation is more influenced by the conduction currents, thereby deviating it from the true current maximum. Further, 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 shows a maximum in the loss modulus versus temperature curve around $160°–170°C$,[15] which is in conformity with the occurrence of α-relaxation around this temperature.

Vectra B950 has 4-aminophenol (AP) as a rigid liquid crystal group connected to HNA and TA groups either by rigid or flexible non-LC spacers. Lenz[21] has found that flexible spacers are particularly important for thermotropic longitudinal plcs for determining their molecular behavior. The type and length of the spacer can determine whether a numetic, cholesteric, or sematic phase is formed. At elevated temperature under the influence of field, a reduction in the length of the spacer results in an increase in the rigidity of the molecules and may shift the peak to higher temperature. In the present case, a slight shift in the current peak (P_2) towards higher temperature with increasing E_P is in conformity with the above. The absence of current peak (P_2) in the second TSPC cycle is obvious owing to the fact that the dipolar component of this peak cannot produce a current maximum for the reasons discussed earlier and the space charge component of this peak is overcome by conduction currents.

Above 150°C after the $\alpha\beta$-relaxation is over, the entire TSPC spectra are dominated by conduction currents. We observe a steady rise in the TSP currents with increasing temperature by several orders of magnitude followed by a saturation in the current around 220°C. Though TSP currents do not form any maximum, certainly there is a possibility of a relaxation process occurring in the temperature region 220°–240°C. High temperature transitions in the plcs usually occur owing to melting, i.e., the movement of large segmental groups in the LC phase. Quamara and Sridharbabu[22] have also observed such a transition in PET/x.PHB liquid crystal polymer and have termed this the δ-relaxation process. The occurrence of such a relaxation process in Vectra B950 is also evident from an abrupt decrease in its tensile modulii around 220°C.[15] A similar crystalline phase transition has also been observed in Vectra-A around this temperature in the form of maximum in tensile loss modulus versus temperature curves.[15] In Vectra B950, since the LC phase arises from the 4-aminophenol (AP) unit, we can associate the δ-relaxation process to the segmental motion of AP units.

We do not hesitate to mention that in many respects the experimental findings of the present investigations do not apparently conform to those predicted on the basis of the theoretical model for FITSC proposed by Vanderschuren and Gasiot[4] or the model calculations for the pure displacement current by Shindo.[23] The absence of any current reversal following the dipolar peak (Figure 1) and the large magnitude of TSP currents in the high-temperature region virtually deviate from the theoretical inferences. However, this can be accounted for in the light of the fact that the assumptions made in the aforementioned model are too simplified and rarely valid in actual practice. Further, the charging currents are inherently superimposed onto the dc conduction currents. Another prerequisite, namely the existence of a single relaxation mode, could also not be satisfied even when the ohmic conduction is negligible.

A differentiation between conduction current and polarization current can also be done by adopting different heating rates during the TSPC process as it affects the characteristics of the latter component but not that of the former.[4] Figure 3 illustrates the TSPC spectra of Vectra B950 samples for different heating rates. A shift in peak (P_1) towards higher temperature with enhanced magnitude with increasing heating rates confirms the dipolar nature of this peak. The TSPC
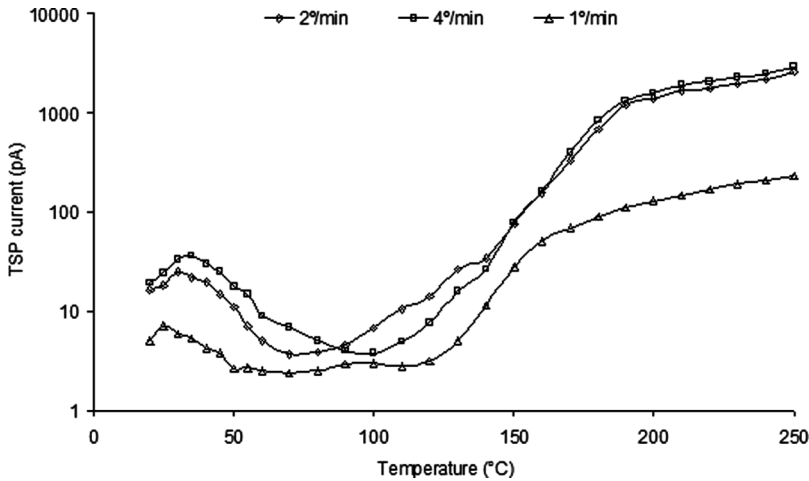
Figure 3. TSPC spectra of Vectra B samples under different heating rates, $E_P = 3.5$ kV/cm.

characteristic for 1°C/min heating rate also shows a maximum around 100°C, which is very close to the glass transition temperature (110°C) of Vectra B950.[24] We can associate this transition with the T_g of Vectra B950. The absence of this transition in TSPC spectra for higher heating rates may be due to fact that sufficient time is not available for the orientation of this transition to take place.

The thermal variation of dielectric constant ($\Delta\varepsilon$) of Vectra B950 with respect to its value at room temperature (20°C) has been estimated from their respective TSPC data using Equation (4). Table I gives the dielectric constant ($\Delta\varepsilon'$) values measured independently using an LCZ meter along with those estimated using TSPC data. We observe good agreement between $\Delta\varepsilon$ and $\Delta\varepsilon'$ in the low temperature region for low values of electric field. However, there is a significant deviation in $\Delta\varepsilon$ from $\Delta\varepsilon'$ at high temperatures and electric fields owing to the dominance of conduction currents in high-temperature TSPC spectra.

Table I. Temperature variation of dielectric constant as deduced from direct measurement, $\Delta\varepsilon'$, and from TSPC data, $\Delta\varepsilon$

T (°C)	$\Delta\varepsilon'$	$\Delta\varepsilon$			
		0.7	3.5	5.6	7.0 kV/cm
30	5.71	6.01	6.18	6.76	6.89
50	5.63	6.45	6.63	6.89	6.99
70	6.16	7.12	7.39	7.53	7.77
100	6.34	7.55	7.99	8.91	10.21
120	6.39	17.89	21.45	33.22	37.99
150	6.45	40.12	47.89	55.34	60.12

CONCLUSIONS

The TSP current characteristics of Vectra B950 polymer liquid crystal obtained for various polarizing fields and heating rates reveal the presence of multiple relaxation processes in this plc. A dipolar relaxation process due to ester linkage occurs in the low temperature region around 30°C. A composite relaxation process ($\alpha\beta$-relaxation) occurs around 140°C. The large conduction currents dominate the TSPC spectra beyond $\alpha\beta$-relaxation followed by saturation around 220°C, revealing the occurrence of a relaxation process due segmental motion of liquid crystalline AP units. At low temperature, there is good agreement between dielectric values obtained from TSPC data and those measured directly using an LCZ meter.

REFERENCES

1. Dreher, S., S. Seifert, H. G. Zachmann, N. Moszner, P. Mercoli, and G. Zanghellini. 1998. Chain orientation in melt-extruded samples of Vectra A, Vectra B, and blends in relation to the mechanical properties. *J. Appl. Polym. Sci.* 67: 531–545.

2. Alfageme, J., J. J. Iruin, and C. Uriarte. 1995. Characterization of acid-base properties of a polyetherimide and two liquid crystalline polymers by inverse gas chromatography. *Int. J. Polym. Anal. Charact.* 1: 349–363.

3. Chung, T. S., M. Cheng, P. K. Pallathadka, and S. H. Goh. 1999. Thermal analysis of Vectra B950 liquid crystal polymer. *Polym. Eng. Sci.* 39: 953–962.

4. Vanderschuren, J., and J. Gasiot. 1979. In *Thermally Stimulated Relaxation in Solids*, ed. P. Bräunlich, New York: Springer-Verlag, pp. 135–224.

5. Turnhout, J. van. 1980. In *Electrets*, ed. G. M. Sessler, New York: Springer-Verlag, pp. 81–216.

6. Quamara, J. K., N. Singh, and A. Singh. 2001. Study of dielectric relaxation processes in poly (*p*-phenylene sulfide) using a thermally stimulated discharge current technique. *Macromol. Chem Phys.* 202: 1955–1960.

7. Khemici, M. W., A. Gourari, and M. Bendaoud. 2006. Study of the effect of annealing and physical aging on PVC by the thermally stimulated currents methods. *Int. J. Polym. Anal. Charact.* 11: 101–114.

8. Khemici, M. W., A. Gourari, and N. Doulache. 2009. Dielectric characterization of poly ethylene naphtalene 2,6 dicarboxylate (PEN) by thermally stimulated currents technique (TSC). *Int. J. Polym. Anal. Charact.* 14: 322–335.

9. Hong, C. M., and D. E. Day. 1979. Thermally stimulated polarization and depolarization current (TSPC/TSDC) techniques for studying ion motion in glass. *J. Mater. Sci.* 14: 2493–2499.

10. Ikeda, S., and K. Matsuda. 1982. Thermally stimulated currents in polytetrafluoroethylene in the neighborhood of room temperature transitions. *Jpn. J. Appl. Phys.* 21: 359–362.

11. Boersma, A., J. van Turnhout, and M. Wubbenhorst. 1998. Dielectric characterization of a thermotropic liquid crystalline copolyesteramide: 1. Relaxation peak assignment. *Macromolecules* 31: 7453–7460.

12. McKeever, S. W. S., and D. M. Hughes. 1975. Thermally stimulated currents in dielectrics. *J. Phys. D Appl. Phys.* 8 (13): 1520–1529.

13. Gill-Zambrano, J. L., and C. Juhanz. 1985. In *5th International Symposium on Electrets (ISE 5), Honoring Professor Bernhard Gross: 4–6 September, 1985, Castle of Heidelberg, West-Germany: Proceedings*, Piscataway, N.J.: IEEE, p. 235.

14. Bhardwaj, R. P., J. K. Quamara, K. K. Nagpal, and B. L. Sharma. 1983. Field-induced thermally stimulated currents in Kapton-H polyimide films. *Phys. Status Solidi A Appl. Mater. Sci.* 80: 559–566.

15. Shepard, D. D., and B. Twombly. 1996. Simultaneous dynamic mechanical analysis and dielectric analysis of polymers. *Thermochim. Acta* 272: 125–129.

16. Jawad, S. A., and M. H. Alhaj-Mohammed. 1992. Dynamic mechanical and dielectric relaxations in liquid crystalline copolymers formed from hydroxynaphthoic acid, terephthalic acid and *p*-aminophenol. *Mater. Lett.* 13: 312–317.

17. Sridharbabu, Y., and J. K. Quamara. 2004. TSDC behaviour of pristine and irradiated PET/0.8PHB polymer liquid crystal samples. *J. Mater. Sci.* 39: 4651–4653.

18. Brostow, W., B. K. Kaushik, S. B. Mal, and I. M. Talwar. 1992. Thermally stimulated depolarization of a copolymer of poly (ethylene terephthalate) and *p*-hydroxybenzoic acid. *Polymer* 33: 4687–4692.

19. Arbe, A., J. Colmenero, and D. Richter. 2003. In *Broadband Dielectric Spectroscopy*, eds. F. Kremer and A. Schonhals, Berlin: Springer-Verlag, pp. 685–707.

20. Singh, R., B. K. Kaushik, and J. K. Quamara. 2008. Investigations of thermally stimulated polarization current in polyetherimide. *Indian J. Pure Appl. Phys.* 46: 491–501.

21. Lenz, R. W. 1985. Balancing mesogenic and non-mesogenic groups in the design of thermotropic polyesters. *Faraday Discuss.* 79: 21–32.

22. Quamara, J. K., and Y. Sridharbabu. 2003. Thermally stimulated depolarization current studies in pristine and 100 MeV Ni-ion irradiated PET/0.3 PHB polymer liquid crystal. *Indian J. Pure Appl. Phys.* 41: 790–800.

23. Shindo, K. 1979. *Shiga Univ. Fac. Lib. Arts Educ. Mem. Nat. Sci.* 29: 19.

24. Baird, D. G., C. G. Robertson, and J. P. de Souza. 1998. Liquid crystalline polymer reinforced thermoplastic fibers. U.S. Patent 5834560.