Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Measurements of polarization reversal current of a ferroelectric liquid crystalline polymer

H. Endo[a]; S. Hachiya[a]; K. Kawasaki[a]
[a] Central Research Laboratories, Idemitsu Kosan Co., Ltd., Chiba, Japan

To cite this Article Endo, H. , Hachiya, S. and Kawasaki, K.(1993) 'Measurements of polarization reversal current of a ferroelectric liquid crystalline polymer', Liquid Crystals, 13: 5, 721 — 728

To link to this Article: DOI: 10.1080/02678299308026344

URL: http://dx.doi.org/10.1080/02678299308026344

LIQUID CRYSTALS, 1993, VOL. 13, NO. 5, 721–728

Measurements of polarization reversal current of a ferroelectric liquid crystalline polymer

by H. ENDO*, S. HACHIYA and K. KAWASAKI

Central Research Laboratories, Idemitsu Kosan Co., Ltd.,
1280 Kamiizumi, Sodeguara, Chiba 299-02, Japan

(*Received 20 July 1992; accepted 4 January 1993*)

The polarization reversal currents of a ferroelectric liquid crystalline polymer were measured. The shape of the current signal was similar to that of low molecular weight ferroelectric liquid crystals. It was found from our calculations that the shape of the current signal was independent of the polydispersity of the polymer. In ferroelectric liquid crystalline polymers, components having different molecular weights respond cooperatively with each other to the applied voltage. From the results of our simultaneous measurements of transmittance and polarization reversal current, the dipole unit and the core moiety in the side chains appear to move in a body.

1. Introduction

Ferroelectric liquid crystals (FLCs) are very interesting materials because of their potential for application in electro-optical display devices. These devices are characterized by their fast switching speed and memory effect [1]. But there are several difficulties in making FLC devices fit for practical use. One of these is the aligning of the FLC molecules along one direction. In order to overcome this difficulty we have polymerized ferroelectric liquid crystals [2–5]. Ferroelectric liquid crystalline polymers (FLCPs) were firstly reported by Shibaev *et al.* [6]. Since then, a number of ferroelectric liquid crystalline polymers have been studied by many researchers [7–18]. We have already discussed the spontaneous polarization [2, 4, 5], the rotational viscosity [4] and the layer structure [2, 5] of some synthetic ferroelectric liquid crystalline polymers. In particular, their rotational viscosities were much greater than those of low molecular weight FLCs.

In the present study we measured the polarization reversal current of a FLCP using an applied square wave voltage. The shape of the polarization reversal current signals was similar to that of low molecule weight FLCs. We discuss now the effect of the polydispersity of the FLCP on the polarization reversal current, since there has been no report discussing polydispersity of FLCPs in our survey. Here we measured simultaneously the polarization reversal current and the transmitted light intensity with the applied square wave voltage. From this result, we compared the motion of the dipole unit with the core moiety in the side chains. We also evaluated the rotational viscosity of our FLCP from the measurements of the polarization reversal currents. The origin of the large rotational viscosity of the FLCP will be discussed.

2. Experimental

2.1. *Materials*

The ferroelectric liquid crystalline polymer used in our experiments was synthesized as follows (see figure 1). 10-iodo-1-decene (0·01 mol; 5·3 g) was added to methyl

---

* Author for correspondence.

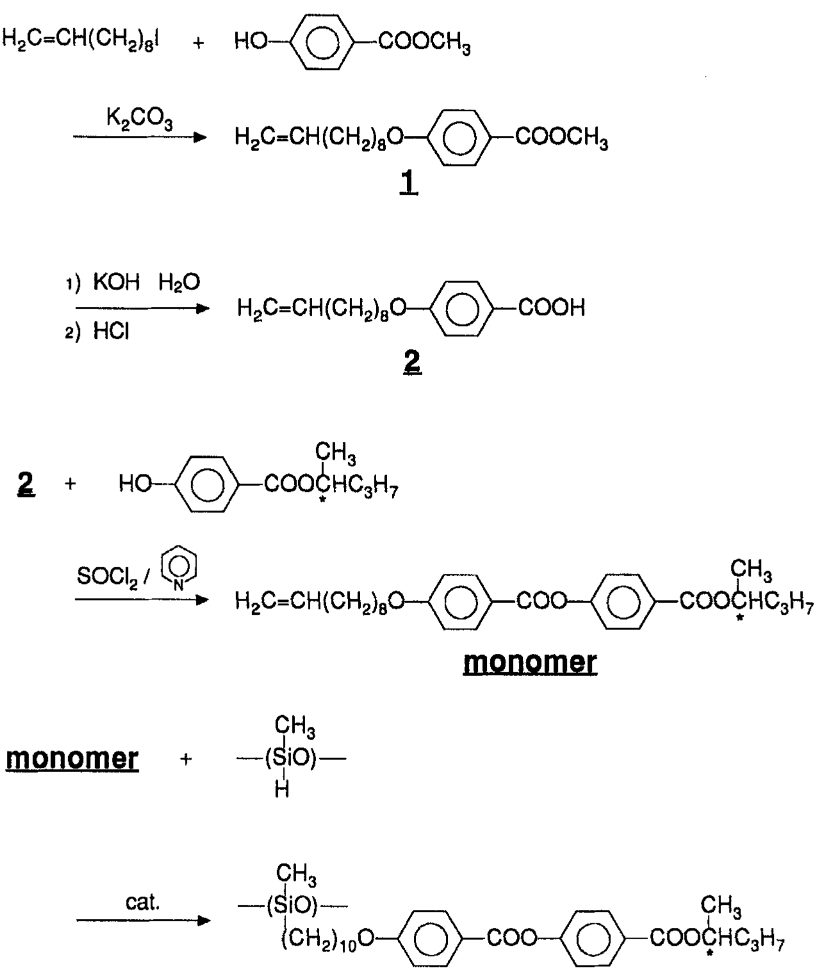

Figure 1. The synthetic route and molecular structure of the ferroelectric liquid crystalline polymer.

4-hydroxybenzoate (0·02 mol; 3·0 g) and potassium carbonate (0·03 mol; 4·1 g). The mixture was heated at reflux in butan-2-one for 8 hours. Insoluble material was filtered off and the solvent was removed by evaporation. The residue was purified by column chromatography; 4·4 g of **1** were obtained.

1 (0·015 mol; 4·4 g), potassium hydroxide (0·045 mol; 2·5 g) and water (0·02 mol; 0·36 g) were dissolved in ethanol. The mixture was heated at reflux for 1 hour. 100 ml of water was added and the mixture was boiled for a second hour. The solution was cooled to room temperature, and 3 M hydrochloric acid was added so that the pH was adjusted to 2. The precipitate was filtered off, washed with water and dried in vacuo; 4·0 g of **2** were obtained.

Thionyl chloride (3 ml) was added to a solution of **2** (0·01 mol; 2·8 g) in toluene. The mixture was stirred for 2 hours at 535 K. The toluene and the excess of thionyl chloride were removed by evaporation to obtain the acid chloride. A solution of 1-methylbutyl 4-hydroxybenzoate (0·01 mol; 2·1 g) and pyridine (0·015 mol; 1·2 g) in toluene was added to a solution of the acid chloride in toluene and the mixture was stirred overnight at room temperature. Subsequently, the resulting reaction solution was washed with water, dried over magnesium sulphate and the solvent removed by evaporation. The residue was purified by column chromatography; 3·8 g of monomer were obtained.

The monomer (0·0064 mol; 3·0 g) and poly(methylhydrogensiloxane) (degree of polymerization $\bar{p}=35$; 0·35 g) were dissolved in toluene under an argon atmosphere, and 2 mg of hexachloroplatinic acid was added as catalyst. The mixture was heated at 358 K for 5 hours. After the reaction, the solvent was removed by evaporation. The residue was purified by column chromatography; 2·9 g of polymer were obtained.

2.2. *Measurements*

The molecular weight distribution of our FLCP, measured using gel permeation chromatography (GPC) with chloroform as solvent, and calibrated with polystyrene as standard, is shown in figure 2. In this measurement we obtained $M_n = 8{\cdot}8 \times 10^3$, $M_w = 1{\cdot}2 \times 10^4$. The transition temperatures determined by using both differential scanning calorimetry (DSC) and polarized optical microscopy are given below

$$\text{Glass-255 K-S}_C^*\text{-338 K-S}_A\text{-348 K-I}$$

The synthesized FLCP was laminated with two ITO coated glass plates. The gap of the cell was controlled by inserting silica beads of diameter 3 μm as spacers. We used no alignment layer on the ITO electrodes. The cell was mounted on a Mettler FP 82 hot stage and the temperature was controlled by a central processor. At first, the cell was heated to form the isotropic phase and then slowly cooled down to the S_A phase. In this phase, alignment of the side chains of the FLCP was achieved by the shearing method. The area of the ITO electrode was 20 mm^2. We took care not to change the effective area of the electrode through displacement of the upper and lower electrode relative to each other. If they deviated, a precise spontaneous polarization value would not be evaluated.

The polarization reversal currents were amplified by a current-to-voltage amplifier and stored in a transient memory using an applied voltage step (±30 V). The hot stage was installed on the polarizing optical microscope. We detected the change in transmitted light intensity using crossed polarizers and a photodiode. The position of the crossed polarizers was suitably determined as described in the next section.

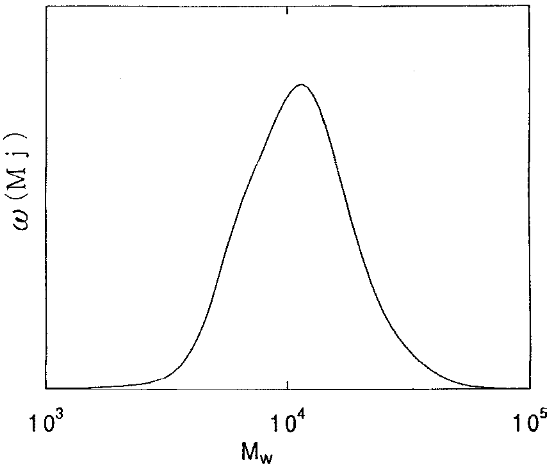

Figure 2. The distribution of molecular weights for the FLCP as measured by GPC.

3. Results and discussion

Figure 3 shows the current change between two electrodes at 313 K in the FLCP cell. The current decay due to the charge accumulation between two electrodes and the polarization current peak due to the dipole reversal were clearly separated after electric field reversal. The shape of the polarization current peak was similar to that of low molecular weight ferroelectric liquid crystals. But the order of the response time (the full width at half-maximum of the peak) was widely different from that of a low molecular weight FLC. The spontaneous polarization was evaluated by integration of the polarization reversal current peak. The value of the spontaneous polarization of this FLCP was $1{\cdot}2\,\mathrm{mCm^{-2}}$ at the temperature of 313 K.

It is obvious from the results of a measurement by GPC that the FLCP is polydisperse. We can regard the FLCP as a mixture of constituents which have different molecular weights. In the case of low molecular weight FLC mixtures, the components have structures differing in their alkyl chains, core moieties, and chiral parts. In such cases, the property of response to an electric field is not dominated by the individual properties of the components of the mixture; rather, the mixture as a whole has unique properties. In the case of the FLCPs we have already reported, that the rotational viscosities depend on their molecular weights [5]. Therefore, we can regard the FLCP as a mixture of various constituents. We then investigated the effect of the polydispersity on the polarization reversal current in a FLCP having a broad distribution of molecular weights. The polarization reversal current i as a function of time t is expressed by

$$i=\frac{d}{dt}P_s\cos\phi=\frac{P_s}{\tau}\sin^2\left[2\tan^{-1}\left\{\left(\tan\frac{\phi_0}{2}\right)\exp\left(\frac{t}{\tau}\right)\right\}\right], \tag{1}$$

$$\tau\equiv\frac{\eta}{P_sE}, \tag{2}$$

where P_s is the spontaneous polarization, η is the rotational viscosity, E is the applied electric field, ϕ is the azimuthal angle of the director and $\phi_0\equiv\phi\ (t=0)$ [19]. In this equation the effect due to the dielectric anisotropy of the molecule (side chain) was

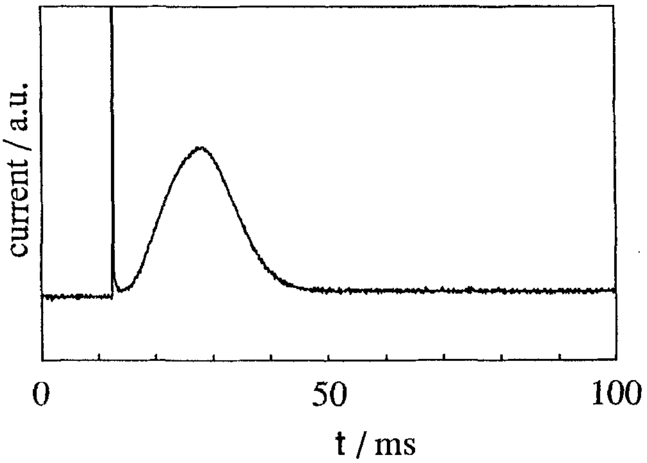

Figure 3. The current change between two electrodes at 313 K for the FLCP cell using an applied voltage step.

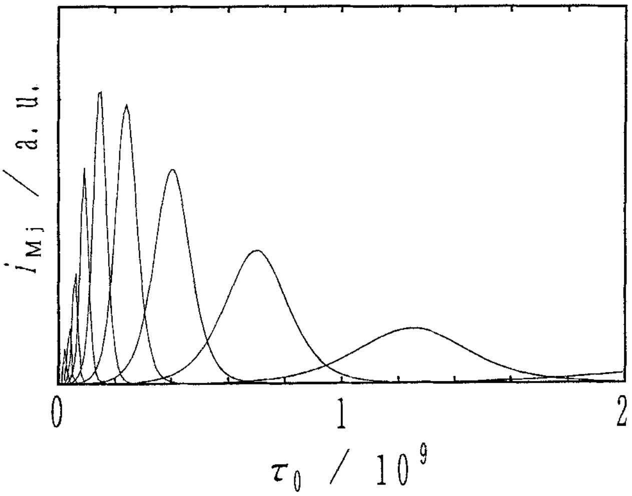

Figure 4. The calculated i_{Mj} as a function of τ_0.

neglected. We express the distribution of the molecular weight in the FLCP as $\omega(M_j)$. $\omega(M_j)$ represents the ratio of the composition j whose molecular weight is M_j. We have investigated the relationship between the rotational viscosity and molecular weight for the FLCP [5] and obtained the result that the rotational viscosity of the FLCP was proportional to about the second power of the molecular weight. We generally write

$$\tau = \tau_0 M_j^a. \tag{3}$$

The polarization reversal current i_{M_j} due to the constituent M_j is expressed as

$$i_{M_j} = \frac{\omega(M_j)}{\Sigma\omega(M_j)} \frac{P_s}{\tau_0 M_j^a} \sin^2\left[2\tan^{-1}\left\{\left(\tan\frac{\phi_0}{2}\right)\exp\left(\frac{t}{\tau_0 M_j^a}\right)\right\}\right]. \tag{4}$$

In these equations we assumed that the spontaneous polarization was independent of molecular weight, and in equation (4) P_s is constant as could be presumed from our previous results [5]. So, the response time τ is proportional to the rotational viscosity η—by using equation (2). In other words τ can be expressed as in equation (3) for FLCPs having the same structure. In this equation $a = 2$. The i_{M_j} were calculated by using equation (4) where we supposed $\phi_0 = 1°$, $a = 2$. We tentatively divided the data obtained by GPC and used them in this calculation. Figure 4 shows i_{M_j} as a function of time τ_0. The total polarization reversal current was assumed to be the sum of each i_{M_j}. The whole signal for the current was calculated by using each i_{M_j} shaped asymmetrically. This was a wide-based shape in the latter half and obviously different from our experimental result. Therefore it can be presumed that the property of a FLCP having a broad distribution of molecular weights is determined cooperatively as a balance of each constituent, in the same way as for a mixture of low molecular weight FLCs. The polarization reversal current reflects the bulk property and not those of individual components, and the property of response to an electric field is not dominated by individual components. The details of the relation between the distribution of molecular weight and the response property are not yet revealed.

Then we investigated the response of the side chains in the FLCP by making a comparison between the change of polarization reversal current and that of the transmitted light intensity using crossed polarizers. The polarization reversal current

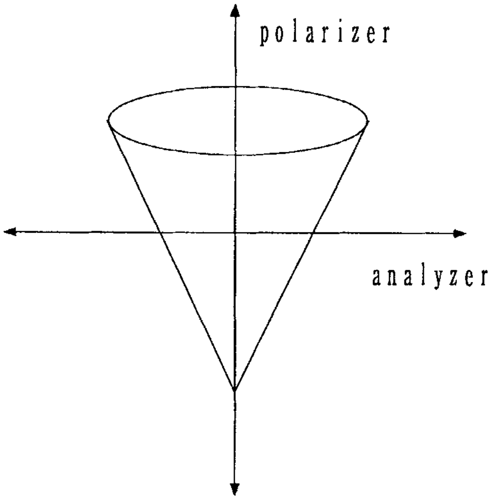

Figure 5. The position of the crossed polarizers with respect to the FLCP cell.

occurs with reversal of the dipole in the molecule and reflects the motion of the dipole as expressed by equation (1). In our FLCP, the C=O bond which is near the chiral carbon has a dipole moment. The C=O bond which is in the core moiety does not contribute to the spontaneous polarization because of its free rotation and separation from the chiral carbon.

On the other hand, the change in light transmittance reflects the motion of the core moiety, which has an optical anisotropy. When the polarization reversal current changed, as in figure 3, its peak position showed the moment when the dipole position ϕ was 90°, if we can neglect the dielectric anisotropy of the side chain. This was evident from equation (1). Even taking the dielectric anisotropy into account, the position of the peak shows the moment when the dipole position ϕ is about 90°. The deviation from 90° will be only 2°–3°.

Then we examined the position of the crossed polarizers in order to know the moment when the position ϕ of the core moiety was 90°. As previously mentioned, we can assess the motion of the core moiety in terms of the change of transmittance in setting the position of the crossed polarizers as in figure 5. This indicated that one direction of the crossed polarizers agreed with the smectic layer normal. In this way, we set up the position of the crossed polarizers so that the transmitted light intensity before field reversal is equal to that after field reversal. The peak position of transmittance showed the moment when the position ϕ of the core moiety was 90°. Figure 6 shows the simultaneous measurements of the change in polarization reversal current and that of the transmitted light intensity in the FLCP cell when a square wave voltage was applied. The positions of their peaks are mostly the same, and were independent of temperature. We deduced from this result that the core moiety of the FLCP moves as one unit with the dipole on applying the electric field. The side chains of FLCP may be regarded as rigid rods, like low molecular weight FLC molecules.

We evaluated the temperature dependence of the rotational viscosity using P_s and t_w, the latter of which is the full width at half-maximum of the peak obtained from the measurement of the polarization reversal currents with respect to changing temperature [19]. The result is shown in figure 7. The rotational viscosity of the FLCP was remarkably larger than that of low molecular weight FLCs. In other words a force of

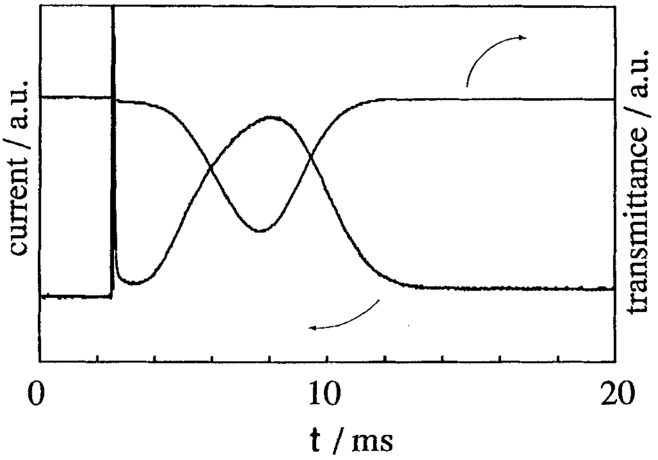

Figure 6. The simultaneous measurement of the change in polarization reversal current and in the transmitted light intensity in the FLCP cell.

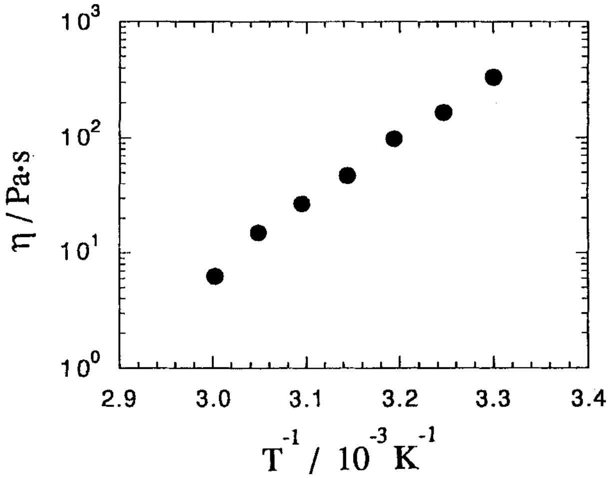

Figure 7. The Arrhenius plot for the rotational viscosity of the FLCP.

resistance, which does not exist in low molecular weight FLC systems, acts on the side chains of the FLCP when an electric field is applied. From our experiments, we know that the dipole moves simultaneously with the core moiety in the FLCP, similarly to the case for low molecular weight FLCs, and we suppose that the origin of the resistance is in the main chains (the backbone). When an electric field is applied, a side chain in the FLCP receives the force caused by the electric field and the dipole, and then moves. This side chain simultaneously exerts a force on other side chains in the same polymer. This force is transmitted through the main chain. So, the side chains receive the resistance from the main chain when they move. We have already observed the motion of the main chain by using Time resolved Fourier transformation Infrared Spectroscopy (FT-IR). It was found that the Si–O bond in the main chain moves at the same time as the side chain moves. The details of this will be described in a subsequent report. We suppose that this resistance is the origin of the apparent large rotational viscosity of the FLCP.

4. Conclusion

The polarization reversal currents of a ferroelectric liquid crystalline polymer were measured with respect to an applied square wave voltage. The shape of the signal did not reflect the properties of individual components having different molecular weights. The motion of the dipole moment and core moiety in the side group were investigated by simultaneous measurements of transmittance and polarization reversal current. It appears that they move together, like a rigid rod. Ferroelectric liquid crystalline polymers have high rotational viscosities. Their high viscosity is considered to originate from the main chain. Experimental investigation into the origin of this high viscosity is important and it is our intention to carry out further research in this area.

References

[1] Clark, N. A., and Lagerwall, S. T., 1980, *Appl. Phys. Lett.*, **36**, 899.

[2] Uchida, S., Morita, K., Miyoshi, K., Hashimoto, K., and Kawasaki, K., 1988, *Molec. Crystals liq. Crystals*, **155**, 93.

[3] Endo, H., Hachiya, S., Uchida, S., Hashimoto, K., and Kawasaki, K., 1991, *Liq. Crystals*, **9**, 635.

[4] Yuasa, K., Uchida, S., Sekiya, T., Hashimoto, K., and Kawasaki, K., 1991, *Ferroelectrics*, **122**, 53.

[5] Endo, H., Hachiya, S., Sekiya, T., and Kawasaki, K., 1992, *Liq. Crystals*, **12**, 147.

[6] Shibaev, V. P., Kozlovsky, M. V., Beresnev, L. A., Blinov, L. M., and Platé, N. A., 1984, *Polym. Bull.*, **12**, 299.

[7] Dubois, J. C., Decobert, G., Barny, P. E., Esselin, S., Friedrich, C., and Noel, C., 1986, *Molec. Crystals liq. Crystals*, **137**, 348.

[8] Guglielminetti, J. M., Decobert, G., and Dubois, J. C., 1986, *Polym. Bull.*, **16**, 411.

[9] Zentel, R., Reckert, G., and Reck, B., 1987, *Liq. Crystals*, **2**, 83.

[10] Suzuki, T., Okawa, T., Ohnuma, T., and Sakon, Y., 1988, *Makromolek. Chem. rap. Commun.*, **9**, 755.

[11] Keller, P., 1988, *Ferroelectrics*, **85**, 425.

[12] Vallerien, S. U., Zentel, R., Kremer, F., Kapitza, H., and Fischer, E. W., 1989, *Makromolek. Chem. rap. Commun.*, **10**, 333.

[13] Kitazume, T., Ohnogi, T., and Ito, K., 1990, *J. Am. chem. Soc.*, **112**, 6608.

[14] Shibaev, V. P., Kozlovsky, M. V., and Platé, N. A., 1990, *Liq. Crystals*, **8**, 545.

[15] Coles, H. J., Gleeson, H. F., Scherowsky, G., and Schliwa, A., 1990, *Molec. Crystals liq. Crystals Lett.*, **7**, 117.

[16] Scherowsky, G., 1991, *Makromolek, Chem. rap. Commun.*, **12**, 381.

[17] Dumon, M., Nguyen, H. T., Mauzac, M., Destrade, C., and Gasparoux, H., 1991, *Liq. Crystals*, **10**, 475.

[18] Naciri, S., Pfeiffer, S., and Shashidhar, R., 1991, *Liq. Crystals*, **10**, 475.

[19] Kimura, S., Nishiyama, S., Ouchi, Y., Takezoe, H., and Fukuda, A., 1987, *Jap. J. appl. Phys.*, **26**, L255.