

# Fluorescence Study of a Field-Induced Director Reorientation in a Liquid Crystalline Polyacrylate

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Received December 20, 1990; accepted December 21, 1990

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The electric field-induced director reorientation is investigated by fluorescence spectroscopy and turbidimetry. The dynamics of this reorientation are studied as a function of temperature, applied voltage, and frequency.

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**KEY WORDS:** Fluorescence; liquid crystals; polymers.

## INTRODUCTION

In an electric field liquid crystalline side-chain polymers show all effects known for low molecular weight liquid crystals, e.g., the Frederickz transition, the DAP effect, the formation of William's domains, and the dynamic scattering [1-14]. Compared to low molecular weight liquid crystals, liquid crystalline polymers display longer response times due to the lower mobility of the polymeric phases.

One of the main deformations known for liquid crystals is the Frederickz transition. Upon applying an electric field the mesogens tend to align themselves with their director parallel to the field, resulting mostly in a homeotropic orientation. Up to now the dynamics of this reorientation have been investigated through electrooptical measurements [10,11].

In this paper the electric field-induced Frederickz transition of a liquid crystalline copolymer is examined by fluorescence spectroscopy and turbidimetry. For this

study a liquid crystalline copolymer with a photophysically active group was prepared.

## EXPERIMENTAL

The polymer samples were prepared between transparent, electrically conducting In/SnO<sub>2</sub>-coated glass plates (GLAVERBEL) separated by a spacing epoxy glue to give electrode separations of 20 μm. The thickness was determined by absorption measurements. To apply AC voltage of variable frequency, a HAMEG function generator HM8030-2 in combination with a self-made linear amplifier was used. This combination produced AC square waves up to 120 V<sub>eff</sub> in a frequency range of 30 Hz to 20 kHz. The applied voltage was checked by a multimeter.

The phase transitions were monitored by microscope examination (Nikon Optiphot) between crossed polarizers using a microfurnace (Mettler FP82). The solvents used (isooctane, diethyl ether, dibutyl ether, ethyl acetate, 1-butanol, acetonitrile, and benzene) are of spectroscopic-grade UVASOL obtained from Merck. The absorption spectra were recorded on a Perkin Elmer lambda 6 spectrophotometer. The turbidimetric measurements were performed on the same spectrophotometer (λ<sub>AN</sub>, 700 nm). The fluorescence spectra were

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taken under thermostated conditions (using the Mettler FP82 hot stage) on a Spex fluorolog.

## RESULTS AND DISCUSSION

### Characterization of the Polyacrylate

The structure of liquid crystalline polyacrylate copolymer is shown in Scheme I. The mesogenic groups are randomly copolymerized at a ratio  $R^1/R^2 = 0.43$ . At room temperature the polymer exhibits a nematic phase, which transforms into an isotropic phase at 90°C. The texture of this nematic phase was examined under the polarization microscope and is displayed in Figs. 1a and 1b. Figure 1a shows the nematic texture of the polymer at 84°C (optical magnification =  $\times 100$ ). The photo in Fig. 1b was taken at the same temperature but at a higher optical magnification ( $\times 400$ ). In this photo the threaded nematic textures can clearly be identified.

### Photophysical Properties of (2,4-Dicyanophenyl)-4-octyloxybenzoate

The dicyanomesogen is the photophysically active group in this copolymer. The monocyano group does not show any fluorescence and its absorption is, compared to that of the dicyano group, more energetically situated (in *n*-hexane  $\lambda_{\text{max,abs}} = 266$  nm). In order to study the photophysical properties of the liquid crystalline polyacrylate, it is worthwhile to examine briefly the photophysical properties of the model compound (2,4-dicyanophenyl)-4-octyloxybenzoate (8DCE) [15].

The absorption spectrum of 8DCE (conc.  $10^{-5}$  M) in diethyl ether shows a maximum at 277 nm (Fig. 2). The maximum of this absorption band is almost inde-

pendent of the solvent polarity. The molar extinction coefficient in diethyl ether amounts to 25,000  $\text{mol}\cdot\text{L}^{-1}\cdot\text{cm}^{-1}$  at 277 nm.

Fluorescence measurements were carried out by excitation in the maximum of the absorption band. The fluorescence spectrum of 8DCE in solution depends strongly on the solvent polarity. In Fig. 2 the fluorescence spectrum of 8DCE in ethyl acetate is shown. A concentration study showed that within the studied concentration domain ( $10^{-5} \rightarrow 10^{-1}$  M), no intermolecular excimer formation occurred.

### Determination of the Phase Transition Temperature

At room temperature the fluorescence spectrum of the polyacrylate shows a maximum around 380 nm. This emission maximum corresponds to the fluorescence maximum of the model compound in ethyl acetate, indicating that the liquid crystalline polymer has polarity characteristics similar to those of ethyl acetate. By monitoring the fluorescence intensity ( $\lambda_{\text{EM}}$ ) with decreasing temperature, the phase transition (N  $\rightarrow$  I) can be determined (Fig. 3). At 92°C a small discontinuity in the relative emission intensity is observed.

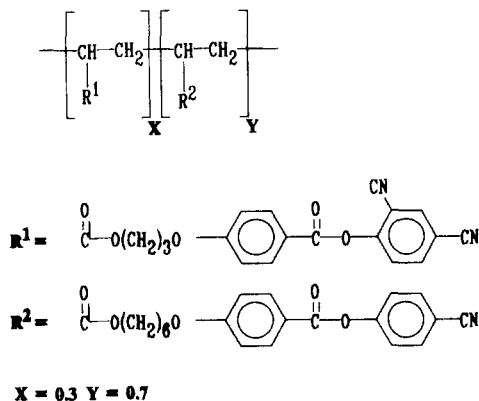
The N  $\rightarrow$  I phase transition can also be determined by turbidity measurements (Fig. 4). The transmission of the sample ( $\lambda_{\text{AN}} = 700$  nm) is measured as a function of the temperature. In the isotropic phase the sample is transparent and the transmission approximates 100%. At the phase transition a strong decrease in transmission is observed, resulting in a small value for the nematic phase (0%).

Due to the large discontinuity that occurs at the phase transition, turbidimetric measurements are even more suitable to determine  $T_{\text{NI}}$ . The transmission changes from 100% in the isotropic phase to a value that approaches 0% in the nematic phase.

Although the discontinuities in the relative fluorescence intensity can be used to investigate the phase transitions in many systems [16–25], in this peculiar case the emission intensity is not very sensitive to the phase transition. Only a small change in the emission intensity is observed (Fig. 4, +). Since the model compound possesses no intermolecular emission properties, the changes that occur in the local order at  $T_{\text{NI}}$  will not result in large fluorescence changes.

### Influence of the Electric Field

The electrically induced deformation was characterized with the polarization microscope. In Fig. 5 the electric field-induced textural changes are shown. On the



Scheme I



Fig. 1a. Nematic texture of PDCE at 84°C (crossed polarizers).  $\times 100$ .



Fig. 1b. Nematic threaded texture of PDCE at 84°C (crossed polarizers).  $\times 400$ .

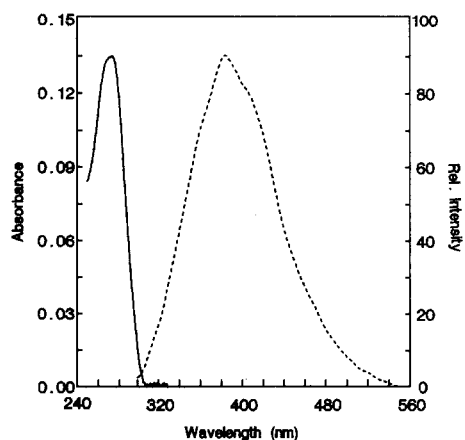


Fig. 2. Absorption spectrum of 8DCE in diethyl ether (—) and fluorescence spectra of 8DCE in ethyl acetate (---) at room temperature (conc.,  $<10^{-5} M$ ).

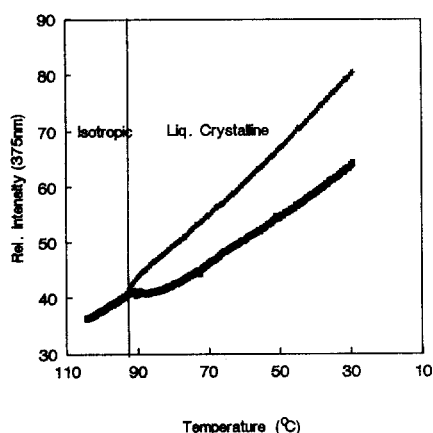


Fig. 3. Plot of the fluorescence intensity ( $\lambda_{EM} = 375$  nm) of the liquid crystalline polyacrylate versus the temperature (cooling cycle): (+)  $\vec{E} = 0$  and (□) AC, 1 kHz,  $100V_{eff}$ .

left side of the photo (optical magnification =  $\times 100$ )  $\vec{E} = 0$  and the original nematic scatter texture is visible. On the right side of the photo the sample is subjected to an electric field (AC  $f = 1.5$  kHz,  $120 V_{eff}$ ). Under influence of this field a homeotropic orientation (Frederickz transition) is achieved which is observed as a black area. In the frequency range of 30 Hz up to 2.5 kHz, a homeotropic orientation was induced. No dynamic scattering deformations were observed.

The influence of the electric field on the fluorescence spectrum is shown in Fig. 6. Upon applying an electric field (AC, 1 kHz) the intensity decreases and the emission maximum undergoes a small shift to lower energy: from 375 nm at  $0 V_{eff}$  to 382 nm at  $100 V_{eff}$ .

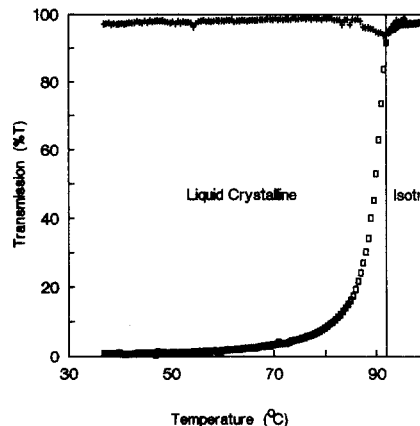


Fig. 4. Plot of the transmission ( $\lambda_{AN} = 700$  nm) of PDCE versus the temperature (cooling cycle): (+)  $\vec{E} = 0^{AN}$  and (□) AC, 1 kHz,  $100 V_{eff}$ .

The electric field has a stabilizing effect on the intramolecular charge transfer state, resulting in a small bathochromic shift.

The decrease in intensity originates from a decreased number of excited mesogenic groups. The experimental setup is built in such a way that at  $\vec{E} = 0$  the transition dipoles of absorption of the mesogenic groups lie in the plane of polarization of the excitation light. As the electric field is switched on, the mesogenic group tends to align parallel to the field. In this configuration the transition dipole of absorption is perpendicular to the plane of polarization of the excitation light. The decreased number of excited mesogens results in a decrease in the emission intensity. If a perfect homeotropic alignment is achieved, no more absorption of the mesogens should occur. However, in Fig. 6 one can observe that the intensity does not drop totally to zero. The reason for this background fluorescence is the incomplete homeotropic ordering at the electrodes. In Fig. 7 the orientation of the mesogenic group at the cell surfaces in the presence of an AC electric field (Frederickz deformation) is given. At the cell surface little or no reorientation is achieved. As a consequence these molecules are able to absorb light and therefore are responsible for the background fluorescence which is detected even at very high electric fields.

The electric field effect is also visible in Fig. 3 (□), where the emission intensity at 375 nm is measured with decreasing temperature in the presence of an electric field (AC, 1 kHz,  $100 V_{eff}$ ). Above  $T_{NI}$  (isotropic phase) no electric field effect is noticeable. Under  $T_{NI}$  a decrease in emission intensity is observed.

The influence of the electric field on the turbidity

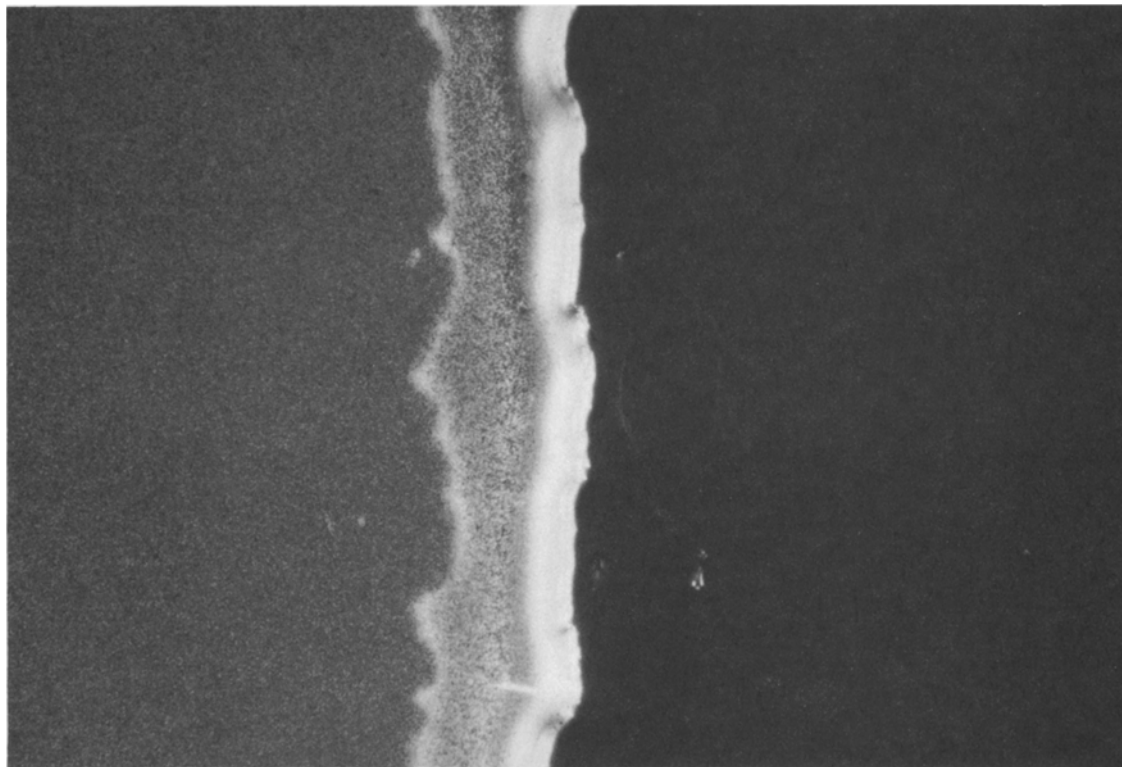


Fig. 5. Photograph of PDCE in the nematic phase. On the left side  $\vec{E} = 0$  and the nematic scatter texture is visible. The right side is subjected to an electric field (AC  $f = 1.5$  kHz,  $120 V_{eff}$ ). As a consequence of the electric field a homeotropic orientation is achieved.  $\times 100$ .

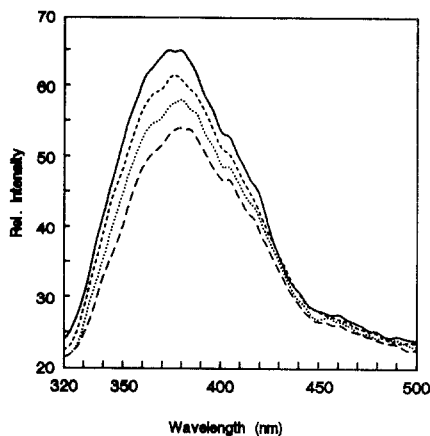


Fig. 6. Fluorescence spectrum of the liquid crystalline polyacrylate in the nematic phase ( $85^{\circ}\text{C}$ ) with varying electric field strengths (AC, 1 kHz) (cell thickness  $\approx 20 \mu\text{m}$ ): 0  $V_{eff}$  (—); 30  $V_{eff}$  (---); 50  $V_{eff}$  (···); 120  $V_{eff}$  (- - -).

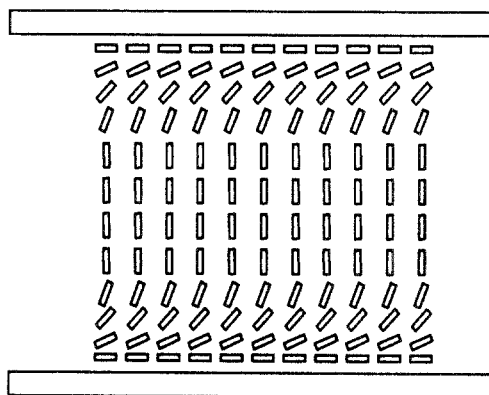


Fig. 7. Schematic drawing of the orientation of the mesogens at the electrode surfaces on application of an electric field. At the surfaces the mesogenic groups possess a homogeneous orientation. With increasing distance, a homeotropic alignment is achieved.

metric measurements of PDCE in the different phases is shown in Fig. 4 (□). Irrespective of the strength of the

electric field, a similar transmission behavior is observed in the isotropic phase. Upon applying an electric field in the nematic phase, a homeotropic orientation is induced, resulting in a transparent sample. As a conse-

quence the transmission of PDCE in the nematic phase under the influence of an electric field approaches 100%.

### Dynamic Aspects of the Frederickz Transition

By monitoring the fluorescence intensity as a function of time upon switching on the electric field, the reorientation times ( $\tau_{or}$ ) can be determined. In this work the reorientation time is defined as the time necessary for the fluorescence to drop to half of its original value. This was studied as a function of the temperature and the applied electric field. The results are compared with the reorientation times obtained from turbidity measurements ( $\tau_{or}$ : time to accomplish half of the total increase in the transmission).

In Fig. 8 the fluorescence intensity decays are shown with increasing electric fields [AC  $f = 1$  kHz; (A) 50  $V_{eff} \rightarrow$  (E) 120  $V_{eff}$ ]. Figure 9 displays the transmission increase in PDCE with decreasing temperatures [AC  $f = 1$  kHz, 120  $V_{eff}$ ; (A) 89°C  $\rightarrow$  (I) 81°C].

Due to the low quantum yield of fluorescence and the relatively small intensity decrease that is associated with the Frederickz deformation, a large experimental noise is introduced in the fluorescence intensity plots. This leads to a less accurate determination of the reorientation time. The turbidity technique, however, offers an excellent technique for accurate determination of the reorientation time.

The results of the transmission ( $\circ$ ) and fluorescence ( $\Delta$ ) measurements are summarized in Figs. 10a, 10b, and 10c. A good correlation between the reorientation times obtained with the two different methods is achieved. The influence of the frequency on the Fred-

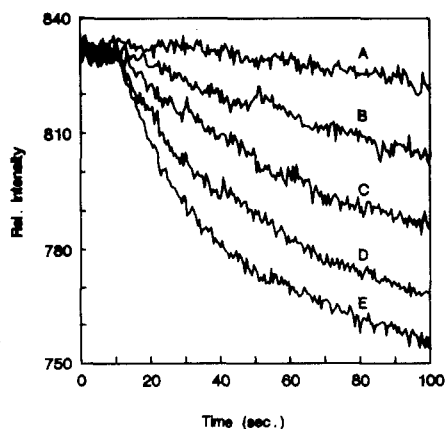


Fig. 8. Fluorescence intensity ( $\lambda_{AM} = 370$  nm) of the liquid crystalline polyacrylate as a function of time, measured with increasing voltages (AC, 1 kHz) (cell thickness  $\approx 20$   $\mu\text{m}$ ): (A) 30  $V_{eff}$ ; (B) 50  $V_{eff}$ ; (C) 70  $V_{eff}$ ; (D) 90  $V_{eff}$ ; (E) 110  $V_{eff}$ .

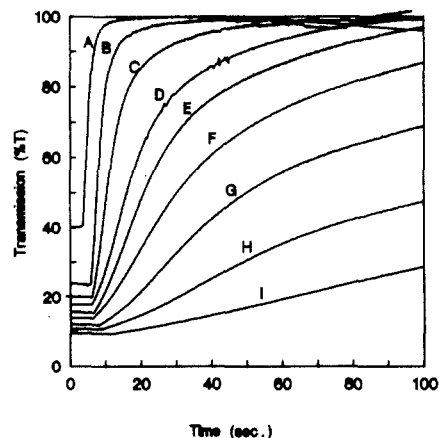


Fig. 9. Transmission ( $\lambda = 700$  nm) of PDCE in the nematic phase as a function of time, measured with decreasing temperatures (A  $\rightarrow$  I): (AC  $f = 1$  kHz, 120  $V_{eff}$ ) (cell thickness  $\approx 20$   $\mu\text{m}$ ): (A) 89°C; (B) 88°C; (C) 87°C; (D) 86°C; (E) 85°C; (F) 84°C; (G) 83°C; (H) 82°C; (I) 81°C.

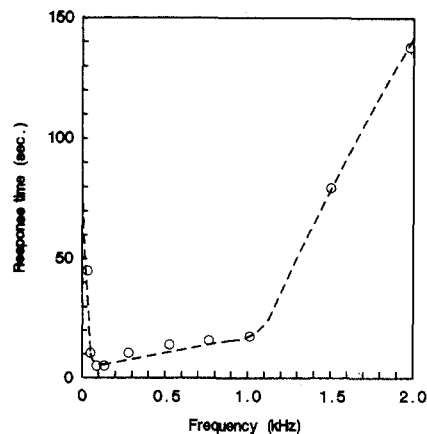


Fig. 10a. Response time for the liquid crystalline polyacrylate as a function of the frequency of the applied field (AC, 120  $V_{eff}$ ) (cell thickness  $\approx 20$   $\mu\text{m}$ ).

erickz transition is presented in Fig. 10a. The reorientation time attains optimal values in the frequency range of 50 Hz to 1 kHz. Lower and higher frequencies lead to longer reorientation times. The increase in the reorientation time at higher frequencies ( $>1$  kHz) is due to the existence of a certain frequency  $f_0$  at which the sign of  $\Delta\epsilon$  changes [9,10]. At  $f > f_0$  the side groups tend to be positioned perpendicularly to the electric field.

For a fixed voltage and frequency the response time decreases markedly with increasing temperature (Fig. 10b). Plotting the logarithm of the response time versus the reciprocal of the temperature results in a linear relationship. From the slope the activation energy of the

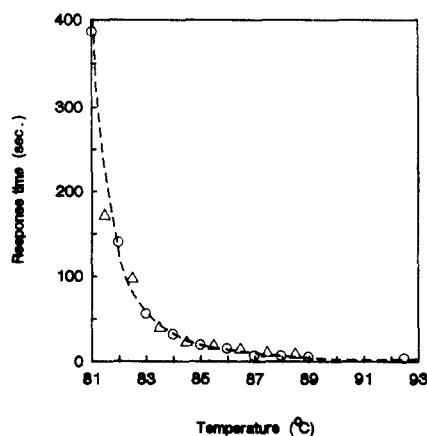


Fig. 10b. Response time for the liquid crystalline polymer as a function of temperature. The applied voltage was  $100 V_{eff}$  at 1 kHz; the cell thickness was  $\approx 20 \mu\text{m}$ .

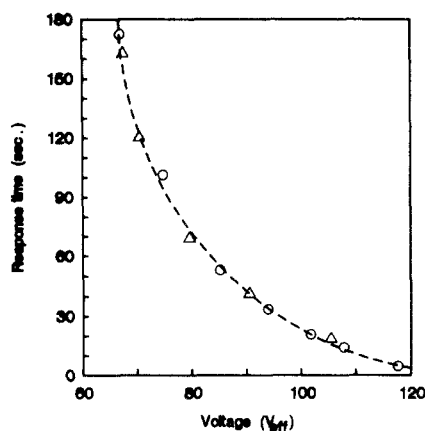


Fig. 10c. Response time for the liquid crystalline polyacrylate as a function of the applied voltage.  $T = 90^\circ\text{C}$ ;  $d \approx 20 \mu\text{m}$ ;  $f = 1 \text{ kHz}$ ; cell thickness  $\approx 20 \mu\text{m}$ .

Frederickz transition can be calculated. For this polymer a value of 526 kJ/mol is obtained.

The reorientation time also decreases with increasing voltage (Fig. 10c). Experimentally the reorientation time is  $\sim V^{-3.5}$ . The same relationship was found by Coles and Simon [2] for a polysiloxane. Shibaev and co-workers [9,10], however, found an inverse square relationship of the applied voltage and the response time.

## CONCLUSION

The influence of the electric field-induced director reorientation on the photophysical properties was investigated. On application of an electric field a homeotropic

orientation is induced. As a result of this deformation the intensity of the fluorescence spectrum decreases, due to the decreased number of excited mesogens in this orientation. The dynamics of the Frederickz transition were studied by means of fluorescence spectroscopy and turbidimetry. A good correlation between both techniques was obtained. Furthermore, the influence of the temperature, the applied voltage, and the frequency was studied. From the influence of the temperature the activation energy of the Frederickz transition was determined.

## ACKNOWLEDGMENTS

The financial support of I.C.I., through a JRS of the ministry of "Wetenschapsbeleid," I.U.A.P.3, and a concerted action, as well as that of the Belgian National Science Foundation is gratefully acknowledged.

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