Polymer-Dispersed Chiral Discotic Liquid Crystals

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POLYMER-DISPERSED CHIRAL DISCOTIC LIQUID CRYSTALS

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Abstract We have investigated the electro-optic properties of a polymer film
which contains a chiral columnar liquid crystal in small cavities. The cavities
were formed due to phase separation during the evaporation of a solvent. A
uniform orientation of the optical axis of the liquid crystal could be achieved
by shearing the sample at a temperature above the softening point of the
polymer. The system shows bistable and linear switching effects due to the
ferroelectric properties of the liquid crystal. When the film is placed between
crossed polarizers, this new system can be used as an electrooptic light valve.
Moreover, the field-induced orientation remains stable when the sample is
cooled to room temperature, i. e. below the melting point of the pure liquid
crystal. This behavior can be used for optical storage effects.

INTRODUCTION

It is well known that the chiral tilted smectic liquid crystals which are formed by
rod-like molecules, can exhibit a spontaneous polarization[1]. The resulting ferro-
electric properties have found great interest with respect to fundamental questions
and possible applications for electro-optic light shutters and displays[2]. However,
only recently the prediction[3] that also chiral discotic columnar phases can show
ferroelectric properties was proved experimentally[4]. The latter phases appear in
systems consisting of disk-like molecules, such as derivatives of dibenzopyrene[4,5],
pyrene[6], phenanthrene[7], benzophenanthrene[7], or chiral mixtures of substituted
triphenylenes[8]. The symmetry of a column consisting of such chiral disk-like
molecules (Fig. 1) is described by the point group C_2 if the director $\underline{n}$ normal to the

preferred plane of the molecules is tilted with respect to the axis $\underline{c}$ of the column. The only symmetry element is a two-fold axis perpendicular to both $\underline{n}$ and $\underline{c}$ and thus a polar physical property such as the spontaneous polarization $\underline{P}_s$ is allowed to occur along this two-fold axis, $\underline{P}_s = P_o \, (\underline{c} \times \underline{n})$. Polar groups in the side chains of the molecules can enhance the value of the spontaneous polarization. However, the columnar phases are characterized by the arrangement of the columns in a hexagonal or tetragonal lattice. The spontaneous polarizations of neighboring columns in the unit cell may either add or cancel each other, depending on their respective tilt direction. Thus, a large variety of ferroelectric, antiferroelectric or ferrielectric phases with different macroscopic polarization can appear in the same material and field-induced phase transitions can occur between these phases[5]. Besides the interesting fundamental questions connected with these new materials, Bock and Helfrich[5] have pointed out that columnar ferroelectric liquid crystals may also have advantages compared to smectic liquid crystals, as far as applications are concerned. The columnar arrangement is expected to show better shock resistivity and can not result in the formation of the chevron texture which exhibits a reduced switching angle. Thus it seems to be a rewarding challenge to overcome the remaining problems connected with the application of columnar liquid crystals, i. e. finding discotic materials with a large liquid crystal temperature range and small switching times, and developing suitable alignment techniques.
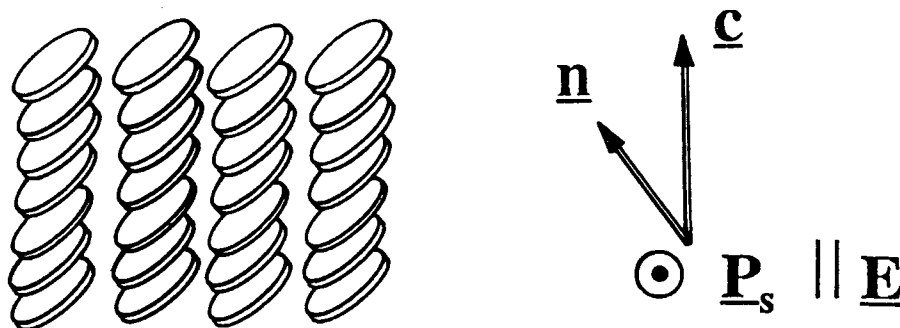

FIGURE 1   Schematic representation of a tilted columnar phase, indicating the relation between the column axis $\underline{c}$, the director $\underline{n}$, and the spontaneous polarization $\underline{P}_s$.

In this paper, we present some results on a polymer-dispersed discotic ferroelectric liquid crystal (PDFLC$_D$), i. e. a polymer film with small cavities in which the liquid crystal is embedded. Polymer-dispersed liquid crystals are known to be suitable for the application as large area flexible light shutters[9,10]. During the last few years, efforts were made to extend the work on these systems from the initially investigated nematic liquid crystals[9,10] to rod-like cholesteric[11] and ferroelectric liquid crystals[12]. The present study shows that also discotic ferroelectric liquid crystals can be embedded in a polymer matrix, that a uniform alignment of the liquid crystal can be achieved and thus a bistable electrooptic switching can occur in such systems.

SAMPLE PREPARATION

The investigated PDFLC$_D$ system consists of the liquid crystal (S)-D8m*10 and the thermoplastic polymer poly-(vinyl-butyral), PVB, Aldrich. The dibenzopyrene derivative (S)-D8m*10
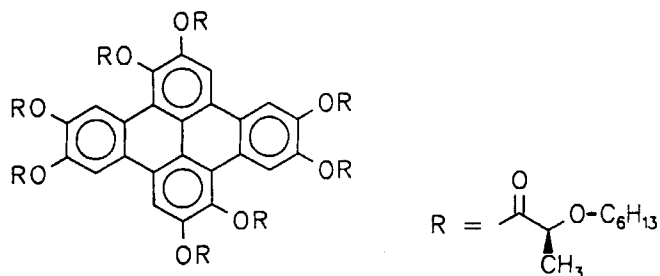
which was described earlier[4,5] shows on heating the transition temperatures K 88.8°C D$_t$ 129.5°C I. The composition of the samples was ≈ 45 % (by weight) (S)-D8m*10 and ≈ 55 % (by weight) PVB. For all of the measurements presented in this paper (except the tilt angle measurement in Fig. 4), a mixture of 44.3 % (S)-D8m*10 and 55.7 % PVB was used. PDLC samples were prepared using the phase separaration due to solvent evaporation. The liquid crystal and the polymer were dissolved in chloroform and small glass cylinders were added which later on serve as spacers, controlling the cell gap. The solution was casted on an ITO-coated glass substrate and the solvent was allowed to evaporate slowly at room temperature. After complete evaporation of the chloroform, the sample was covered by the

second ITO-coated substrate and baked for about one hour at 120°C. A gentle pressure was exerted on the substrates in order to achieve spreading of the liquid crystal/polymer mixture over the whole electrode area. Finally, the samples were cooled to room temperature. Investigations by electron microscopy indicated cell gaps between 14 μm and 28 μm.

Examination of the samples in the polarizing microscope indicates a heterogeneous structure with liquid crystal droplet sizes close to the resolution of the microscope, i. e. with diameters of about 1 μm. After the preparation described above, the liquid crystal droplets are randomly oriented and thus the PDFLC$_D$ film shows no macroscopic birefringence. If the sample is placed between crossed polarizers, the transmitted light intensity does not depend on the azimuthal orientation of the sample (Fig. 2a). However, a uniform orientation could be achieved due to a shear flow induced by sliding the substrates gently with respect to each other. The lowest possible temperature where the polymer is sufficiently soft to allow the shearing, was 115°C, well below the clearing temperature of the liquid crystal. Due to the shear-induced macroscopic birefringence, the samples show a dependence of the transmitted intensity on their azimuthal orientation φ, according to the well-known relation $I = \frac{1}{2} I_o \sin^2(2\{\varphi-\varphi_0\}) \sin^2(\pi \, \Delta n \, d \, / \, \lambda)$, where I_0 is the intensity of the incident light, φ_0 the azimuthal angle between optical axis of the liquid crystal and the plane of polarization of the incident light, and Δn is the effective birefringence of the liquid crystal. Rotating the sample between crossed polarizers corresponds to a contrast ratio $I_{max}(\varphi)/I_{min}(\varphi) \approx 10 : 1$ (Fig. 2a). This contrast ratio due to rotation of the sample corresponds approximately to the maximum contrast ratio expected for the ferroelectric switching since the electrooptic effect in ferroelectric liquid crystals is mainly due to a field-induced rotation $2 \, \varphi_t$ of the optical axis. Immediately after the shearing process, the optical contrast is even higher than 10 : 1 (Fig. 2b). Unfortunately, the softness of the polymer leads to a relaxation of the shear-induced alignment. Nevertheless, the remaining contrast is still sufficient, e. g. a sample with $I_{max}(\varphi)/I_{min}(\varphi) = 14 : 1$ immediately after shearing showed still a contrast ratio of about 7 : 1 after the sample was kept at 115°C for one day.
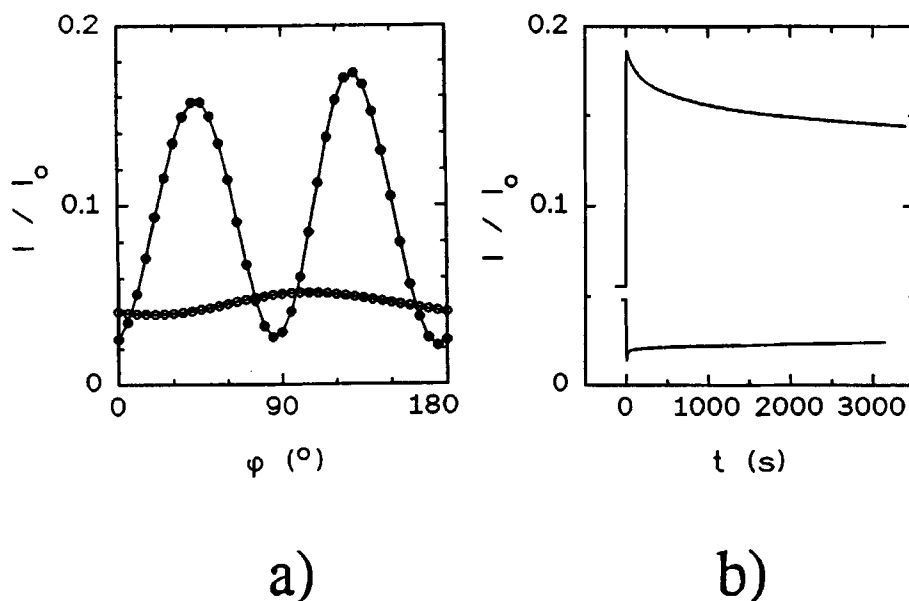
a)   b)

FIGURE 2   (a) Intensity of the transmitted light as a function of azimuthal orientation φ when the sample is placed between crossed polarizers and rotated, (o) before shearing and (●) after shearing at 115°C. The intensity values are normalized with respect to the intensity of the light source I_0. (b) Time dependence of the transmittance (for φ = 0° and 45°) after the shearing process. Composition: 44.3 % (S)-D8m*10; 55.7 % PVB. Sample thickness: d = 22μm.

ELECTRO-OPTIC PROPERTIES

The investigated samples show the bistable switching behavior (Fig. 3) which is typical for ferroelectric liquid crystals. Sufficiently high dc voltages of opposite polarity cause an increase and a decrease of the initial intensity, respectively, if the initial azimuthal orientation of the optical axis is adjusted at φ_0 = 22.5°. The critical field which reverses the polarization and thus rotates the optical axis is E_{cr} ≈ 170 V / 14 μm = 12 V / μm. Examination of the dependence of the transmittance on the azimuthal orientation of the sample between crossed polarizers shows (Fig. 4a) that the electrooptic effect corresponds to a rotation of
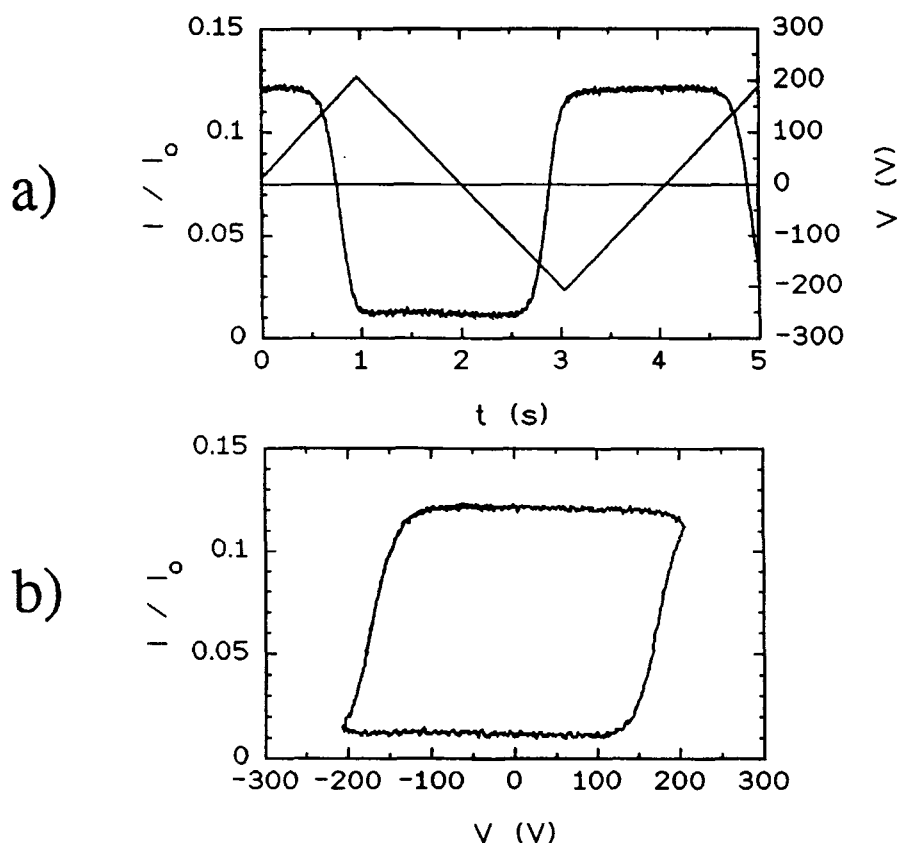
a)

b)

FIGURE 3   (a) Time dependence of the transmitted light intensity (for φ = 22.5°) due to a triangular wave voltage applied to the sample. (b) Optical hysteresis corresponding to the data presented in Fig. 3 (a). d = 14 μm.

the optical axis. The amplitudes of the curves in Fig. 4a differ only slightly which indicates that the effect of the field on the birefringence is rather small. Thus, we can describe the switching behavior by the field-dependence of the induced tilt angle φ_t of the optical axis (which we define as one half of the angle of rotation observed due to a sign reversal of the field). This tilt angle varies up to 20° (Fig. 4b). Previous work on the pure liquid crystal has shown[5] that two different phases can appear in (S)-D8m*10 for the same temperature at different field strengths. The low-field phase exhibits a field-induced tilt angle of φ_t = 20 - 25°, whereas the high-field phase shows a much larger tilt angle of $\varphi_t \approx$ 35° - 38°. The critical field

for the field-induced phase transition has been found between $E_{cr} \approx 10$ V/μm[5] and $E_{cr} \approx 18$ V/μm[8]. Comparing our data (Fig. 4b) to these previous results, we conclude that the effective value of the highest voltage which we applied to the PDFLC$_D$ sample (200 V / 14 μm, limited by the power supply) is below the threshold voltage for the field-induced transition. Erdmann et al.[13] have pointed out that the liquid crystal droplets in a PDLC sample are exposed to an effective field strength $E_{loc} = 3 E (\rho_P / \rho_{LC} + 2)^{-1}$, where E is the applied external field, and ρ_P
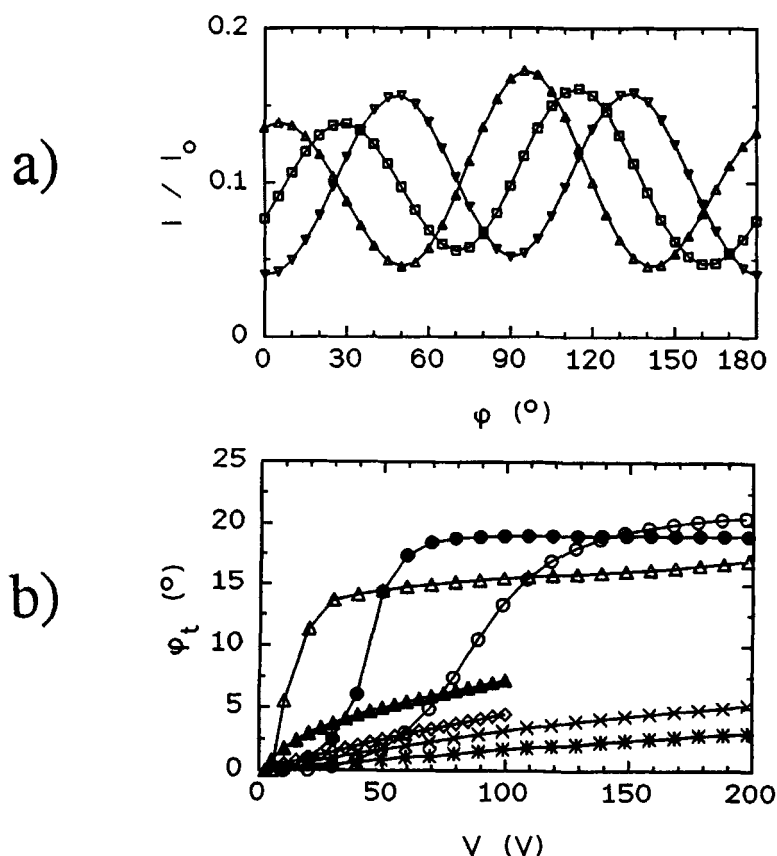

FIGURE 4   (a) Transmitted light intensity as a function of the azimuthal orientation of the optical axis of the sample with respect to the plane of polarization of the incident light, (□) immediately after preparation of the sample, (▲) for V = 0 V, after application of a V = +200 V pulse, and (▼) for V = 0 V, after application of a -200 V pulse; d = 14 μm. (b) Field-induced tilt angle of the optical axis as a function of the applied voltage for different temperatures. (○) 115 °C, (●) 120°C, (△) 125°C, (▲) 130 °C, (◇) 135 °C, (×) 140 °C, and (*) 145°C. Composition: 46.1 % D8m*10, 53.9 % PVB. Sample thickness d = 28 μm.

and ρ_{LC} are the resistivities of the polymer and the liquid crystal, respectively. Thus, the fact that we did not observe the high-field phase in the $PDFLC_D$ sample can also be attributed to the relation $\rho_P > \rho_{LC}$, i. e. $E_{loc} < E$. It is interesting to note that we observed a weak electrooptic transmittance variation of the $PDFLC_D$ sample even in the temperature range above the clearing point of pure D8m*10. The contrast ratio is very small in this temperature range. The apparent tilt angle depends linearly on the applied voltage which indicates that this behavior is not due to the Kerr effect. Possibly, this unusual phenomenon can be explained by an impurity of the liquid crystal, i. e. the presence of a compound which has a higher clearing temperature. However, we can not exclude that the surface-induced order which is known to occur in polymer-dispersed liquid crystals[14] causes exceptionally large effects in columnar phases.

Turning to the dynamic behavior, we note that the response of the $PDFLC_D$ samples is rather slow. The switching times τ_{90} presented in Figure 5 correspond to the time interval between the reversal of the voltage and the reach of 90% of the total intensity change. These response times vary between a few ms and about 10s. The dependence of the switching times on the applied voltage can approximately be described by a power law $\tau \propto E^{-\alpha}$, with $\alpha(115°C) = 2.37$ and $\alpha(125°C) = 2.19$ (see solid lines in Fig. 5a). This behavior is in disagreement with the behavior of smectic ferroelectric liquid crystals which show $\alpha = 1$. However, similar results for D8m*10 have been found by other authors[5,8]. The value of the exponent α close to 2 confirms our assumption that only the low-field phase appears in our $PDFLC_D$ samples for the field strengths applied so far. For the high-field modification, an even stronger dependence of the switching times on the applied field, $\tau \propto E^{-5}$, has been reported. For 130°C, i. e. close to the clearing point of D8m*10, the switching times in our samples become even less dependent on the field, $\alpha(130°C) = 0.85$. The linear dependence of the tilt angle on the applied voltage and the small field-dependence of the switching time τ are similar to the electroclinic effect occuring in smectic liquid crystals. However, we have no evidence that D8m*10 shows a non-tilted modification above 130°C which may exhibit an electroclinic effect.

The temperature dependence of the response times for constant field strength (Fig. 5a) can be described by an Arrhenius law, i. e. $\ln \tau = E_a/(k \cdot T) + const$. From the fit of this function to the experimental data we obtain an apparent activation energy of $E_a = 5.54 \cdot 10^{-19}$ J $= 3.46$ eV which is in agreement with earlier observations on the pure liquid crystal. In the temperature range above 130°C, the switching times depend only slightly on the temperature.
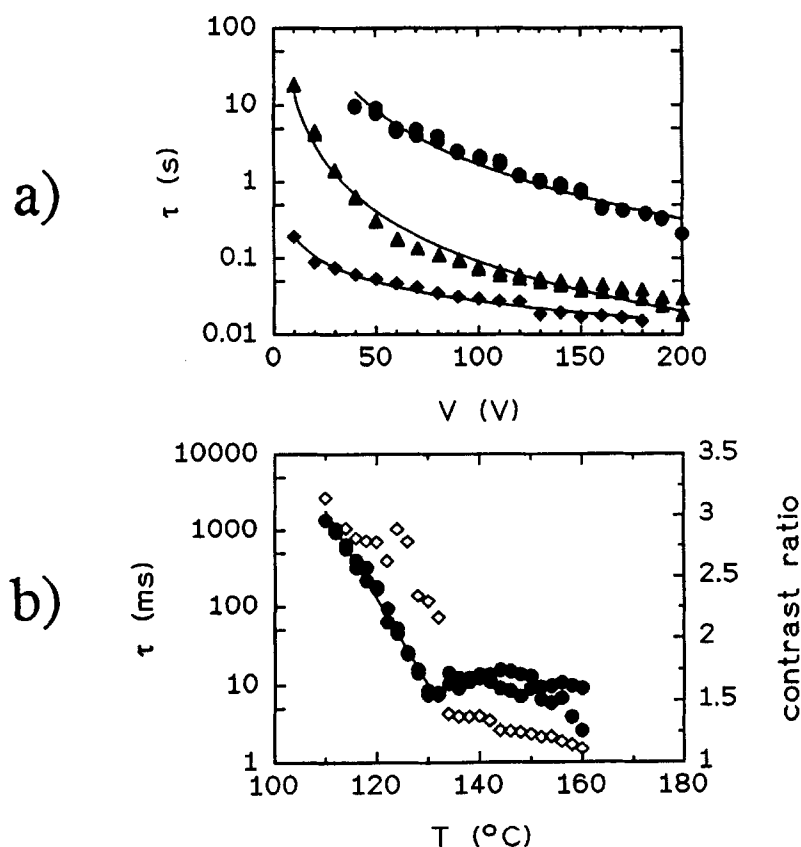

FIGURE 5 (a) Switching time versus applied voltage (cell gap d = 14 μm) for different temperatures (●) 115°C, (▲) 125°C, and (◆) 130°C. (b) Switching time (●) and optical contrast ratio (◇) versus temperature at E = 200 V / 22 μm.

STORAGE EFFECT

Due to the transition temperatures of (S)-D8m*10, the investigated system shows electrooptic switching only at high temperatures. However, we found that the field-induced orientation is preserved if We cool the sample to room temperature. The change of the transmission due to rotation of the sample between crossed polarizers remains almost unchanged during the cooling process (Fig. 6a). Thus it is possible to store the information which is induced by an electric field without keeping the sample in the temperature range of the columnar phase. Moreover, it is possible to induce a reorientation from the parallel to the homeotropic alignment by heating above the clearing point and subsequent cooling, e. g. due to exposure of the sample to a laser beam (Fig. 6b). The pattern generated by local heating can be erased by a new shearing process which leads again to a uniform parallel alignment.
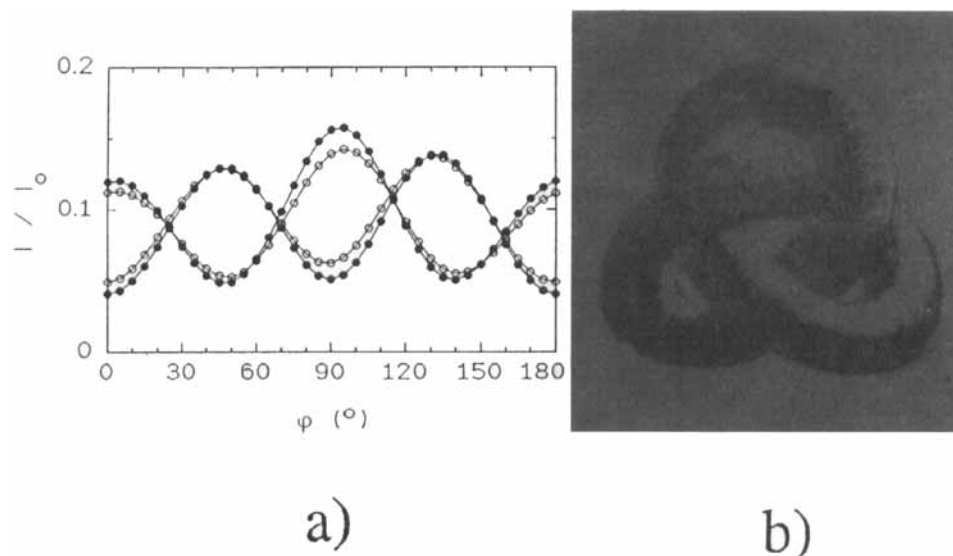

a)   b)

FIGURE 6   (a) Transmitted intensity versus azimuthal orientation of the optical axis in the two field-off states, demonstrating a memory effect. (●) 120°C, after application of ± 200 V / 14 μm;   (○) 25 °C, after having applied ± 200V / 14μm at 120°C and subsequently cooled. (b) Test image ("The Knot" by M. C. Escher) created by a laser beam (514nm, 50mW, 256*256 dots) due to thermally induced reorientation.

SUMMARY

In conclusion, we have performed first electrooptic investigations on a polymer-dispersed ferroelectric columnar liquid crystal. Our results indicate that the latter can be embedded in a polymer matrix and aligned by shearing the substrates with respect to each other. The high tilt angles of (S)-D8m*10 make reasonable values of the contrast ratio available. Comparison of our electrooptic measurements with previous results on the pure liquid crystal[5] shows that only the low field phase of two known modifications appears in the range of field strengths which we have investigated so far. Thus, it seems to be possible to observe even larger tilt angles by applying higher voltages or using smaller sample thicknesses. However, the high transition temperatures of the studied material and the large electrooptic switching times are not suitable to improve the characteristics of electrooptic light shutters. To overcome these problems may be a challenge for future work on the synthesis of chiral discotic columnar phases. Nevertheless, the investigated PDFLC$_D$ system shows an interesting storage capability, since the field-induced orientation of the liquid crystal is preserved after cooling the sample to room temperature. To study this behavior in more detail and to investigate the pretransitional behavior of the columnar phase above its clearing temperature will be the subject of further studies.

ACKNOWLEDGEMENTS

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