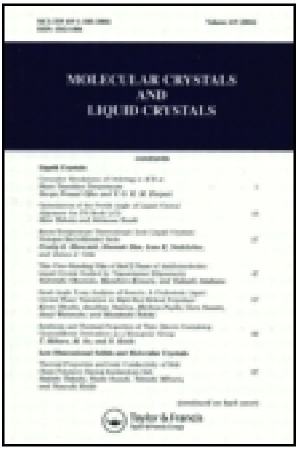

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Time-Resolved Polarized FTIR-Spectroscopy on Structure and Mobility in Banana-Shaped Liquid Crystal Molecules

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Time-Resolved Polarized FTIR-Spectroscopy on Structure and Mobility in Banana-Shaped Liquid Crystal Molecules

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By use of time-resolved polarized Fourier-transform infrared (FTIR-) spectroscopy the molecular structure and mobility of B2 phase LC banana-shape molecules is investigated. Two samples are investigated: an achiral banana-shaped (B14) system and a mixture of achiral (B14) and chiral (B7*) banana-shaped molecules. The molecules are oriented by shearing the substance between ITO-coated CaF_2 windows. The measurements give detailed information about a) the average orientation, b) the orientational order, c) the reorientation time, d) the reorientation angle and e) the phase relation between the different segments for the different molecular moieties. The experiments are performed in dependence on frequency and strength of the external electric field. The corresponding molecular response of the different moieties is recorded by means of step-scan FTIR spectroscopy with a time resolution of 5 microseconds.

Keywords: Banana-shaped molecules; FTIR-spectroscopy

INTRODUCTION

The induction of chiral smectic phases by achiral banana-shape molecules has been observed recently [1]. While their structure are – in the meantime – well explored [2,3] the knowledge concerning the molecular mechanism of the switching behavior is sparse. To analyze that time resolved FT-IR-spectroscopy with polarised light is an ideal tool. It is the purpose of this paper to employ this technique to study structure and mobility of banana-shaped molecules in response to an external electric field.

EXPERIMENTAL PART

The chemical composition of the investigated substances is shown in Fig. 1a for the achiral molecule B14 and in Fig 1b for the chiral molecule B7*. The doped sample consists of achiral banana shaped molecules (B14) with less than 10 percent of chiral banana shaped molecules (B7*). The sample was oriented by shearing the liquid crystalline melt (at 135°C) between CaF2 windows coated with an indium tin oxide (ITO) layer in order to make the surface conductive (Fig.2). Furthermore, a SiO layer protected the ITO electrodes against short-circuits during shearing. These cell windows are transparent to infrared and visible light.

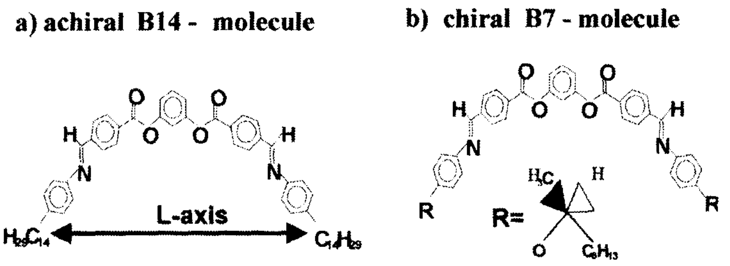

FIGURE 1: Chemical composition of the investigated substance: a) achiral B14 molecule and b) chiral B7* molecule

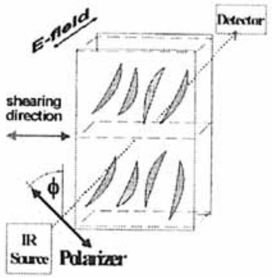

FIGURE 2: Schema of the experimental setup and the orientation of the molecular system

RESULTS AND DISCUSSION

Undoped sample

The shearing of a fresh sample at 135°C produces stripes of approximately 20 μm width which show different switching behavior in response to an external electric field [7]. Domains of a bigger size (~1mm) can be achieved by annealing the sample at this temperature and further reciprocate shearing. Two types of domains could be observed which are named orientation type I and orientation type II in this paper. The electro-optical response of domains of orientation type I to a triangular voltage is shown in Fig. 3a and in Fig 3b for domains of orientation type II. As can be seen from Fig. 3a, the orientation type I shows switching over three states with the same transmittance at maximum positive and negative voltage and can therefore be called as a racemic domain. The electro-optical response for domains of orientation type II is completely different: the sample is also switched over three states but all states are optically distinguishable. This can be related to a rotation of the optical axis. The observation of two different orientation types in the B2 phase indicates that two smectic structures coexist at the same temperature.

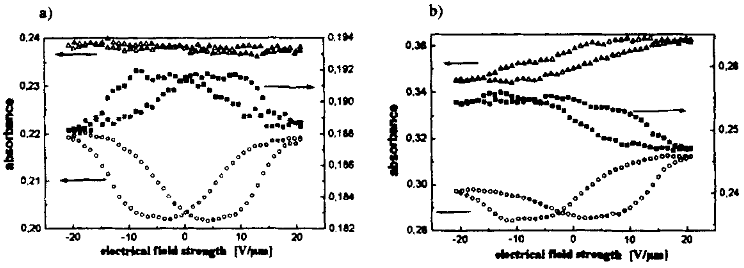

FIGURE 3: Electro-optical response of the system for orientation type I (a) and orientation type II (b) to an external electrical triangular field of 100 Hz and 2400 Hz (respectively 2300Hz)

The response of the different molecular moieties is investigated by use of the following bands $\nu_{as}(CH_2)$ at 2924 cm^{-1}, $\nu(C=O)$ at 1736 cm^{-1}, $\nu(C\text{-}C)_{ar}$ at 1603 cm^{-1} (Fig.2). In order to analyze the molecular motion of the banana-shaped molecules of the undoped sample, the IR-absorbance as response to an external triangular electrical field (±10V/µm, 2405 Hz) has been recorded as time-resolved (time-resolution 5 µs) FT-IR spectra for a complete set of polarization (0° to 170° in steps of 10°). The absorbance (Fig. 4a and 4b) of different molecular moieties changes with the electrical field likewise as the electro-optical response. The response for the orientation type I (Fig. 4a) is symmetric, an asymmetric behavior with respect to the applied field is found for orientation type II (Fig. 4b). Additionally, a hysteresis is observed which is more or less characteristic for the different molecular moieties. From the complete set of the polarization

dependent spectra for the different molecular units ($C\text{-}C_{ar}$, C=O, CH_2), the deflection angle is deduced. It is projected in the plane perpendicular to the direction of the light propagation ("apparent" angle γ) (Fig. 5a,b). $\Delta\gamma$ describes the difference in γ for a positive and negative electric field. In the symmetric case (Fig. 5a), no change is observed while an asymmetric response is found for a sample in orientation type II with indication for a plateau around the zero field.

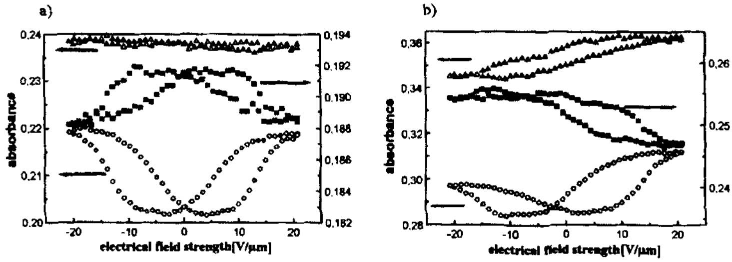

FIGURE 4: Time resolved absorbance for orientation type I (a) and orientation type II (b) for the $\nu(CH_2)$ [△], $\nu(C=O)$ [○], and $\nu(C\text{-}C)_{ar}$ [■] bands at a fixed polarizer angle of ϕ=50° and a modulation frequency of 2405 Hz.

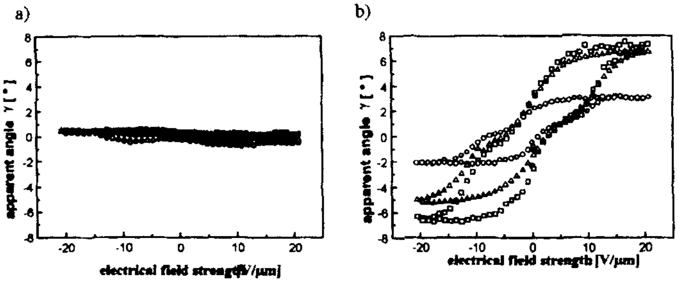

FIGURE 5: Angular excursion for orientation type I (a) and orientation type II (b) of the different molecular moieties as measured in the projection of the plane perpendicular to the direction of the light propagation and as determined from the polarization dependence of the time resolved FT-IR spectra.

The orientational behavior of type I can be assigned to racemic and that of type II to homachiral domains [4,5,6]. For the latter, maximal tilt angle variations of $\Delta\gamma \approx 14° \pm 2°$ (5b) are observed in the $\nu(C\text{-}C)_{ar}$ and the $\nu_{as}(CH_2)$ transition moments. These changes are the results of a rotation of the molecular axis L under the influence of the external electric field. The tilt angle ϑ between the L-axis and the smectic layer normal can be deduced from the response of $\nu(C\text{-}C)_{ar}$ transition moment as $\vartheta = \Delta\gamma/2 = 7° \pm 1°$. The lowest $\Delta\gamma \approx 5°$ angle changes were observed for the carbonyl band ($1736 cm^{-1}$). A similar observation has been made for carbonyl bands of ferroelectric and antiferroelectric liquid crystals with linear mesogens [8-10]. Calculations carried out for these molecules proved that the lower value of the apparent angle for the carbonyl bands is related to a biased rotation of carbonyl groups around the mesogenic axis [10]. Our investigations show that this is also true the for banana-shaped molecules under study.

Our results led to a model of two coexist molecular arrangements in the B2 phase of this substance. For the orientation type I, where changes in the polarity of the electric field do not affect the optical axis of the sample (Fig. 6a), we can not distinguish whether the molecular axis is parallel to the smectic layer normal or whether it is tilted to the right or to the left in every other smectic layer. In orientation type II the L axes are tilted relative to the smectic layer normal. In this case, the optical axis changes with reversion of the electric field polarity. This leads to rotation of the L axes around the smectic layer normal (Fig. 6b).

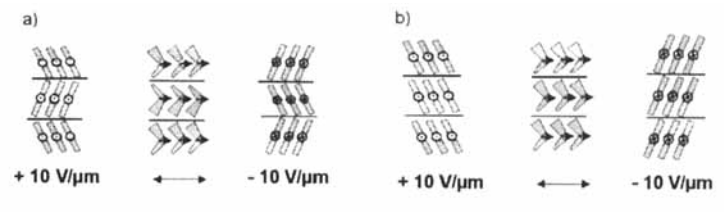

FIGURE 6: Model of arrangements of banana-shaped molecules a) for orientation type I and b) for orientation type II

Undoped sample

The doped sample is a mixture of >90% of achiral B14 molecules and <10% of chiral B7* molecules (Fig. 2) and is not thermally stable. After repeated shearing, domain sizes similar to the undoped sample have been achieved. In contrast to the undoped sample the shearing of the sample produced domains with a unique switching behavior. The electro-optical response to an external triangular electric field (20V/μm, 2405 Hz) of these domains is shown in Fig. 7. The sample also switches within three states. The response to the external field is asymmetric like in the orientation type II of the undoped substance.

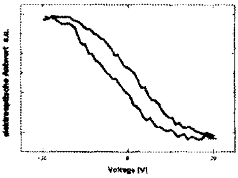

FIGURE 7: Electro-optical response of the system to an external electrical triangular field of 2400 Hz

With the same experimental setup as for the undoped sample (except the electric field strength, maximal ±20V), FT-IR spectra have been recorded for a complete set of polarization. The absorbance (Fig. 8a) shows an asymmetric response to the electric field for the different molecular moieties similar to the electro-optical response. From these two measurements, a homochiral arrangement like in orientation type II of the undoped sample can be deduced. The apparent angle γ was calculated (Fig. 8b) from the time resolved absorbance. The tilt angle $\vartheta=\Delta\gamma/2$ for the mesogen deduced from the transition moment $\nu(C\text{-}C)_{ar}$ is more than four times larger ($\vartheta=30°\pm1°$) than for the undoped sample. In accordance with the undoped sample, the tilt angle for the carbonyl group has a lower value of $\vartheta=17°\pm1°$.

The domains of the doped sample show the same behavior like the domains of orientation type II. Thus the same model for the arrangement of the molecules like in orientation type II was proposed.

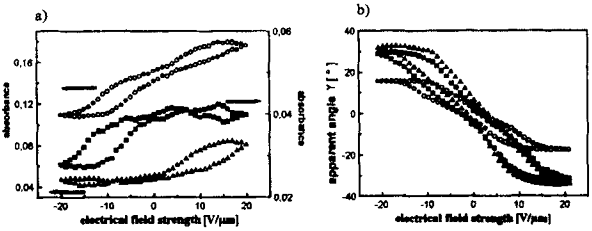

FIGURE 8: a) Time resolved absorbance for the $\nu(CH_2)$ [△], $\nu(C{=}O)$ [○], and $\nu(C\text{-}C)_{ar}$ [■] bands at a fixed polarizer angle of $\phi=50°$ and a modulation frequency of 2405 Hz. and b) apparent angle of the different bands

CONCLUSION

The undoped sample shows two types of domains with different switching. Both types switch over three states but orientation type I has the same transmittance at maximum positive and negative voltage and orientation type II shows an asymmetric response to the external electric field. In contrast to this the doped sample shows only one kind of domains. The behavior of these domains is similar to the orientation type II , thus these domains are homochiral. The doping with chiral B7* molecules suppresses the racemic arrangement in the sample. The tilt angles of molecular moieties in the doped samples are much larger than in the undoped case.

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