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Reorientation behaviour of bent core molecules in response to an external electric field as detected by time-resolved FTIR spectroscopy

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Time-resolved polarized Fourier transform infrared spectroscopy (FTIR) is employed to analyse the segmental orientation and mobility of achiral bent core molecules in response to an external electric field. By shearing the substance between ITO coated CaF_2 windows two types of domain, racemic and homochiral, are formed in the high temperature B_2 phase. Each of these domains is characterized by two spontaneous symmetry-breaking instabilities which yield a symmetric and an antisymmetric electro-optical response, respectively. Taking advantage of the specificity of IR spectroscopy, this switching behaviour is analysed on a molecular level for the moieties of the bent core liquid crystal materials. In this way, the electrically induced reorientation of the different segments on a cone and the suppression of the antiferroelectric structure at higher frequencies can be followed in detail. Furthermore the biased rotation of the two carbonyl groups around the molecular long axis is determined. It is shown that all molecular units move synchronously on the time scale of the experiment (10 μs).

1. Introduction

In the SmC* phases of rod-like ferroelectric liquid crystals, the chirality of the molecules leads to a break in the centrosymmetry of these systems and thus to the existence of a polar axis. In 1996 it was discovered that achiral bent core molecules can form polar smectic phases as well [1]. For these phases, ferroelectric [1, 2] as well as antiferroelectric switching [2–5] has been reported. The molecular structure of these systems is characterized by two spontaneous symmetry-breaking instabilities: a polar ordering about the smectic layer normal and a molecular tilt in the plane normal to the polar axis [2, 3, 6, 7]. Through this, a handedness is defined and two different types of domain can coexist in one phase: domains with homogeneous chiral stacking of the layers and racemic domains with alternating stacking [2, 3, 6, 7]. While the structural properties of this new class of materials have been well explored [2–7], dynamic investigations on a molecular level are sparse. By use of FTIR spectroscopy with polarized light, the average orientation and the orientation order of the different molecular moieties (long mesogenic axis, the alkyl tails and the carbonyl group) can be observed. In performing these measurements with a time resolution of 5 μs, the mobility of these different molecular moieties in response to an external electric field, as well as their detailed path of reorientation, is obtained. In that way, a refined model for the molecular structure of the two coexisting domains in these phases is deduced, the observation of both ferroelectric and antiferroelectric switching behaviour is analysed and the synchronous reorientation of the different molecular groups on a 10 μs scale is proven.

2. Experimental

The experimental set-up and the chemical structure of the substance investigated are shown in figure 1.

The polar B_2 phase (phase notation according to the rules given in [8]) is found within the temperature interval 129–153°C. The sample was oriented by shearing the liquid crystalline melt [9] (at 135°C) between CaF_2 windows coated with a conducting ITO layer. An additional SiO layer protects the ITO electrodes from

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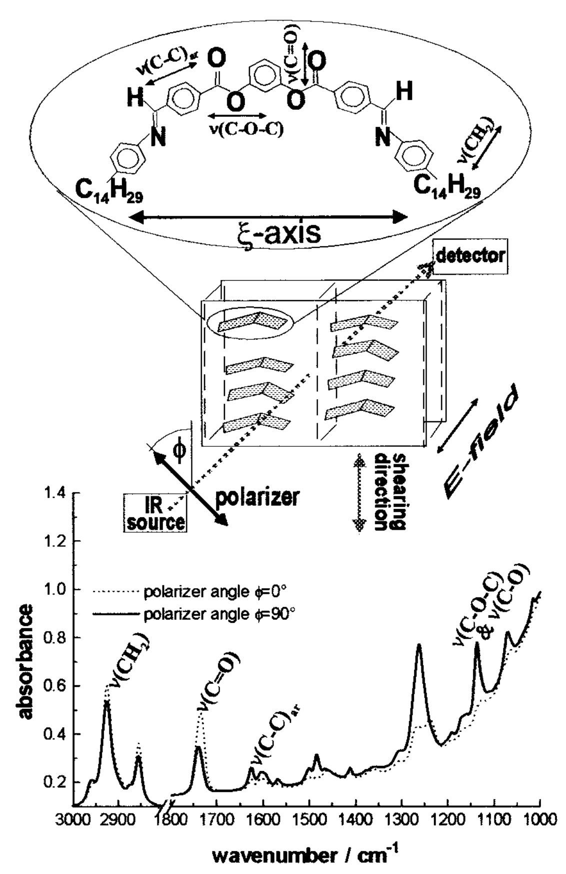

Figure 1. Scheme of the experimental set-up and the sample geometry. Dichroic static spectra (.... polarizer angle $\phi = 0°$, — polarizer angle $\phi = 90°$) of the bent core molecules. Sample thickness: $\approx 2\,\mu m$, temperature 135°C.

short-circuits during shearing. The FTIR spectrometer (FTS-6000, BioRad) equipped with an IR microscope (UMA-500) allowed measurements on an identical spot (size: $200\,\mu m \times 200\,\mu m$) in the visible (with the sample placed between crossed polarizers) and in the infrared wavenumber region as well. The incident light propagates normal to the CaF_2 windows (figure 1). Therefore the electric field vector of the polarized IR beam ε_ϕ always lies in the plane normal to the external electric field. By use of the step-scan technique time-resolved IR spectra were recorded for different infrared polarizer positions ϕ with a time resolution of $5\,\mu s$ and a spectral resolution of $8\,cm^{-1}$.

3. Results and discussion

3.1. *Electro-optical investigations*

The shearing of a fresh sample at 135°C produces stripe-like domains of approximately $20\,\mu m$ width. These domains possess different switching behaviour in response to an external electric field. By further shearing, these domains can be enlarged to sizes of approximately 1 mm, such that we can perform measurements on monodomains. The electro-optical response of the sample to a triangular voltage is shown in figures 2(*a*) and 2(*e*) for domains of type I and II, respectively. The transmittance of visible light at maximum positive and negative voltage is the same for domains of type I, but different for domains of type II. The observation of two different orientation types in the B_2 phase indicates that two structures coexist at the same temperature. For low frequencies of the external electric field, the switching is tristable (with the formation of a plateau at about $0\,V\,cm^{-1}$) and becomes bistable for frequencies in the kHz range.

3.2. *Band assignment and static FTIR measurements*

The response of the different molecular moieties is analysed by use of the following infrared bands: $\nu_{as}(CH_2)$ at $2924\,cm^{-1}$, $\nu(C{=}O)$ at $1736\,cm^{-1}$, $\nu(C\text{–}C)_{ar}$ at $1603\,cm^{-1}$ and $[\nu(C\text{–}O\text{–}C) + \nu(C\text{–}O)]$ at $1127\,cm^{-1}$ (figure 1). For several bands, the absorbance A is found to be dependent on the polarizer angle ϕ (figure 1). This results from the fact that A is proportional to $\int(\mathbf{m}\varepsilon_\phi)^2$ with $\mathbf{m}$ and ε_ϕ being the corresponding transition moment and the electric field vector of the polarized IR beam, respectively. The dichroic ratio for the $\nu(C\text{–}C)_{ar}$ band of $R = 1.3$ ($R = A_{max}/A_{min}$) is low compared with ferroelectric systems with linear mesogens [10, 11]. Considering that the transition moment for the $\nu(C\text{–}C)_{ar}$ bands is nearly parallel to the *para*-axis of the benzoate ring, this low R value reflects the bent shape of the molecule. The $[\nu(C\text{–}O\text{–}C) + \nu(C\text{–}O)]$ band ($1127\,cm^{-1}$) shows a strong dichroism with $R = 15$ for both orientations (types I & II). Due to the fact that the transition moment of this band is nearly parallel to the molecular long axis ('ξ-axis', figure 1) an order parameter $S = (R-1)/(R+2)$ of 0.82 is found which is in good agreement with NMR measurements [5] on homologues of this substance. This gives evidence for a monodomain orientation in the measurement spot.

3.3. *Time-resolved FTIR measurements*

In order to follow the molecular motion of the bent core molecules in response to an external triangular electric field ($\pm 10\,V\,\mu m^{-1}$, 2405 Hz), time-resolved FTIR spectra have been recorded for a complete set of polarizer angles ϕ (0° to 170° in steps of 10°). Similarly to the electro-optical response, figures 2(*a*) and 2(*e*), the absorbance of the different bands changes with the electrical field: while for orientation of type I, figure 2(*b*), the absorbances for maximum positive and negative electric fields are identical, an asymmetric behaviour with respect to the applied field is found for orientation of type II, figure 2(*f*). Additionally a hysteresis is observed which is more or less pronounced for the different molecular moieties.

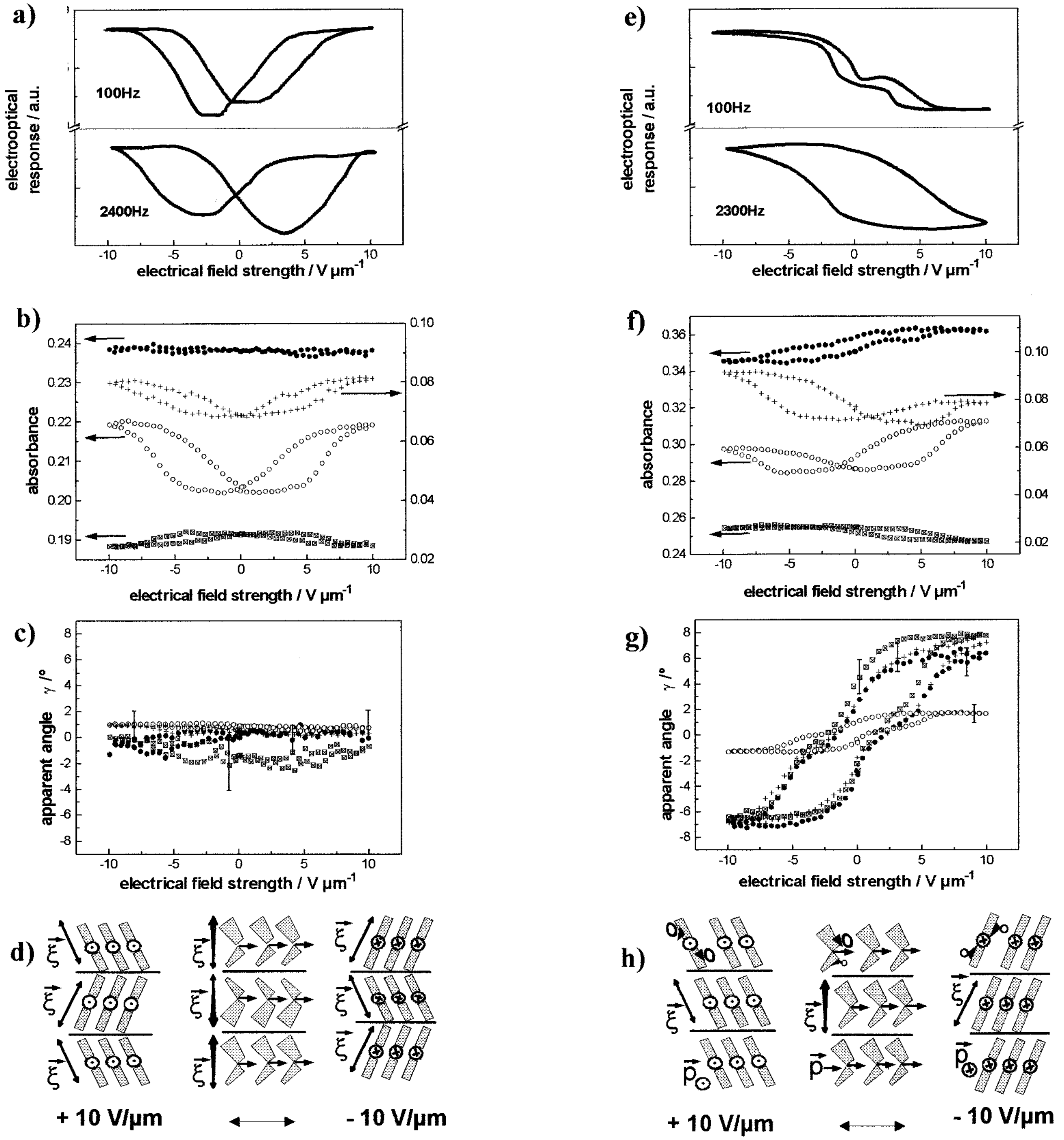

Figure 2. Dynamic response of bent core molecules in orientations of type I (*a*–*d*) and type II (*e*–*h*). (i) Electro-optical response of the system for orientation type I (*a*) and orientation type II (*e*) to an external electric triangular field of 100/2400 Hz and 100/2300 Hz, respectively. The sample was rotated between crossed polarizers until maximum transmission modulation was obtained. (ii) Time resolved absorbance for orientation type I (*b*) and orientation type II (*f*) for the $\nu_{as}(CH_2)$ [●], $\nu(C{=}O)$ [○], $\nu(C{-}C)_{ar}$ [⊠] and $\nu(C{-}O{-}C)$ and $\nu(C{-}O)$ [+] bands at fixed polarizer angle of $\phi = 50°$ and a modulation frequency of 2405 Hz. (iii) Angular excursion for orientation type I (*c*) and orientation type II (*g*) 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 FTIR spectra. (iv) Sketch of the molecular orientation as deduced from time-resolved, polarized FTIR spectra for orientation type I (*d*), and orientation type II (*h*). The spatial orientation of the two carbonyl groups pointing out on opposite sides of the polar plane ($\xi \times \mathbf{p}$) is indicated (◀ O, ▶ O).

From the complete set of the polarization dependent spectra, the polarizer angle with greatest absorbance can be determined for the different molecular units (C–O–C, C–C$_{\mathrm{ar}}$, C=O, CH$_2$). This angle determines the average direction of the corresponding transition moment projected in the plane perpendicular to the direction of the light propagation. This is denoted as the 'apparent angle γ' of the molecular moiety under study. In the case of orientation type I, figure 2 (*c*), the apparent angle γ for all bands equals 0°, whereas in the case of orientation of type II, figure 2 (*g*), the electric field induces a change in the apparent angle, $\Delta\gamma$. For the ν(C–C)$_{\mathrm{ar}}$, the combined [ν(C–O–C)+ ν(C–O)] and the ν_{as}(CH$_2$) bands, $\Delta\gamma$ is approximately 14° and for the ν(C=O) band it is $\approx$ 3°.

In accordance with [2, 3, 6, 7], the orientation behaviour of type I can be assigned to racemic domains. The alternating chirality in these domains leads to an alternating tilt of the ξ-axis if an external electric field forces the polar vector **p** of each layer in the same direction—anticlinic ferroelectric structure, left and right sketch in figure 2 (*d*). Both ferroelectric structures have the same optical axis (apparent angle $\gamma = 0°$). The results for domains of type II can be explained by a homochiral structure introduced in [2, 3, 6, 7]. In these domains the mesogens in each layer are tilted to the same side under the influence of a sufficient electric field—synclinic ferroelectric structure, left and right sketch in figure 2 (*h*). With reversal of the field polarity, this mesogen tilt changes its sign. Therefore a change in the apparent angles for the ν(C–C)$_{\mathrm{ar}}$, the combined [ν(C–O–C)+ ν(C–O)] and the ν_{as}(CH$_2$) bands of $\Delta\gamma \approx 14° \pm 2°$ is observed, figure 2 (*g*). One should note that after shearing, the sample also possesses homochiral domains of type II with an opposite handedness, as was first shown by Jakli *et al.* [9]. The opposite switching characteristic of these domains was observed by polarized optical microscopy. Equivalent results (i.e. negative apparent angles for positive electric fields and *vice versa*) are to be expected for time-resolved FTIR measurements.

In order to determine how the molecular reorientation takes place in the dynamic experiment, the modulation of the IR absorbance for the different polarizer angles is analysed. While for a polarizer angle $\phi = 90°$, no change in the IR absorbance for the ν(C–C)$_{\mathrm{ar}}$ band is observed during the switching cycle, for $\phi = 0°$ a modulation similar to that in figures 2 (*b*) and 2 (*f*) is found. From this one has to conclude that the tilt angle between the director—assigned to the ν(C–C)$_{\mathrm{ar}}$ and ν(C–O–C) and ν(C–O) bands—and the smectic layer normal (represented by $\phi = 90°$) is not changed in the course of the switching. In other words, the reorientation takes place on a cone for both orientations of types I and II, as indicated in figures 2 (*d*) and 2 (*h*).

For the polarizer angle $\phi = 0°$, maximum absorbance of the ν(C–C)$_{\mathrm{ar}}$ and ν(C–O–C) and ν(C–O) bands is just obtained for maximum positive and negative voltage (where ferroelectric structures are induced). For an antiferroelectric arrangement of the smectic layers as reported in [2, 3, 6, 7], this maximum absorbance would also be obtained as the term $\int(\mathbf{m}\varepsilon_{\phi=0°})^2$ is the same for both the antiferroelectric and the ferroelectric arrangements. Therefore one can conclude that in the course of the observed switching between the two ferroelectric states, an antiferroelectric structure is not established. The bistable behaviour in this experiment is obviously due to the fact that the frequency of the external electric field exceeds the relaxation rate of the mesogen. In the electro-optical experiment, the change from tristable switching at low frequencies to bistable switching at high frequencies, figures 2 (*a*) and 2 (*e*), supports these findings as well.

In type II domains, the apparent angle for the carbonyl band, ○ in figure 2 (*g*), is less than the angles for the other bands. This proves a biased rotation of the carbonyl groups around the ξ-axis by analogy with the findings for ferroelectric and antiferroelectric liquid crystals with linear mesogens [10–13]. Furthermore this shows that the carbonyl groups are pointing out of the polar plane formed by the ξ-axis and the polar vector **p**, figure 2 (*h*). The question arises whether the two carbonyl groups in the bent core molecular are pointing out of this plane on the same side or on opposite sides. In the first case, the carbonyl distribution would be symmetric with reference to the plane normal to the ξ-axis, resulting in equal apparent angles for the carbonyl and the phenyl band. Hence the observed difference in the apparent angles, figure 2 (*g*), shows that the normal of the symmetry plane of the carbonyl distribution is inclined to the ξ-axis, thus proving that the two carbonyl groups are pointing out on opposite sides of the polar plane, figure 2 (*h*).

In order to detect asynchronicities in the reorientation behaviour for the different molecular units, the corresponding apparent angles γ in figure 2 (*g*) have been normalized, figures 3 (*a*) and 3 (*b*). All γ_{n}-charts coincide within margins of $\pm 10\,\mu$s, proving that all different molecular moieties respond in phase on this time scale.

4. Conclusion

Two types of molecular arrangement coexist in the B$_2$ phase of the bent core molecules under study. Their molecular reorientations in response to an external electric field can be analysed on a microsecond scale by time-resolved spectroscopy. In domains of type I the switching is symmetric in its optical response and takes place between two anticlinic states. In contrast, the optical switching in domains of type II is antisymmetric.

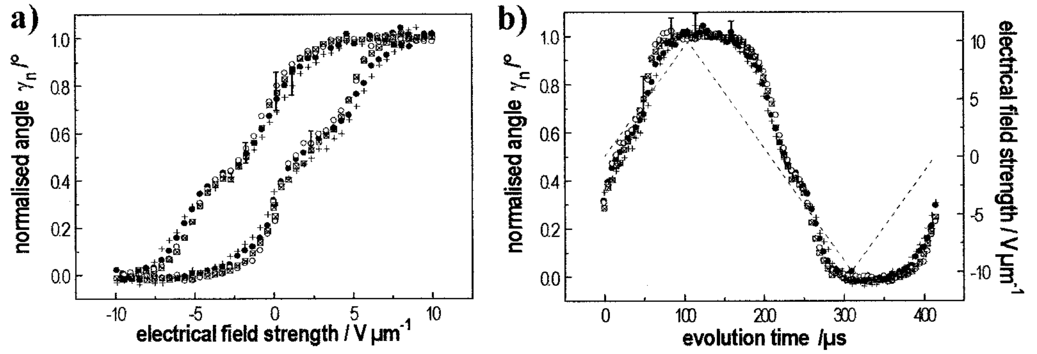

Figure 3. (*a*) Normalization of the apparent angle γ vs. electrical field strength E [figure 2(*g*)] according to $\gamma_n(E) = [\gamma(E) - \gamma_-]/(\gamma_+ - \gamma_-)$ with γ_+ and γ_- being the apparent angles for positive and negative maximum field strength, respectively, averaged over the corresponding plateaus. (*b*) Normalization of the apparent angle γ vs. evolution time. The time dependence of the external field is indicated by the dashed line. The coincidence of the normalized plots shows the synchronous reorientation of the different molecular moieties on a time scale of 10 µs.

For modulation frequencies ≤ 100 Hz, a tristable response is observed. With increasing frequency, the molecular motion becomes bistable and resembles that on a cone. From the analysis of the molecular response to an external electric field for the phenyl and the carbonyl groups, it can be deduced that the latter obeys a biased rotational distribution. It is shown that all molecular moieties move synchronously on the time scale of the experiment (10 µs).

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