Electrooptical investigation on the three switching states of a chiral smectic side group polymer

Frank Gießelmann, Peter Zugenmaier*

Institut für Physikalische Chemie, Technische Universität Clausthal,
Arnold-Sommerfeld-Str. 4, D-3392 Clausthal-Zellerfeld, FRG

Günter Scherowsky

Institut für Organische Chemie, Technische Universität Berlin,
Straße des 17. Juni 135, D-1000 Berlin, FRG

Kurt Kühnpast, Jürgen Springer

Institut für Technische Chemie, Technische Universität Berlin,
Straße des 17. Juni 135, D-1000 Berlin, FRG

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Introduction

Recently, investigations on chiral ferroelectric liquid-crystalline (lc) side group polymers (flcp's) have been reported[1-3] which exhibit three switching states in an alternating electric field. The existence of the third switching state was interpreted by Chandani et al.[4-6] for a low-molecular-weight lc compound as an antiferroelectric modification of the SmC* phase, an SmC_A* phase. Skarp et al.[2] and Bömelburg et al.[3] came to the same conclusion with analogous experimental results on a chiral smectic side group polymer. Electrooptical investigations presented in this paper suggest that the formation of three switching states for a side group polymer occurs upon conformational interactions between the side group and the main chain.

Experimental part

Material

The polymer investigated consists of a 1,3-dioxolane-4-carboxylic acid as chiral building block which is attached terminally to the phenylpyrimidine mesogenic moiety and linked via a C_{11} spacer to a polyacrylate main chain:
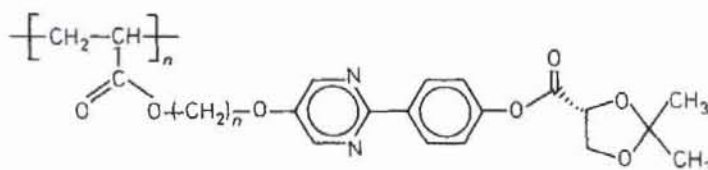
The synthesis has been reported elsewhere [1, 7], and the weight-average molar mass was determined to $\widetilde{M}_w = 7600$ g · mol^{-1}, the polydispersity to $\widetilde{M}_w/\widetilde{M}_n = 1{,}38$ and the phase sequence to SmX · 45 °C · SmC* · 85 °C · SmA · 110 – 115 °C · isotropic.

Cells

The polymer was filled into 4 µm thick cells (E. H. C. & Co. Ltd., Tokyo) with the temperature gradient method for the electrooptical investigations. The glass plates of the cells were coated with transparent ITO (indium tin oxide) electrodes and parallel rubbed polyimide layers which provide homogeneous orientation of the lc phases.

Measurements

The setup for the electrooptical measurements and their evaluation has been described elsewhere [8]. The light beam of the polarizing microscope was monochromatized by an interference filter with $\lambda_{max} = 633$ nm and a half width of $\Delta\lambda_{1/2} = 10$ nm. The measurement of the polarization reversal current was performed with a Sawyer-Tower bridge in connection with a differential amplifier (Tektronix AM 502). A Berek compensator (Olympus AH-CTP) was used for the static determination of the optical path differences.

Results

The investigations were carried out at 75 °C, 10 °C below the SmA → SmC* phase transition. It was clearly confirmed that the polymer exhibits three switching states in an alternating-current electric field. Fig. 1 represents the optical apperance in the
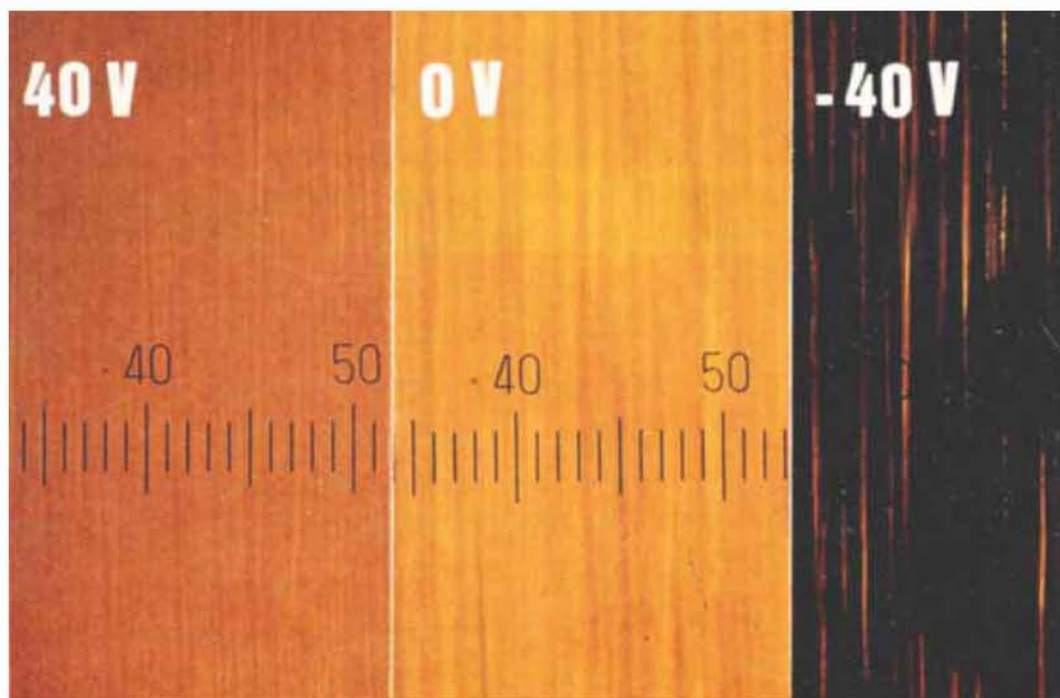

Fig. 1.   Polarizing microscopic texture of the three observed switching states in a 4 µm cell at 40 V, 0 V and −40 V; crossed polars (10 scales ≙ 60 µm)

polarizing microscope at static field conditions. The transmission and colours are obviously different at constant crossed polarizer and analyzer position.

Each of the three switching states can be set to a dark position by a rotation of the cell between crossed polars. An optical uniform structure is concluded from these observations with almost uniform, constant orientation of the optical axis (or the director) across the cell in all three switching states. A continuous change of the orientation of the optical axis along the cell thickness, as e.g. in the cholesteric or helical SmC* phase, does not lead to a dark position between crossed polars because of waveguiding effects. The apparent tilt angle amounts to $+15°$ at $+40$ V, $-15°$ at -40 V and $0°$ at 0 V.

The three switching states are confirmed in a dynamic experiment using a 2 Hz/40V triangular voltage (Fig. 2a). The corresponding transmission curve between crossed polars at 633 nm (Fig. 2b) exhibits, besides the two stationary switching states in the range of high positive and negative electric field strength, a clear breaking point in the range of low electric field strength. The transmission does not become stationary in this range anymore caused by the high internal viscosity of the polymer.

An even more informative picture of the switching behaviour is provided by the time-dependent curves of the polarization reversal current (Fig. 2c). Two peaks of the current are observed for each gradient of the applied electric field which indicates two switching procedures separated in time between three switching states. It should be noted that the ohmic and capacitive contributions to the current in Fig. 2c have not been completely compensated.

The optical path difference between the extraordinary and ordinary beam after passing through the 4 μm cell amounts to 469 nm at -40 V and 418 nm at 0 V and
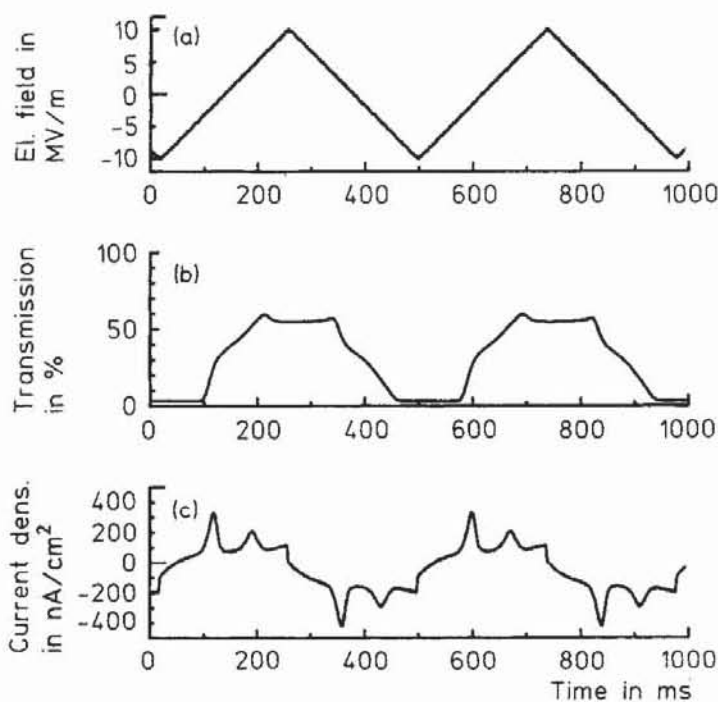

Fig. 2. Representation of applied electric field (a), optical transmission response at $\lambda = 633$ nm and crossed polars (b), and polarization current response (c) at 75 °C
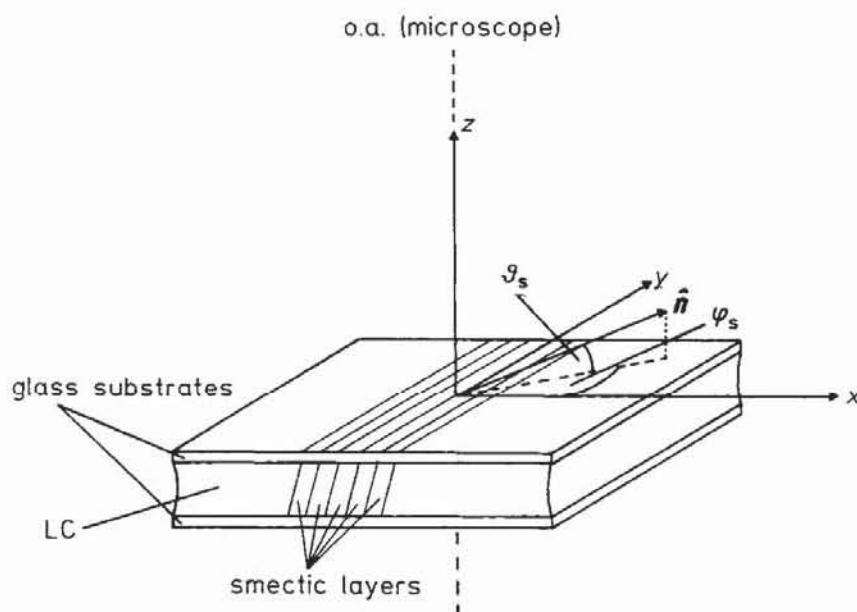
Fig. 3. Schematic representation of the laboratory coordinate system x, y, z for a description of the director orientation $\hat{n}$; φ_s: in-plane angle (apparent tilt angle); ϑ_s: off-plane angle
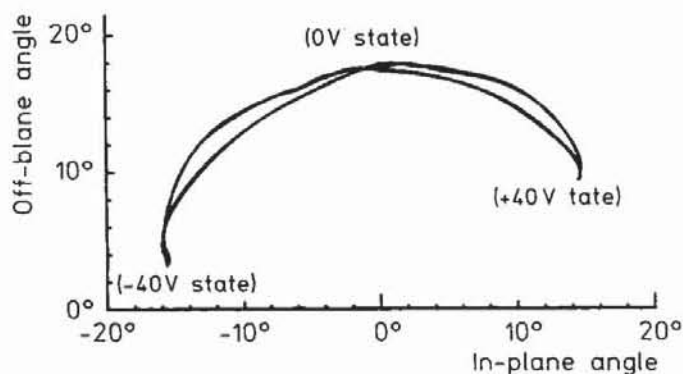

Fig. 4. Trajectory of director reorientation in a 4 μm cell at an applied 2 Hz/40 V triangular voltage at 75 °C

have been determined with a compensator. The smallest effective birefringence corresponding to the smallest path difference was observed at the 0 V switching state.

Hints towards the mechanism are available by a dynamic study of the reorientation of the optical axis or, at uniform orientation, of the mean director of the lc cell during the switching procedure[8]. The orientation of the director is described in the laboratory coordinate system x, y, z (Fig. 3) by two angles, the in-plane angle φ_s (azimuth angle of the polar coordinate system in x, y, z), which is often denoted as apparent tilt angle, and the off-plane angle ϑ_s (copolar angle of the polar coordinate system in x, y, z). The trajectory which is described by the director during a field-induced reorientation can be determined from electrooptical measurements for a given electric field[8] and plotted for φ_s, ϑ_s as variables, e.g. in Fig. 4 (view direction $-x$ in Fig. 3).

The result for the electric field represented in Fig. 2a is depicted in Fig. 4. The ordinary refractive index, necessary for an evaluation of the trajectory, was estimated to $n_0 = 1,5$ and the extraordinary one n_e determined from the maximal birefringence ($\Delta n = \Delta_{\text{opt,max}}/d = 470 \text{ nm}/4000 \text{ nm} = 0,117$) to $n_e = 1,617$.

The director describes an approximate semicircular trajectory during the reorientation. Assuming the layer normal at $\varphi_s = 0°$ and $\vartheta_s = 2°$, which means a slight layer tilt angle of $2°$, the angular distance between the director positions along the trajectory and the layer normal, which is the tilt angle θ of the SmC* phase, is approximately constant at $\theta \approx 15°$. This confirms that the reorientation of the director occurs along the SmC* tilt cone at constant tilt angle around the smectic layer normal. The small variations in θ leading to a loop-like motion is most probably caused by the electroclinic effect.

The apparent tilt angles observed in the polarizing microscope at static field conditions agree with the corresponding in-plane angles of $-15°$ at -40 V, $0°$ at 0 V and $+15°$ at 40 V (Fig. 4). At high electric fields, the director moves into the substrate plane ($\vartheta_s = 0°$) and the spontaneous polarization lies parallel to the applied field as common in ferroelectric lc's ($+40$ V and -40 V states in Fig. 4). At low electric field, the director orientation is stabilized at an additional third switching state (0 V state in Fig. 4), with maximal angle of $17°$ to the substrate plane and an apparent tilt angle (in-plane angle) of $0°$.

This result agrees with the observed birefringence which is maximal with the director perpendicular to the light beam ($\vartheta_s = 0°$, Fig. 3). The birefringence becomes smaller when the director moves out of the substrate plane and vanishes at $|\vartheta_s| = 90°$ (homeotropic orientation). Consequently, the optical path difference measured with the compensator is at -40 V (off-plane angle ≈ 0) with 469 nm much larger than the one at 0 V (off-plane angle $\vartheta_s \approx 17°$) with 418 nm. The dynamics of the optical path difference during the switching procedure is available by the electrooptical transmission curves[8] and depicted in Fig. 5 and corresponds to the electric field, represented in Fig. 2a. The values agree quite well with the static ones.

Fig. 5. Optical path differences of the 4 µm cell with an applied 2 Hz/40 V triangular voltage (cf. Fig. 2a) at 75 °C. In brackets the corresponding values from static measurements
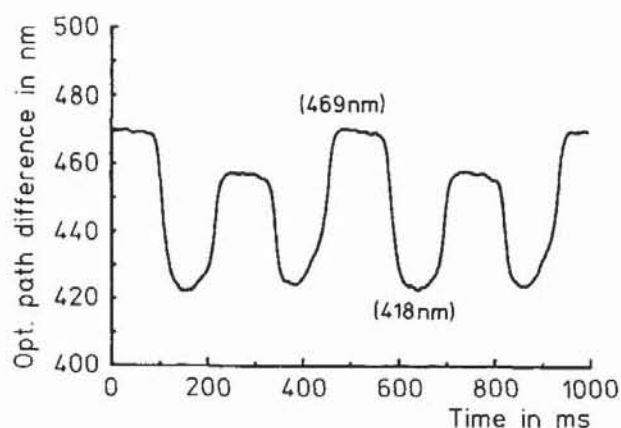
Discussion

The results indicate that the director orientations in all three switching states are directed along the SmC* tilt cone with $\theta = 15°$. Assuming optically uniform and uniaxial transmission and birefringence behaviour, the stationary states are connected by a semicircular trajectory during the switching procedure. The layer tilt angle is about 2°.

Low-molecular-weight ferroelectric lc's exhibit optically nonuniform director re-orientations at low electric fields [9, 10] which serve as explanation of various switching phenomena [11]. This is not the case for the investigated side group polymer, since the cell forms an optically uniform switching state at 0 V as proven by its optical behaviour.

The question still remains, how do the three switching states occur with a uniform state at low electric fields? The clue for an explanation may be found in the relative position of the side groups in relation to the main chain. Today, it is generally accepted that the main chains are placed between the smectic layers and, therefore, the smectic layer normal $\hat{z}'$ is positioned perpendicular towards the main chains. The side group direction and the director $\hat{n}$ of the SmC* phase form the tilt angle θ with the layer normal $\hat{z}'$. The symmetry of the SmC* phase will not be violated for all orientations of the side group relative to the main chain, which are directed along the SmC* tilt cone. In the SmC* phases of low-molecular-weight compounds, all director orientations along the tilt cone are equivalent without fields applied. This is no longer valid if the mesogenic units are connected to main chains, and various conformations (side group orientations) possess different potential energies. As the symmetry of the SmC* phases in surface-stabilized ferroelectric lc cells (SSFLC cells) is broken by the surface, the tilt cone symmetry is broken by the main chain as well as the energetic equivalence of the various orientations along the tilt cone.

With these assumptions, the existence of three switching states of a ferroelectric SmC* side group polymer may be explained as follows: Fig. 6 indicates the main chain (mc), the perpendicular layer normal ($\hat{z}'$), the direction of the director $\hat{n}$ and the side group on the director tilt cone (tc), respectively, the projection of the director c onto the smectic layer plane (sp) and the direction of the spontaneous polarization P_s at various states. Application of a sufficient high electric field E (Fig. 6a) leads to a spontaneous polarization oriented parallel to the field vector E. The direction of $\hat{n}$ on the tilt cone results with $P_s \sim \hat{z}' \times \hat{n}$ as depicted in Fig. 6a. This side group orientation is energetically favoured as regards to the P_s, E interaction. However, it is an un-favourable direction considering the repulsive forces between main chain and side group, since the side group orientation $\hat{n}$ or its projection onto the layer plane c is in eclipsed conformation with regard to the main chain. If the external field is switched off, the repulsive interaction dominates the P_s, E interaction and the side group is turned into a conformational more favourable orientation towards the main chain. The projection of the side groups c as represented in Fig. 6b lies perpendicular to the main chain which should minimize repulsive conformational interactions between the side groups and the main chain and lead to an additional switching state of the polymer. A strong applied negative field leads to the director orientation represented in Fig. 6c, symmetric to the position in Fig. 6a, which is favoured regarding the P_s, E inter-action.
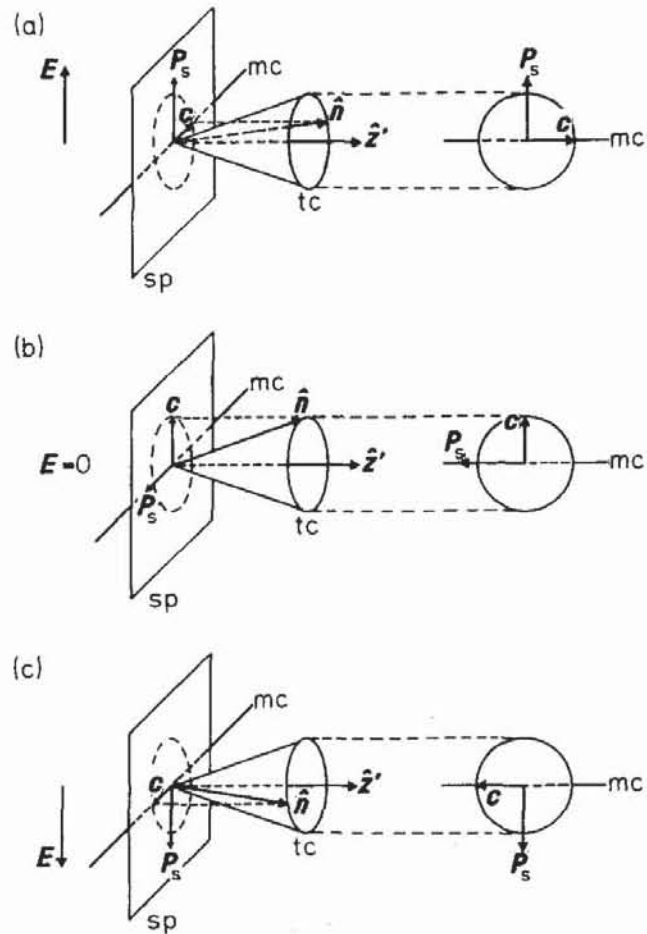
(a)

(b)

Fig. 6. Schematic representa-
tion of side group orientations
relative to the main chain at
different switching states of the
SmC* phase. Explanation and
abbrevations see text

(c)

Regarding the simple case of bookshelf geometry of the smectic layers, the director
in Fig. 6a and c lies within the substrate plane and represents an apparent tilt angle
(corresponding to the in-plane angle φ_s) of $+\theta$ (Fig. 6a) and $-\theta$ (Fig. 6c),
respectively, as observed for an applied voltage of $+40$ V or -40 V at the cell. In
Fig. 6b the director exhibits an apparent tilt angle of $0°$ and is tilted by θ out of the
substrate plane, causing a lower birefringence, as experimentally verified for the 0 V
state. The predictions from this model agree with the experimentally determined
director orientations in all three switching states.

Further verification of the proposed model is provided by simulation calculations
which are described for low-molecular-weight ferroelectric liquid crystals in refs. [12]
and [13]. The simulation for the polymeric system in this paper was carried out with a
simplified procedure, and the elastic energy is not considered in a first approximation.
An additional conformational energy term with a potential well

$$g_c = -K_c \cdot \sin^2\theta \exp(-\beta \sin^2 \Phi)$$

has to be added to describe the discussed model. The parameter β influences the half
width, K_c the depth of the potential and the angle Φ, introduced as azimuth angle, is
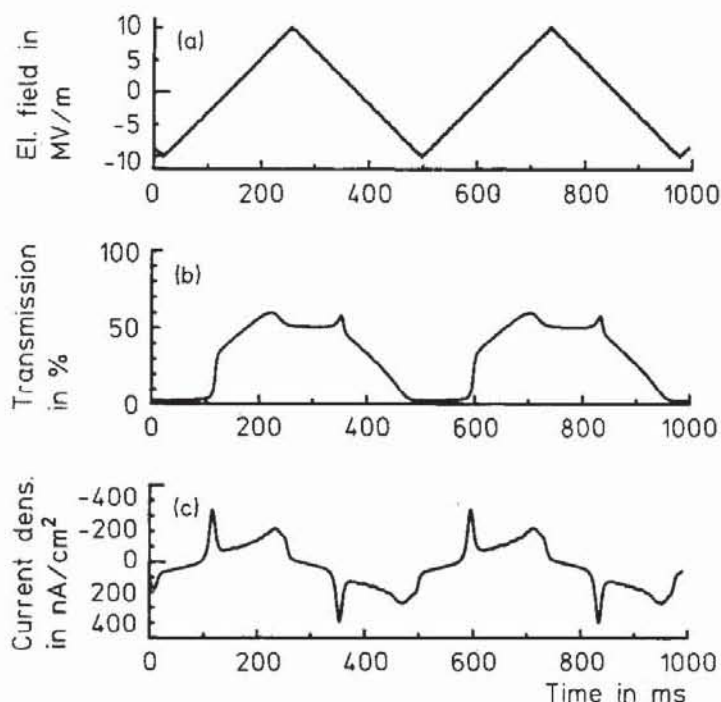related to the orientation of the side group projection c.

Fig. 7. Simulation results of the switching procedure investigated. Optical response at $\lambda = 633$ nm and crossed polars (b) and current response (c) to a 2 Hz/40 V triangular field (a)

The best fit is represented in Fig. 7 and was obtained with the following parameters: $\beta \approx 1$, $K_c = 22$ kJ $\cdot$ m^{-3}, $P_s = 25$ nC $\cdot$ cm^{-2} ($\theta = 14°$) and an effective rotational viscosity $\gamma = 6$ Pa $\cdot$ s^{-1}. The assumed model leads to the calculated transmission response in Fig. 7b and compares well to the experimental transmission curve of Fig. 2b. Both transmission curves exhibit a contrast of 60%, a pronounced optical overshoot and breaking points in each of the rises and decays of the curves which are caused by the third switching state. The calculated current response (Fig. 7c) shows characteristic double peaks although the additional peak appears too flat and occurs too late as compared to the measurement. Experiment and simulation agree in linear, electrolinic behaviour at low field amplitudes.

The energy barrier for the side group rotation along the SmC* tilt cone ($\theta = 14°$) is calculated to g_c ($\Phi = 90°$) $- g_c$ ($\Phi = 0°$) ≈ 830 J $\cdot$ m^{-3} from the model and compares to the maximum value for the P_s, E-interaction of 2500 J $\cdot$ m^{-3} and may be easily surpassed. Assuming a molar mass of ≈ 500 g $\cdot$ mol^{-1} and a density of 1 g $\cdot$ cm^{-3}, the rotation barrier amounts to $5 \cdot 10^{-6}$ eV for a single side group. This value is extremely small, if compared to the rotation barrier of the C—C bond in ethane of $1,5 \cdot 10^{-1}$ eV. It can be concluded from these estimations that the experimental results are consistently explained by a conformational interaction between main chain and side groups with an extremely small rotational barrier between the switching states.

Despite the simplicity of the model for the explanation of the switching states which does not include the packing of the polymers, the considerations remain valid as long as a certain long-range orientation correlation exists between different main chains. An average degree of polymerization of 15 and a length of the extended main chain of 30 Å can be concluded from the mean molecular weight of the polymer which is comparable of the length of the side groups. The orientation behaviour of such a short

main chain will predominantly be influenced by the SmC* order of the side groups and will lead to an extended chain necessary for the proposed model.

Similar results have been reported in refs.[2,3] for a different chiral side group polymer and explained by an antiferroelectric behaviour caused by an (unknown) polymer effect which has to account for the resulting optical properties (birefringence, apparent tilt angles) at constant tilt angle, leading to constant smectic layer thickness.

In our opinion, the polymeric SmC* phase has to be clearly distinguished from the low-molecular-weight SmC* phase, since the tilt cone symmetry will be broken by the main chain. If the resulting phase can be classified as antiferroelectric is at the present open for discussion.

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