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# Evidence for a tilted smectic phase in Anopore membranes by dielectric spectroscopy

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Collective relaxation processes are completely undetectable in a ferroelectric liquid crystal confined in porous Anopore membranes, as a result of perfect orientation of the smectic layers perpendicular both to the long axis of the pores and the direction of the measuring electric field. In the ferroelectric liquid crystal – Anopore composite only one relaxation process, assigned to rotation of the molecule around the molecular short axis, appears throughout all smectic phases. The temperature dependence of the relaxation frequency and of the dielectric strength of this process also shows no irregularity at the point of polarization sign reversal. The temperature dependence of the relaxation frequency follows the Arrhenius law with an activation energy slightly higher in the ferroelectric SmC* phase. Analysis of the non-linear changes of temperature dependence of the dielectric strength at the SmA–SmC* phase transition enables one to obtain the temperature dependence of the tilt angle of the molecules in the SmC* phase in the Anopore membrane. Dielectric measurements confirm the existence of the tilted smectic phase in Anopore cylindrical channels with no tilt anomaly at the point of polarization sign reversal.

## 1. Introduction

The influence of geometric restrictions on liquid crystal (LC) phases manifests itself mainly in two important aspects: (i) significant and sometime unexpected changes in the dynamics of the molecular and collective relaxation processes; (ii) influence of confinement on the structure and molecular arrangement of the mesophases. In particular, the influence of confinement on the dynamics of the collective modes and on the thermodynamic properties of the SmA–SmC* phase transition in ferroelectric liquid crystals (FLCs) remains an open question. What is the orientation and arrangement of the smectic layers in porous materials? What is the role of the main physical parameters characterizing the ferroelectric phase—such as tilt angle, spontaneous polarization and helical pitch—on the observed changes in dynamics of the relaxation processes? If the tilted smectic phase exists in confinement is it still ferroelectric? Moreover, there is only limited experimental evidence of the arrangement and structure of the SmC* phase in confinement.

Common experimental methods used to describe and characterize the structure and molecular arrangement of the different mesophases under geometric restriction include X-ray diffraction (XRD) [1–3], NMR spectroscopy [4–7], infrared absorption dichroism spectroscopy [8], conoscopy [5], selective reflection [9], measurements of birefringence and optical activity [5], and dielectric spectroscopy [10–13]. Powder XRD measurements of the temperature dependence of the tilt angle in FLC CE8/aerosil dispersions reveal smectic layer compression leading to a distribution of layer thicknesses, and pretransitional tilted order that increases with increasing degree of confinement [1]. In the FLC A7/Anopore system XRD shows that the tilted phase still exists in this porous membrane. Additionally, in the composite a smooth temperature variation of the layer spacing in the SmA–SmC* transition appears, in contrast to abrupt changes in the bulk smectogen [2]. Also, in the FLC DOBAMBC/Synpor system X-ray spectroscopy revealed the existence of the SmA and SmC* phases in confinement [3]. Deuterium NMR ($^2$H NMR) shows a structural transition in nematic LCs doped by chiral agents in cylindrical pores of Anopore membrane. It was found that the stability of the radially or axially twisted structure depends on the helical pitch length [4]. Also, $^1$H and $^{13}$C NMR studies of a nematic mixture doped by a cholesteric agent implied a conical helical director field in the pores, as in a common SmC* phase, with the helical axis parallel to the cylindrical channel

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axes in Anopore membrane [5]. Infrared dichroism measurements of the 4-*n*-pentyl-4′-cyanobiphenyl (5CB) nematic LC confined in Anopore membrane reveal that an increase in the chiral dopant causes an increase in tilt of the molecules in the pores [8]. These results were interpreted in terms of a conical helicoidal or a radially twisted axial arrangement of the LC molecules.

Usually, optical measurements complete the results from other experimental methods and allow conclusions to be drawn regarding orientation and structure of the LC phase. The sign of the optical rotatory power of the twisted nematic and FLC phases under cylindrical geometric restriction is reversed in comparison with the bulk materials [5]. The observed changes in optical activity can be caused by a significant reduction of the pitch in confinement, or a reversal of the rotatory sense of the helical structure. In antiferroelectric LCs confined in Anopore membrane, selective reflection of light in the blue region was observed, which suggests the existence of a helical structure within the pores, with the helical axis along the pores [9].

Dielectric spectroscopy of different LC phases enables one to draw conclusions concerning the structure of the mesophases from the changes of the main parameters characterizing the dynamics of the relaxation processes. An example is seen in the determination of temperature dependence of the tilt angle in chiral and non-chiral bulk compounds from analysis of the dielectric strength changes at the phase transition for homeotropically oriented smectogens [10–12]. It is also well established, and confirmed from dielectric experiments, that in untreated Anopores the molecules in the nematic phase orient parallel to the axis of cylindrical channels, while in treated membranes the molecules orient homeotropically to the walls of the pores [14, 15]. However, dielectric spectroscopy is less sensitive to the different possible orientations of the director field in pores, and more accurate results can be obtained using NMR [4–7].

Some dielectric measurements of FLCs, with small spontaneous polarization and relatively large helical pitch of the pore diameter scale, in untreated Anopore membranes, show complete suppression of the soft and Goldstone modes [16, 17]. These results do not contradict the above described optical activity of the FLC/Anopore composites, but in fact greatly support the existence of a perfectly oriented structure of smectic layers within pores, with the helical axis parallel to the pores. Additionally, in FLCs with high spontaneous polarization and short pitch confined in untreated [13] and treated Anopores [2], a significant modification of the collective processes was detected. A new collective relaxation process observed in untreated membranes, in the MHz range, was assigned to a relaxation of flexoelectric polarization near the splayed regions at the pore walls [13]; whereas the dramatic increase of the Goldstone mode frequency in treated membranes was assigned to substantial unwinding of the helix [2].

In this study, experimental evidence is given of the existence of a tilted smectic phase in the cylindrical channels of Anopore membrane, based on dielectric measurements.

## 2. Experimental

The influence of cylindrical geometric restrictions on molecular and collective relaxation processes near the SmA–SmC* phase transition, and on the point of polarization sign reversal, was investigated in the ferroelectric liquid crystal *S*-(-)-2-methylbutyl 4-*n*-nonanoyloxybiphenyl-4′-carboxylate with the phase transition temperature sequence Cr 312.15 K SmC* 315.65 K SmA 332.65 K I, supplied by AWAT Sp. z o.o. (Warsaw, Poland). The ferroelectric SmC* phase appears over a broad temperature range and can be easily supercooled to about 265 K. Polarization sign reversal is observed at a temperature of about 292 K [18–22]. The material is characterized by a small spontaneous polarization of about $2\,\mathrm{nC\,cm^{-2}}$ and a rather high helical pitch near the SmA–SmC* phase transition of 3–3.8 μm [18–21].

Tilt angle measurements were performed in ITO-coated electro-optic cells with a 5 μm thickness and a $12.7 \times 12.7\,\mathrm{mm^2}$ pixel area covered on both sides by rubbed polyimide to induce homogeneous orientation of the LC (AWAT Sp. z o.o.). The temperature dependence of the tilt angle $\theta$ was determined from the two angular readings of the successive positions of the extinction corresponding to the switching of the optic axis on the cone observed under a Leica polarizing microscope equipped with turn-table. The LC in the cell, mounted in an Instec hot stage, was switched using a low frequency square wave signal ($f$=0.1 Hz, $V_{\mathrm{pp}}$=20 V). The temperature stabilization was about ±0.1 K.

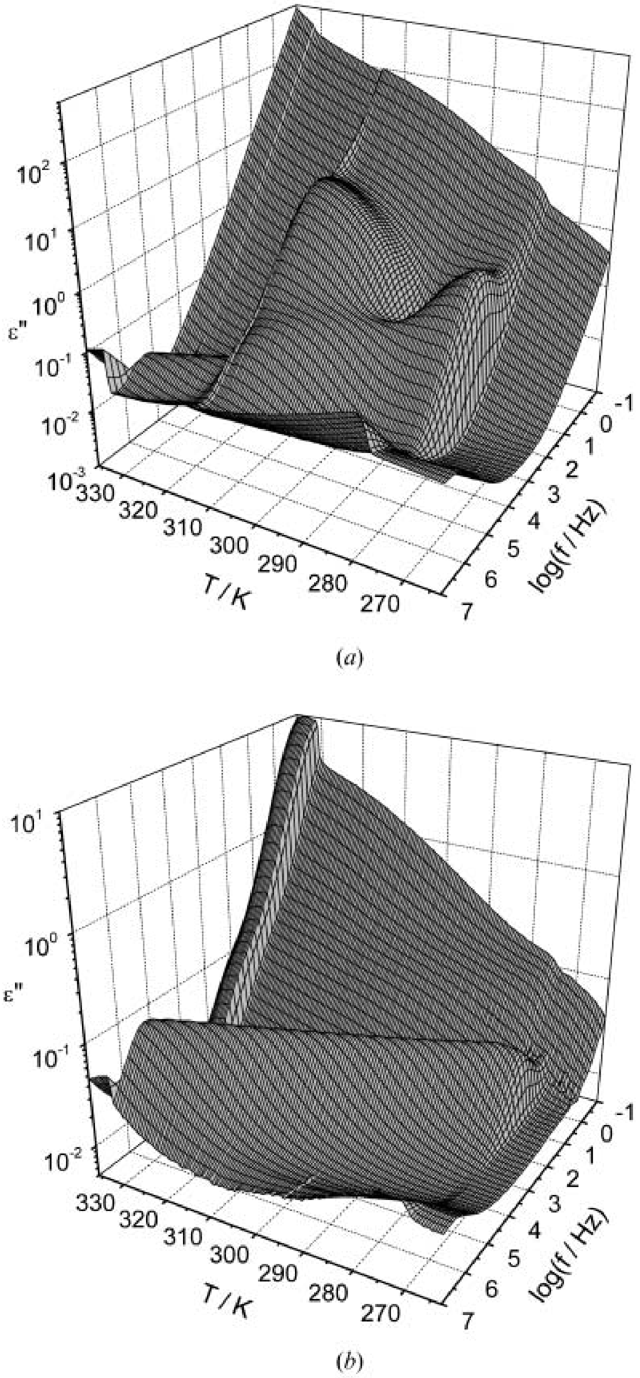
Inorganic alumina oxide Anopore membranes with thickness about 60 μm and 0.20 μm cylindrical diameter, well oriented and separated pores, were used to prepare FLC/Anopore composite samples [23]. Pieces of Anopore membrane of diameter about 10 mm were annealed at a temperature of about 473 K in a vacuum oven overnight to avoid water and other impurities. The membrane was then filled by the action of capillary forces, staying immersed in the liquid crystal in the isotropic phase for about one hour. Finally, the outer surfaces of the membranes were carefully cleaned with filter paper and by sliding the membrane on a glass surface, to avoid undesired dielectric signal from the possible leakage and of a thin surface layer of the liquid crystal between the membrane and capacitor electrode.

A Novocontrol broadband dielectric spectrometer with a high resolution dielectric impedance analyser Alpha, and an active sample cell, were used to measure the complex dielectric permittivity $\varepsilon^*(\omega, T)=\varepsilon'(\omega, T)-i\varepsilon''(\omega, T)$ in the frequency range $10^{-1}$ to $10^7$ Hz. The FLC/Anopore samples were directly placed between the gold-plated electrodes of the measuring capacitor. Dielectric measurements on the bulk FLC have already been presented and described in previous papers [22, 24, 25], and will be used here for comparison with FLC/Anopore composites. The measurements were performed on cooling the sample in the temperature range from 336 to 263 K, in temperature steps of about 0.5 K. The temperature stabilization was better then ±0.01 K.

The dielectric spectra of the FLC/Anopore composites were analysed using superposition of Havriliak and Negami relaxation functions [26] and a conductivity contribution:

$$\varepsilon^*(\omega, T)=\varepsilon_\infty+\frac{\Delta\varepsilon}{\left[1+(i\omega\tau)^{1-\alpha}\right]^{\gamma}}-\frac{i\sigma_0}{\varepsilon_0\omega^n} \qquad (1)$$

where $\tau$ is the relaxation time and $\Delta\varepsilon$ the relaxation strength, while the exponents $\alpha$ and $\gamma$ describe broadening and asymmetry, respectively, of the relaxation time distribution. $\varepsilon_0$ and $\varepsilon_\infty$ are the permittivity of free space and the high frequency limit of the permittivity, respectively. In the low frequency range the conductivity related to the free charge carriers present in the liquid crystal dominates, and its contribution is expressed by the term $i\sigma_0/\varepsilon_0\omega^n$, where $\sigma_0$ is the Ohmic conductivity and $n$ a fitting parameter.



(*a*)

(*b*)

Figure 1. Three-dimensional plot of the temperature and frequency dependence of the imaginary part of the permittivity in (*a*) the bulk FLC and (*b*) FLC confined in Anopore membrane.

## 3. Results and discussion

The dielectric measurements were performed both in bulk FLC and in FLC/Anopore composites. Figure 1 presents the temperature and frequency dependence of the dielectric losses in the bulk smectogen (*a*) and in the FLC/Anopore system (*b*). In the isotropic phase, losses related to the conductivity of the LC dominate. After the transition to the paraelectric SmA phase, one relaxation process assigned to the rotation of the molecules around the molecular short axis is observed. Close to the SmA–SmC* phase transition, in the SmA phase, the characteristic behaviour for the soft mode appears, with a decrease of the characteristic relaxation frequency and an increase of the dielectric strength. In the ferroelectric SmC* phase the soft mode splits into the soft amplitude mode and the Goldstone mode (GM), assigned to the formation of the helical structure and the azimuhal fluctuations of the direction of the director on the cone. In the SmC* phase the soft mode is covered by the GM, characterized by a relatively high dielectric strength and nearly temperature-independent characteristic relaxation frequency. In the FLC investigated the polarization sign reversal phenomenon appears, which is visible in figure 1 (*a*) as a clearly pronounced saddle shape of the 3D surface. At the polarization sign reversal temperature the Goldstone mode disappears, but below this temperature it appears again with somewhat lower dielectric strength.

The temperature and frequency dependence of the dielectric losses in the FLC/Anopore composite, figure 1 (*b*), differ considerably from that for bulk material. Besides the conductivity contribution, which decreases with decreasing temperature, only one relaxation process, assigned to the rotation of the molecules around the molecular short axis, appears throughout all mesophases. This decrease of conductivity in the isotropic–SmA phase transition, and appearance of one relaxation process in all phases, can only be explained by assuming the formation of a perfect smectic layer structure with layer planes perpendicular to the axes of the Anopore cylindrical channels. In this configuration a significant drop in the conductivity is observed in the isotropic–SmA phase transition. No sign of an anomaly is visible at the point of polarization sign reversal. Qualitatively comparable dependences of the relaxation losses and conductivity have already been observed in other FLC/Anopore systems [17].

Figure 2 shows the temperature dependence of the dielectric losses in the bulk smectogen and in the FLC/Anopore system, both in the SmA (*a*) and in the SmC* (*b*) phases far from the SmA–SmC* phase transition. The solid lines represent fits of the experimental data to equation (1). The fitting parameters for bulk FLC in the SmA phase are: $\Delta\varepsilon=0.11$, $\alpha=0.13$ and $\gamma=1$. For the FLC/Anopore system, $\Delta\varepsilon=0.28$, $\alpha=0.14$ and $\gamma=1$. The quantities $\alpha$ and $\gamma$ are practically the same, reflecting bulk-like dynamics behaviour of the molecular process in Anopore confinement. However, the dielectric strength of this relaxation process is higher in Anopore membrane because of perfect orientation of the molecules parallel to the pores compared with the mainly planar ordered bulk sample. For the bulk FLC in the SmC* phase, besides the soft mode present very close to the SmA–SmC* phase transition, two other relaxation processes appear: the Goldstone mode with fitting parameters $\Delta\varepsilon=5.3$, $\alpha=0.07$ and $\gamma=1$; and a molecular process with $\Delta\varepsilon=0.20$, $\alpha=0.01$ and $\gamma=0.94$. In the FLC/Anopore system the Goldstone and soft modes are dielectrically inactive and only a molecular process is observed with fitting parameters $\Delta\varepsilon=0.21$, $\alpha=0.01$ and $\gamma=0.69$. In the Anopore membrane the dielectric peak of the molecular process is more asymmetric than in the bulk material, which can be caused by more pronounced surface interactions in the frustrated SmC* phase.

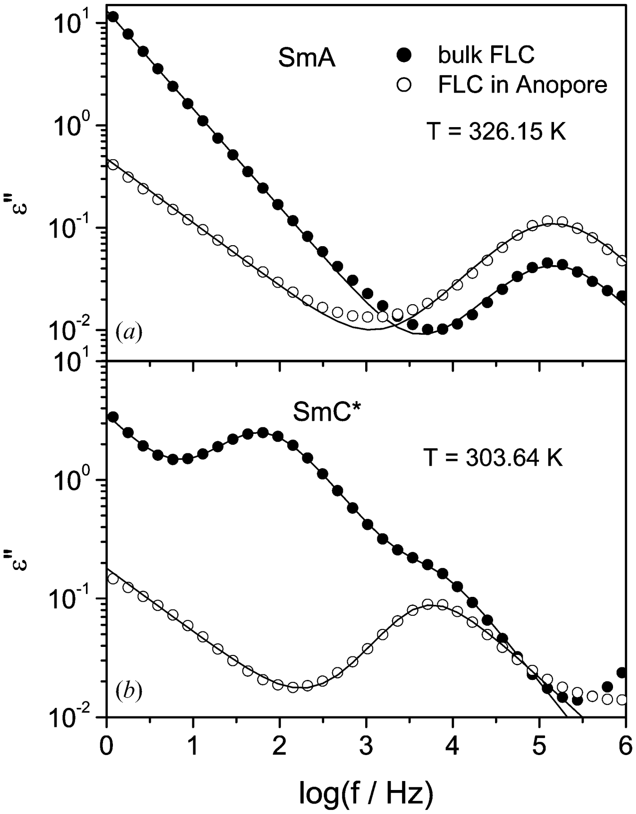


Figure 2. Comparison of the temperature dependence of the dielectric losses in the bulk ferroelectric liquid crystal and confined in Anopore membrane in (*a*) the SmA and (*b*) the SmC* phases. The solid lines represent fits to equation (1).

Figure 3 compares the temperature dependence of the characteristic frequencies of the relaxation modes observed in the bulk FLC and in FLC/Anopore composite. In the SmA phase of the homogeneously oriented bulk smectogen, the characteristic behaviour for the soft mode is observed, with frequency degeneration in the phase transition. In the SmC* phase the double degenerated soft mode splits into the Goldstone and soft amplitude modes. The frequency of the Goldstone mode is almost temperature-independent. However, a characteristic dip in the temperature dependence of the relaxation frequency is related to the disappearance of the spontaneous polarization at the point of polarization sign reversal. Across all phases the characteristic frequency for the molecular process assigned to the rotation around the molecular short axis is observed, which results from imperfection in the planar orientation of the sample. However, in the FLC/Anopore system the molecules are almost perfectly oriented perpendicular to the axis of the Anopore channels, and only one relaxation process is present with a relaxation frequency in good agreement with the

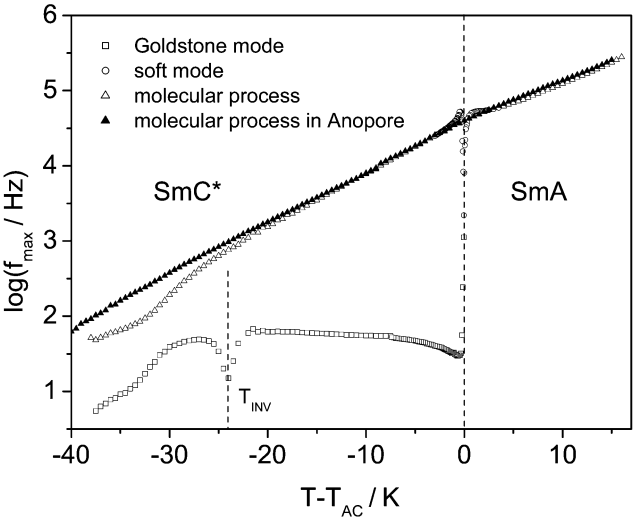


Figure 3. Temperature dependence of the relaxation frequency of different modes observed in the bulk FLC and FLC confined in Anopore membrane.

frequency of the molecular process observed also in bulk FLC.

The relaxation frequency and dielectric strength of the molecular relaxation process observed in the FLC/Anopore system were retrieved by fitting experimental data to equation (1). Figure 4 presents the temperature dependence of the relaxation frequency and dielectric strength in the SmA and SmC* phases. The relaxation frequency follows the Arrhenius law and decreases with decreasing temperature. The activation energy in the SmA phase is about 105 kJ mol$^{-1}$, and is slightly higher in the SmC* phase at about 115 kJ mol$^{-1}$. This negligible difference in the activation energies suggests that molecules rotate in a comparable environment in confinement. Additionally, no other noticeable changes are observed either in the SmA–SmC* phase transition or at the point of polarization sign reversal. However, the temperature dependence of the dielectric strength exhibits several characteristic features: (i) the dielectric strength in the SmA phase, $\Delta\varepsilon_A$ decreases linearly with decreasing temperature as a result of the antiparallel correlations of the parallel component of the dipole moments; (ii) after crossing the SmA–SmC* phase transition the temperature dependence of the dielectric strength in the SmC* phase should be a simple extrapolation of this dependence from the SmA phase, $\Delta\varepsilon_{\text{ext}}$ (straight line in figure 4). However, the non-linear decrease in the dielectric strength in the SmC* phase ($\Delta\varepsilon_{C^*}$) with decreasing temperature results from the temperature dependence of the tilt angle of the molecules, and indicates the existence of a tilted phase in the channels of the Anopore membrane. Knowing $\Delta\varepsilon_{\text{ext}}$ and $\Delta\varepsilon_{C^*}$, it is possible to determine the temperature dependence of the tilt angle from the equation [10]:

$$\theta = \arccos\left[\left(\frac{\Delta\varepsilon_{C^*}}{\Delta\varepsilon_{\text{ext}}}\right)^{\frac{1}{2}}\right]. \qquad (2)$$

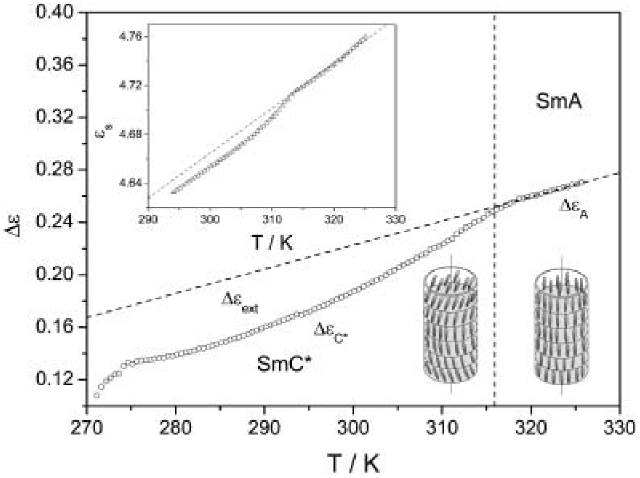


Figure 4. Temperature dependence of the dielectric strength (circles) of the relaxation process related to rotation of the molecule around the molecular short axis in confinement. The straight-dash line represents the extrapolation of dielectric strength from the SmA to the SmC* phase. The drawings in the figure present possible configurations of the smectic layers in the pores of the Anopore membrane in the SmA and SmC* phases. The inset shows temperature dependence of the static value of the permittivity of the FLC in Anopore membrane.

Additional evidence for a tilt angle of the molecules in the pores below the SmA to SmC* phase transition temperature is also visible in the non-linear change (below the transition) of the static permittivity, as displayed in the inset in figure 4. Although this change is the result of the tilt, it is not possible to deduce the tilt angle from it because different (tilt angle-dependent) terms contributing over the whole frequency range cannot be separated [10].

Figure 5 shows the temperature dependence of the tilt angle calculated from equation (2). It can be expressed by the following formula: $\theta = \theta_0(T_{AC} - T)^{\beta}$, where $T_{AC}$ is the phase transition temperature, $\theta_0$ is a fitting parameter while $\beta$ is a critical exponent. The solid line in figure 5 was obtained with fitting parameters $\theta_0 = 0.15$ rad and $\beta = 0.37$. It should be noted that the Landau mean-field theory predicts a value of 0.5 for the critical exponent $\beta$. Also, the value of $\beta$ is significantly influenced by the experimental method used to determine it, and the temperature range considered during the fitting procedure. The dielectrically found tilt angle

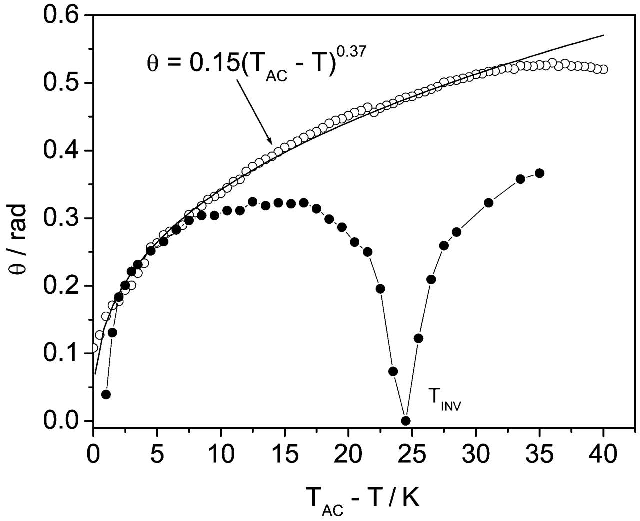


Figure 5. Comparison of the temperature dependence of the dielectric tilt angle obtained from equation (2) (circles) with optical tilt angles (dots) measured by an electro-optic method.

is related mainly to the tilt of the longitudinal component of the dipole moment with respect to the direction of the measuring electric field.

Figure 5 also compares the dielectric tilt angle with our new electro-optically measured tilt in a homogeneously oriented sample. The obtained temperature dependence of our optical tilt angles agrees well with results previously presented for this compound [18, 19]. However, the very surprising temperature dependence of the optical tilt angle, with a pronounced dip at the point of polarization sign reversal, requires some comment. The obtained temperature dependence, which suggests the disappearance of the tilt angle at the point of polarization sign reversal, is simply an artifact from the inadequacy of the electro-optic method in this special case. With decreasing temperature the spontaneous polarization continuously drops to zero and the applied electric field is unable to switch a sample because there is no coupling between electric field and polarization. This leads to the wrong temperature dependence of the tilt for this compound. On the other hand, the dielectric tilt angle is higher than that obtained from optical measurements, but shows no anomaly at the point of polarization sign reversal. This result is consistent with optical measurements of the tilt angle in very thin samples [19] and of optical rotatory power [21].

## 4. Conclusions

Dielectric measurements of a ferroelectric liquid crystal with polarization sign reversal, confined in Anopore membranes with well defined structure of the cylindrical pores, confirm the significant influence of surface interaction on the orientation of liquid crystal molecules in the pores. The liquid crystal molecules orient in untreated Anopore parallel to the walls of the cylindrical pores, and enforce perfect orientation of the smectic layers perpendicularly to the pore axes. As a consequence, the axis of the helical superstructure in the SmC* phase should be parallel to the pores. This assumption was confirmed in several optical experiments. In the considered geometry of the experiment, the soft mode and Goldstone mode are inactive dielectrically because the measuring electric field can only be parallel to the pores and perpendicular to the local spontaneous polarization. However, perfect orientation of the smectic layers perpendicular to the pores and the electric field enables one to measure the dynamics of molecular rotation around the molecular short axis.

The temperature dependence of the relaxation frequency of this process is an Arrhenius one throughout all phases, with slightly higher activation energy in the SmC* phase. However, the temperature dependence of the dielectric strength changes non-linearly after the transition to the SmC* phase. This change is assigned to the tilt of the molecules in the SmC* phase and was exploited to determine the temperature dependence of the tilt angle in the confined SmC* phase. The obtained temperature dependence of the dielectric tilt angle and critical exponent agree in general with other known experimental results. Additionally, neither the temperature dependence of the relaxation frequency or dielectric strength, nor dielectric tilt angle shows any anomaly at the point of polarization sign reversal. It should also be stated that the dielectric measurements undoubtedly confirm the existence of the tilted phase in the cylindrical pores after transition to the SmC* phase. However, the present dielectric results do not settle the question of the presence of the helix in the SmC* phase in Anopore membranes, and complementary measurements of the optical rotatory power are needed and in progress.

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