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Properties of Non-Tilted Bent-Core Orthogonal Smectic Liquid Crystal

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We present the properties of different achiral orthogonal polar smectic phases observed in a homologous series of bent-core molecular compounds. The macroscopically uniaxial SmAP_R phase transforms to biaxial state by the application of higher electric fields and biaxial SmAP_A phase undergoes biaxial-uniaxial-biaxial texture transformation with increasing electric fields, i.e., initial antiferroelectric structure transforms into ferroelectric state under higher electric fields and it shows three different optically distinguishable states. The SmAP_{AR} phase shows an entirely different response compared to other polar smectic phases under study. The dielectric measurements in the SmAP_{AR} phase is the evidence of antiferroelectric behavior of uniaxial state. The polarizing microscopy texture observation supports the corresponding biaxiality measurements.

Keywords Bent-core molecules; orthogonal biaxial polar Smectic; electro-optic effects; dielectric relaxation; polarization

1. Introduction

After the discovery of ferroelectricity in tilted smectic phases of chiral molecules by Robert Mayer et al. in 1975, the idea of having a spontaneous electric polarization in the liquid crystalline state was revolutionary [1] and a model of ferroelectricity for an orthogonal smectic phase (Cp) formed by non-chiral bent core molecules were recommended by Brad et al. in 1995 [2]. In 1996, Niori et al. reported the experimental proof of ferroelectricity for the first time [3].

In addition to conventional banana phases such as B1-B8 [4] orthogonal smectic phases and biaxial nematic (N_b) phases have been reported. The bent core materials consist of biaxial nematic phase offers fast switching by the rotation of secondary short axis *m* around the fixed long axis *n* due to the coupling of dielectric anisotropy ($\epsilon_m - \epsilon_l$) with the fields. Although the N_b phase has offered some newer possibilities in display applications, it is very difficult to obtain an independent short axis (*m*) switching and this is usually accompanied by unnecessary tilt of the primary director.

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A homologous series of achiral orthogonal Sm-A like phases have been synthesized and studied recently [4–8]. Upon the reduction of temperature, some bent core molecules exhibit a number of lower temperature polar orthogonal SmAP_R , SmAP_{AR} and SmAP_A phases in addition to conventional non-polar uniaxial Sm-A phase. Under crossed polarizers in SmAP_R phase, dipoles form small polar domains and the direction of polar director is randomly arranged in layers in the absence of electric field, leading to macroscopic uniaxial texture and exhibit polar switching. Recently, Gomola et al. reported SmAP_{AR} phase in asymmetrical bent-core compound containing 3-aminophenol central unit [5]. This paper presents the physical properties of different non-tilted orthogonal polar smectic phases observed in a homolog series of 4-cyanoresorcinol bisbenzoate with two terephthalate-based wing compounds.

2. Experimental

The measurements are carried out in three different 4-cyanoresorcinol bisbenzoate compounds with two terephthalate-based wings of different chain lengths, synthesized in Halle, Germany. The molecular structure of LC materials is shown in Fig. 1 and Table 1 lists the orthogonal achiral smectic compounds investigated. Among these LC materials PAL30 compound exhibits of all three polar orthogonal SmAP_R , SmAP_{AR} and SmAP_A phases.

The homeotropic alignment is obtained by two glass substrates coated with polymer AL60702 (JSR Korea), for electro optic measurements. The electrodes are arranged to apply in-plane electric field of frequency 110 Hz by etching indium tin oxide (ITO) stripes on the bottom substrate and the electrode distance is $\sim 80\ \mu\text{m}$. A tilting optical compensator is used for biaxiality measurement so that it can take extremely small optical retardation. As the smectic layers lie parallel to the substrate the homeotropic cell shows perfect alignment of very large extinction on cooling from Isotropic to SmA and then to SmAP_R phases. The dielectric study is carried out using broadband high resolution dielectric spectrometer (Novocontrol GmbH, Germany) on planar cells of $10\ \mu\text{m}$ thickness.

3. Results and Discussion

3.1 Textures and Biaxiality in a Homeotropic Cells

The effect of electric field on different orthogonal smectic phases has been studied in a $7\ \mu\text{m}$ homeotropic cell under crossed polarizers with an angle of 45° between the electric field and polarizer axis.

Figure 2 presents the electric field of induced biaxiality SmAP_A phase in PAL31 material.

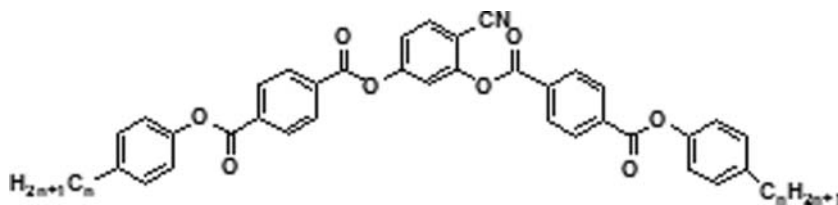


Figure 1. Chemical structure of orthogonal achiral smectic liquid crystals.

Table 1. List of orthogonal achiral smectic materials under investigation.

Material	Chain length	Phase sequence
PAL 31	8	SmAP _A 121°C SmA 163°C I
CK 64	12	SmAP _A 111°C SmAPz 157.5°C SmA 163.9°C I
PAL 30	14	SmAP _A 95°C SmAPz 108°C SmAP _{AR} 111°C SmA 164°C I

The properties of SmAP_A and SmAP_R phases were studied in CK 64 material ($n = 12$). Figure 3 presents the field induced biaxiality measurements and textures in homeotropically aligned cell.

When CK 64 sample is cooled down from SmA to, SmAP_R phase the sample looks dark under crossed polarized state. Since the polar (secondary) directors in different smectic layers are randomly ordered in the absence of electric field and the primary director is orthogonal to the smectic layer plane, this SmAP_R phase [8, 10] is macroscopically uniaxial. An application of electric field disturbs the random distribution of the secondary director and therefore induces optical biaxiality. The value of induced biaxiality increases with lowering temperature and is stronger near the phase transition to SmAP_A (compare 116°C and 112°C).

While cooling down from SmAP_R phase to SmAP_A the Schlieren texture with $s = 1, 1/2$ declinations appears at 110°C. In this phase, the application of in-plane electric field of 100 Hz shows a transformation of Schlieren in to biaxial bright state corresponding to antiferroelectric structure with $\delta n_{AF} = 0.0035$. The further application of field shows a transformation to the dark uniaxial intermediated level. In this uniaxial state the secondary directors in the neighboring smectic layers perpendicular to one another are resulting in macroscopically uniaxial structure [9]. On further increase in field, this uniaxial dark state transforms in to bright biaxial ferroelectric state with $\delta n_F = 0.012$. In higher temperature range of SmAP_A phase $\delta n_{AF} < \delta n_{AF}$. With reduction in temperature the biaxiality δn_{AF}

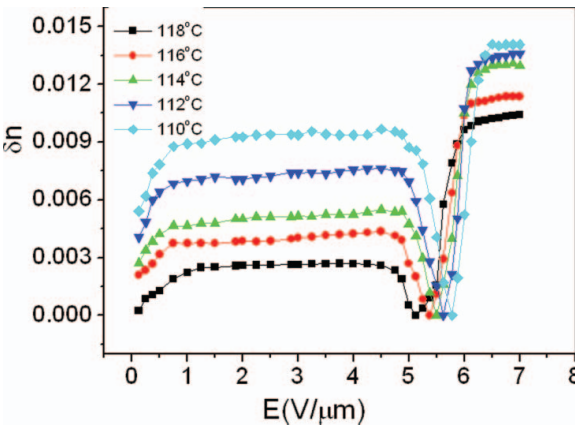


Figure 2. Electric field induced biaxiality measurements in SmAP_A phase of PAL 31 material with decreasing of temperature (cell thickness 7.6 μm and $f = 100$ Hz).

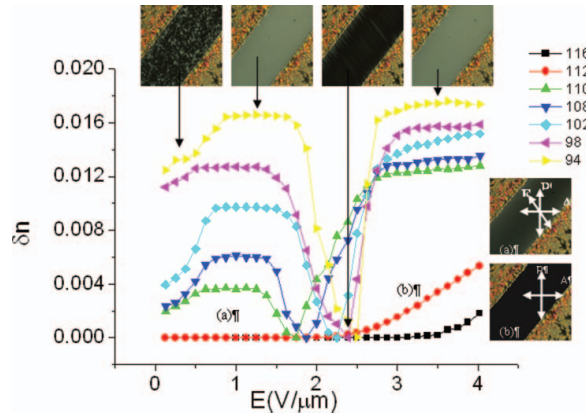


Figure 3. Electric field induced biaxiality measurements in CK 64 material with decreasing of temperature and the POM textures corresponding to the biaxiality values at 112°C and 94°C (cell thickness 7 μm and $f = 100$ Hz).

increases faster than δn_F and at 94°C the biaxiality values are almost equal for both antiferroelectric and ferroelectric states, $\delta n_{AF} = \delta n_{AF'}$.

The material PAL 30 ($n = 14$), shows another new phase SmAP_{AR} in the temperature range (96°C–109°C) in addition to SmAP_R and SmAP_A phases. The optical texture observations in SmAP_A and SmAP_{AR} phases are similar to the corresponding field induced biaxiality measurement for CK-64 (Fig 3). The electric field effect of new phase SmAP_{AR} with reduction in temperature is shown in Fig. 4.

When the homeotropically aligned cell is cooled down from SmAP_R to SmAP_{AR} phase at 104°C, it remains completely dark under crossed polarizers for the applied electric field less than ~ 0.95 V/ μm . On the application of in-plane electric field ~ 1 V/ μm it transforms to the biaxial (bright) state with $\delta n = 0.002$ up to 1.2 V/ μm . On further increase of field this biaxial state goes to a uniaxial dark state with the secondary directors in the neighboring

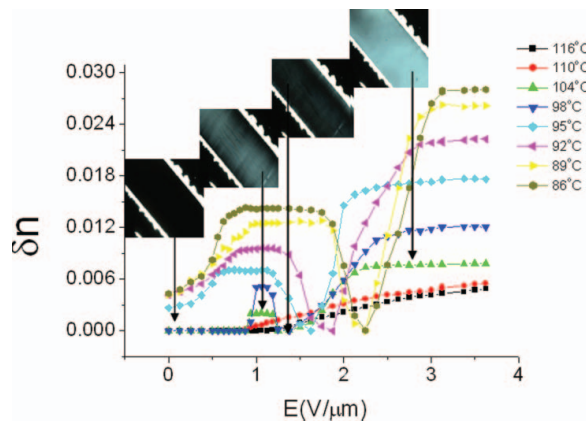


Figure 4. Electric field induced biaxiality measurements in PAL30 compound with decreasing temperature and the POM textures corresponding to the biaxiality value at 104°C (cell thickness 7 μm and $f = 100$ Hz).

smectic layers perpendicular to one another, similar to intermediate state in SmAP_A and again goes to biaxial ferroelectric state and then saturates at higher field with $\delta n_F = 0.007$. The SmAP_{AR} phase under electric field exhibits two macroscopically uniaxial dark states separated by two biaxial bright states. All the materials under study (Table 1) show similar behavior in their SmAP_A phase and the field response of SmAP_R phases is similar for CK64 and PAL 30 samples.

3.2 Spontaneous Polarization Measurements

The polarization measurement is carried out in a $5.5 \mu\text{m}$ planar cell for different applied square wave voltages (2V–58V) of 110Hz. The polarization is measured using the integral current technique. The important feature of this sample is the absence of P in the entire temperature range when the field applied for its measurement is low.

The temperature dependence of macroscopic spontaneous polarization of PAL 30 compound is shown in Fig. 5. Application of E above a threshold changes the distribution of the dipole moments (polar directors) and consequently gives rise to the net polarization P . In the higher temperature range of SmAP_R phase, we find that the induced polarization is linearly proportional to the applied field. It is observed that $P(T)$ increases on approaching the SmAP_R – SmAP_{AR} phase transition.

In the temperature range corresponding to SmAP_{AR} and SmAP_A phases, the net polarization is initially proportional to the applied field and then it jumps to a saturated value. It may be remarked that while the field-induced polarization shows a smooth-like normal dependence on E , the biaxiality (Figs. 3 and 4) shows sharp step-like behavior. This arises from the principal difference of the manner used in arriving at the results using the two techniques. The birefringence/biaxiality is measured for a localized small area in the cell, whereas the macroscopic polarization is measured over the entire area of the cell. The latter may consist of up to three different structures and hence the measured P corresponds to an integrated response over the entire area.

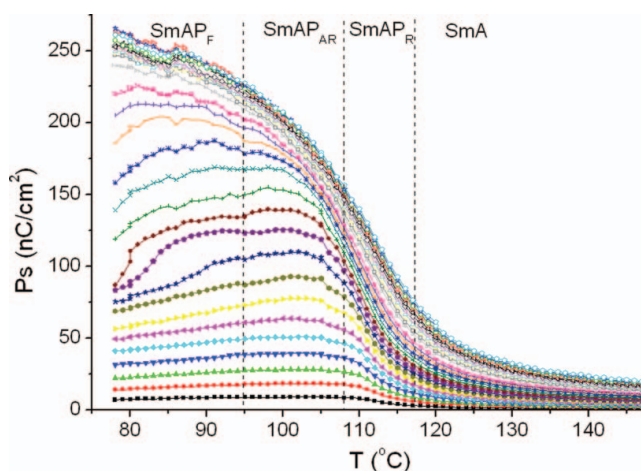


Figure 5. Temperature dependence of macroscopic spontaneous polarization in $5.5 \mu\text{m}$ planar cell for different applied square wave voltages (2V–58V) of 100 Hz with a 2V step.

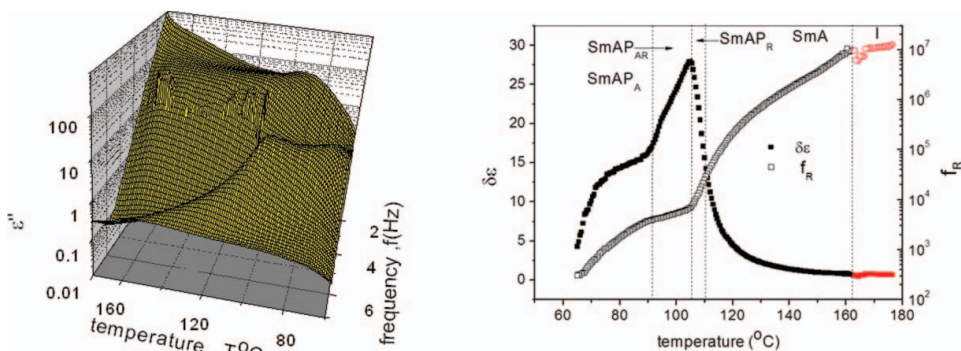


Figure 6. Dielectric behavior in 10 μm planar cells (a) dielectric loss spectra (ϵ'') and (b) dielectric amplitude ($\delta\epsilon$) and relaxation frequency (f_R) of process P2 with temperature.

3.3 Dielectric Spectroscopy

The dielectric response of PAL-30 material over a frequency range of from 10 Hz to 10 MHz is measured in 10 μm (brass electrodes) planar cell using broadband high resolution Alpha-A frequency analyzer (Novocontrol GmbH, Germany). Figure 6(a) shows temperature dependence of dielectric loss spectra. On cooling from isotropic to SmAP_A phase a relaxation peak is appeared in the lower frequency region, which is due to the contribution of longitudinal dipole moments. The dielectric spectrum is fitted to Havriliak-Negami equation and the fitting parameters of the dominant process, e.g. dielectric strength (amplitude) and relaxation frequency are shown in the Fig. 6(b).

From this figure it is clearly seen that the dielectric amplitude $\Delta\epsilon$ increases with lowering temperature and reaches a maximum at SmAP_R-SmAP_{AR} transition.

4. Conclusions and Perspectives

In summary, field-induced biaxiality in different achiral orthogonal smectic phases in bent core banana-shaped liquid crystal compounds are investigated. The SmAP_R phases is macroscopically uniaxial since secondary directors are randomly ordered in the absence of field, and the phase exhibits transformation from uniaxial to biaxial by an application of rather high electric field. In biaxial polar SmAP_A phase molecules undergo biaxial-uniaxial-biaxial transformation with the strengthening electric fields, i.e., initial antiferroelectric structure transforms into ferroelectric state with increasing electric fields and it shows three optically distinguishable different levels. The SmAP_{AR} phase shows an entirely different response compared to other smectic phases under study. The initial uniaxial state comes to biaxial state with field and with further increasing field strengths it shows again uniaxial dark state to biaxial bright state transformation. The dielectric measurements in SmAP_{AR} phase is the evidence of antiferroelectric behavior of uniaxial state. The POM texture observation in CK64 and PAL 30 materials supports the corresponding biaxiality measurements. All materials under study (Table 1) show similar behavior in their SmAP_A phase and the field response of SmAP_R phases is similar for CK64 and PAL 30 samples.

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