Mechanical and Electro-Optical Properties of Unconventional Liquid Crystal Systems

A dissertation submitted to Kent State University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

by

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Chapter 1

Introduction

In 1888 an Austrian Chemist Friedrich Reinitzer observed a cloudy intermediate phase in melting cholesteryl benzoate\(^1\), which later became known as a cholesteric liquid crystal. Since then, hundred thousands of liquid crystal materials have been synthesized and studied. Liquid crystal technology has a wide range of applications in our daily life such as in LCD panels. Most of liquid crystals research and application is focusing on thermotropic liquid crystals and more often, liquid crystals composing of rod-shape molecules, which are defined as the conventional liquid crystals system in my thesis. Different from the conventional liquid crystals, in my thesis three unconventional liquid crystals systems are studied: thermotropic mesophases formed by the bent-core molecules and their mixtures (liquid crystal molecular structure different from conventional liquid crystals), amphiphilic glycolipids (liquid crystal properties difference) and colloidal crystals and liquid crystals system (liquid crystal compositions difference).

1.1 Thermotropic properties of Bent-core liquid crystals

Bent-core liquid crystals refer to the liquid crystals whose molecular shapes are bent through some linked group in the middle. Most bent-core molecules link through the
aromatic benzene groups by attaching to 1,3 position of benzene ring (Figure 1.1). The angle between two linking arms ranges from $100^\circ$ to $170^\circ$. The first bent-core liquid crystal was synthesized in the research group of Vorländer by Schröter in 1923\(^2\), but the mesophase properties of the compound were not reported. In 1932, the report of bent-core mesophases appeared in the literature for the first time\(^3\).

Bent-core molecules did not get too much attention until Matsunaga\(^4\) synthesized new mesogenic compounds with “banana-shaped” molecular structures, but no polarization was reported. In 1996 at 6\(^{th}\) International Liquid Crystal Conference in Kent, Ohio Niori\(^5\) presented the first mesophase with antiferroelectricity formed by non-chiral bent-core molecules without electro-optic switching. This phase was later known as the B2 phase (tilted polar smectic phase). This discovery is the beginning of interests in these new mesophases which are not comparable by smectic phases formed by calamitic (rod-like) molecules. Most of the research effort has focused on the bent-core smectics, because nematic phases were absent or rather uncommon in the early series of compounds synthesized.

Till now a great number of bent-core mesophases have been predicted theoretically, or reported from experiments. Among them there are some classical phases such as nematic\(^6\), smectic A\(^7\) and the new ones actually classified with names ranging from B1 to B7 defined at the 1997 Berlin workshop\(^8\) and after. The B1 to B7 series represent phases in the sequence of their discovery and do not correspond to their real
Figure 1.1: Molecular structure of typical bent-core liquid crystals: (a) typical molecular structure of a bent-core liquid crystal; (b) first bent-core liquid crystal synthesized by Vorländer\textsuperscript{3}; (c) first recognized bent-core liquid crystal in 1994\textsuperscript{9}. 

\textsuperscript{3}Vorländer, ...
layer structures in the mesophases. The B1 phase exhibits a two-dimensional order. There are strong arguments that it is necessary to subdivide phase B1 into modifications with different columnar structures. The B2 phase corresponds to the phase first discussed by Niori and is of a special interest because it is the first liquid crystal showing antiferroelectric behavior. Another phase which shows similar electro-optical switching properties was named as B5. B3 and B4 are crystalline-like modifications, the B4 phase is also designated as the “blue phase” of bent-core mesophases. The B6 phase can be compared with an interdigitated smectic C phase generated by bent-core molecules. The growing of helical filaments along with myelinic, ribbons, spirals has been the hallmark of B7 phase. In our thesis we focus on the electro-optical properties of banana-shaped mesophases and bent-core molecules orientations in the smectic layer structures. Based on that, a review of switch-able banana-shaped mesophases is presented:

- SmAP: orthogonal bent-core smectic liquid crystals

In calamitic smectic liquid crystals, two axes are sufficient to define the orientation of molecules in smectic layers (the molecular directors and the layer normal). However for bent-core molecules, three axes are needed to locate the orientation of molecules in layer plane: the molecular plane, the ‘director’ of the molecules (average direction of line connecting the ends of the molecules), and the layer normal. SmAP is the phase in which both the bent-core molecular plane and molecular director are parallel to the layer normal. The SmAP phase is named after the SmA phase of calamitic liquid crystal mesophases due to the similar orientation of molecules in the layer plane, with
molecular directors perpendicular to the layer plane. Here ‘A’ means ‘orthogonal’ and ‘P’ refers to ‘polar’. In the SmAP phase, focal conic textures appear on the planar treatment substrates and Schlieren textures with defect of $s=1$ and $s=\pm\frac{1}{2}$ form on homeotropic alignment substrates. The first theoretical model of the SmAP phase was proposed by Niori et al\textsuperscript{5}. Due to its $C_{2v}$ symmetry, spontaneous polarization can be formed in the layer plane through molecular close packing, which is the difference between SmAP and SmA. Whether the SmAP is ferroelectric or antiferroelectric depends on the polarization direction in the adjacent layer. If the polarization directions are the same for the adjacent layers, the polarization behavior is ferroelectric. If the polarization direction alternates between layers, the polarization is anti-ferroelectric (shown in Figure 1.2).

The first bent-core compound with SmAP phase was experimentally confirmed recently\textsuperscript{7}. It is worthwhile to mention that this material also forms Smectic A at high temperature range (Figure 1.3). Small energy needed in the transition between SmAP and SmA (1.2kJ/mol) indicates the transition is of weakly first order\textsuperscript{7}. Also the layer spacing and the tilt angle do not change obviously from SmA to SmAP\textsuperscript{7}. In fact it can be proposed that at high temperatures, the rotation speed of bent-core molecules along their long axis is very fast, the short axes of molecules can not be distinguished and on average they behave like uniaxial molecules; Therefore the SmA phase forms. As the temperature decreases, rotation speed decreases, and molecules could form polar packing into SmAP phase without other layer parameters changing, such as layer thickness, and tilt angle. The packing model is proved by the continuous increase of the static dielectric constant\textsuperscript{7},
Figure 1.2: Schematic representation of the structures of polar smectic banana phases.

⊗ and ○ indicate that the in-plane layer polarization component $P_t$ points outward (inward) from the plane of the drawing. $\perp$ and $\top$ : upper (lower) part of the director tilt toward the observer. $\downarrow$ and $\uparrow$ indicates that out-of-plane polarization component $P_n$ points down (up)$^{16*}$.
Figure 1.3: First experimentally proved SmAP bent-core mesophase\textsuperscript{7}: (a). Molecular structure of 4CN-3F-OPIMB, which shows SmAP mesophase\textsuperscript{7}; (b) SmAP type of arrangement of bent-core molecules in smectic layer\textsuperscript{7}; (c) polarization of 4CN-3F-OPIMB at the function of electric field\textsuperscript{7}. (d) polarization of 4CN-3F-OPIMB at the function of temperature\textsuperscript{7}; (e) corresponding textures under cross-polarized microscope at 170\textdegree C-SmA (f) 130\textdegree C-SmAP. The black bar represents 100\textmu m length.
which indicates the formation of a stronger dipole-dipole interaction between molecules as the temperature decreases. This is a very good example of the transition of a non-polar SmA to a polar smectic A phase.

- SmCP & SmCP\textsuperscript{L}: single tilted Bent-core smectic liquid crystals

When bent-core molecules tilt in layers, they could form SmCP or SmCP\textsuperscript{L} which are polar smectic phases. In SmCP & SmCP\textsuperscript{L} ‘C’ stands for molecular tilt and ‘P’ stands for polar, ‘L’ means leaning. As bent-core molecules tilt in smectic layer, two ways are possible: either the molecular planes tilt with the layer normal (clinic) or the molecule directors (average direction of the line connecting the ends of molecules) tilt with the layer normals (leaning) (shown in Figure 1.2). Phases of bent-core molecules with a monoclinic tilted layer structures is called B\textsuperscript{210} or SmCP\textsuperscript{17} (‘P’ stands for polar). These phases are similar to SmAP with polarization in the layer plane. Due to tilt and polar packing, the layers have no reflection symmetry, i.e. they are chiral\textsuperscript{17}. So SmCP smectic layers are monoclinic chiral symmetry C\textsubscript{2}. Depending on the relative orientations of the two fold symmetry axes and the tilt direction, the layers can be right (+) or left handed (-) (shown in Figure 1.4). The SmCP is called racemic if chirality of adjacent layer is alternate and chiral and if the adjacent layer has same chirality. Most of the known SmCP phases are antiferroelectric (AFE) in their ground state without net polarization\textsuperscript{18} and they can be switched to ferroelectric (FE) with an external electric field applied. The SmCP with the ferroelectric ground state has also been found\textsuperscript{19,20}. It is assumed that the chirality of layer is conserved\textsuperscript{17} during the switching from AFE to FE. This assumption is basically true during the short period of electric field applied, although gradual change of
the layer chirality was observed in some cases. This provides a useful tool to analyze layer properties of the SmCP: The chiral switching is accompanied with optic axis rotation with polarity of electric field during switching. The optic axis in the racemic SmCP does not respond to the sign of electric field during switching. Polarization properties of SmCP can be recognized by a polarization current as a function of time under triangular electric field or as a function of electric field measured by Diamant-bridge method. Racemic AFE SmCP i.e. SmC\textsubscript{s}P\textsubscript{A} (‘s’ stands for synclinic and ‘a’ stands for antiferroelectric) is synclinic (Figure 1.4): the molecules tilt the same way in adjacent layer. The textures of the SmC\textsubscript{s}P\textsubscript{A} always contain fan domains with a few micrometers wide stripes (Figure 1.5). In every stripe the molecular planes tilt at the same direction but polarization directions are opposite in the adjacent layers. SmC\textsubscript{s}P\textsubscript{A} can be switched to FE state (SmC\textsubscript{a}P\textsubscript{F}) as sufficient high electric field is applied. SmC\textsubscript{a}P\textsubscript{F} is an anticlinic tilted layer structure with the optic axis parallel to the layer normal. In SmC\textsubscript{a}P\textsubscript{F}, optic axis is independent of the sign of the external a.c. field during switching. Therefore no linear optical switching can be observed under a square wave electric field (Figure 1.4). Chiral AFE SmCP i.e. SmC\textsubscript{a}P\textsubscript{A} is an anticlinic layer structure and its optic axis is parallel to the layer normal. SmC\textsubscript{a}P\textsubscript{A} can be switched to FE state and it changes to the synclinic structure (SmC\textsubscript{s}P\textsubscript{F}). During the switching of AFE of the SmC\textsubscript{a}P\textsubscript{A} to FE of the SmC\textsubscript{s}P\textsubscript{F}, the optic axis rotates to the polarity of the external electric fields.

The phase formed by bent-core molecules with a single leaning (molecular director tilted with layer normal) tilted layer structure is called SmCP\textsuperscript{L}. In SmCP\textsuperscript{L},
molecular directors tilt with respect to the layer normal but the molecular planes are not tilted. The SmCP\(^L\) has a non-chiral monoleaning symmetry \(C_\text{s}\). Therefore in the SmCP\(^L\)

Figure 1.4: handness and chirality of SmCP: P is polarization of layer, n is the layer normal. (c) is the side view of bent-core molecules in a layer structure. \(\bigotimes\) and \(\bigcirc\) indicate that the in-plane layer polarization component \(P_t\) points inward (outward) from the plane of the drawing. Chirality is defined according to the left /right hand rule shown in (a). SmC\(_{\text{s}}\)P\(_A\) is racemic, with synclinic tilting, and antiferroelectric with the chirality of layer different in alternate layers. The optic axis does not change with sign of electric field during switching. SmC\(_{\text{s}}\)P\(_A\) is chiral smectic phase. As the electric field is applied, the optic axis rotates with an angle of twice the tilt angle.
Figure 1.5: Typical textures between crossed polarizers of SmC₃Pₐ (b) at ground state and switched to SmC₃Pₕ (a)¹⁸*. Pictures represent 100μm x 150μm areas.

The layers can have two polarization components: the polarization in the layer plane (tangential component \(P_t\)) and normal to the layer plane (normal component \(P_n\)). In SmCPₜ, switching process may need layer realignment because of the out-of-layer polarization component. But banana mesophases with such a structure have not yet been experimentally discovered.

- SmCₐ: double tilted smectic phase

The SmCₐ was predicted by De Gennes²² about thirty years ago, but there was no experimental proof for the existence of this kind of mesophase because liquid crystal research focused mainly on calamitic liquid crystals. As bent-core liquid crystals appeared, more new mesophases formed by bent-core molecules were found. In 2001 Jákli showed that some B7 textures have SmCₐ structures by studying binary mixtures of
bent-core materials with B2 and B7 textures and showing evidence for the SmCG phase in the bulk\textsuperscript{23}. He found that ribbon B7 textures can either grow or shrink under DC field.

Figure 1.6: Possibilities for the packing of the banana-shaped molecules into layers (left).

Shading illustrates tilt out of the plane of the drawing: Brighter areas are closer to the observer. The structures can be characterized by three vectors: the smectic layer normal $n$, the molecular plane normal $m$, and layer polarization $\vec{P}$ which (a) $n \perp m$ , $\vec{P}$, $C_{2v}$ symmetry. (b) $n \perp \vec{P}$ but not $\perp m$. (c) $n \perp m$ but not $\perp \vec{P}$, $C_s$ symmetry (d) $n$ not $\perp \vec{P}$ and not $\perp m$, and a double tilted smectic phase with $C_1$ symmetry results. This is the SmC\textsubscript{G} phase. Eight possibilities of molecular packing in two layers SmC\textsubscript{G} (right): A-D indicates the anticlinic arrangements whereas A’-D’ are synclinic. $<\vec{P}>$ is resulting polarization vector. The end of the molecules with nail sticks out from the plane of the drawing.
and the direction of motions reverses under electric field reversal. However during switching no polarization showed up. This observation ruled out a chiral/achiral SmC_{a}P_{F} structure and indicated that there was an out-of-layer polarization component corresponding to the SmCG structures shown in Figure 1.6(C) and (C’). The eight different arrangements of packing bent-core molecules could be named according to the tilted situation as shown in Figure 1.2: for example AC&SL means molecules have anticlinic and synleaning packing structures in layers.

Materials with B_{7} textures have been attracting a lot of research interest for their unusual textures during cooling from the isotropic phase. Four kinds of domains of SmC_{G} had been observed coexisting at same temperature^{14,15}(Figure 1.7). Exact reasons for multiple textures coexistence are still argued: Based on numerous experiments, the Boulder group proposed that the B7 is a structure of stacked smectic layers, periodically modulated/undulated (PM/UL) on microscopic level^{24}, which may form the SmCG structure macroscopically. The undulation wavelength varies from ~40Å to ~700Å. This would be another broken symmetry, corresponding to the spontaneous periodic modulation of the polarization density into splay domains. But the PM/UL state places two basic constraint on the layer structure of B7: 1) molecules must have synclinic structures to reduce layer strains from undulation 2) AFE could not appear in layer structures since global splay of polarization is suppressed when polarization alternates from layer to layer. Therefore, the PM/UL state is a feature of only the SmC_{a}P_{F} group.

Switching properties of SmCG are more complicated compared with switching of SmCP due to out of layer polarization components^{24}. But in some SmCG subphases
Figure 1.7: Various B7 textures in cooling from the isotropic phase: (a) myelinic textures 
(b) growth of spiral domains (c) thread-like and spiral nuclei (d) Oval domains with equistant stripes\textsuperscript{14*}.

molecular packing results in a cancellation of the out of layer polarization, as in SC&AL and AC&AL of Figure 1.6. In most cases the out-of-layer polarization does not cancel out, and layer tilting is involved during switching, which requires additional energy i.e. higher electric fields. Threshold electric field is directly related to the leaning angle of molecules in the layer, which always decreases as temperature decreases. As the leaning angle decreases, the threshold electric field decreases, which is a good way to distinguish
SmCP (whose threshold voltage remains unchanged during whole temperature range) from the SmCG phase.

In our study we are going to explore phase properties of novel bent-core liquid crystals including optically isotropic ferroelectric mesophase, asymmetric bent-core liquid crystals, chiral and achiral bent-core liquid crystal mixtures, bent-core and glycolipids mixtures. By studying their electro-optical switching properties, we will understand layer structures behind unusual phase behavior. Also through mixtures we studied the relationship between the molecular chirality and the induced polarity.

1.2 Amphotropic Liquid Cyrstals- Glycolipids

Glycolipids molecules are amphiphilic, containing polar sugar (hydrophilic) heads and non-polar carbon chains (hydrophobic). Glycolipids are also amphotropic liquid crystals: They behave as thermotropic liquid crystal in their dry form and they form lyotropic liquid crystal mesophase when mixing with solvents. Glycolipids with one sugar head are named glucosides whereas those with two sugar heads are called maltosides. Lyotropic properties of glycolipids have been intensively studied over the last century. However their thermotropic properties have been rarely touched. Short-tailed glycolipids have been mainly used in surfactant industry. Glycolipids with much more complicated molecular structures play a very important role in the cells of living system: Glycolipids are one of the three lipids existing in the cell membrane. They control numerous cell membrane functions such as ion transportation, cell fusion process, and more, cell surface recognition process. It is interesting to point out that most such
processes are electrical-related\textsuperscript{29}, for example, ferroelectric behavior had been observed in muscle and nerve system\textsuperscript{29}.

Lyotropic properties of glycolipids have been widely studied. However due to different observation methods and apparatuses, different lyotropic phase diagrams are depicted for glycolipids, especially for those with high Kraft temperature. A schematic phase sequence of amphiphilic-water systems as a function of water concentration is shown in Figure 1.8.

Figure 1.8: Binary phase diagram of typical lyotropic liquid crystal behavior as a function of water concentration.

Due to the amiphilic properties of the glycolipids, most glycolipids have a long temperature range for the thermotropic SmA phase\textsuperscript{30}. Columnar phases appear for glycolipids with long hydrocarbon tail. In the SmA phase, glycolipids form a head-to-
head, tail-to-tail bilayer structure. This kind of structure is in favor of hydrogen bonding forming between glycolipids molecules, of which the hydroxyl groups on the sugar head serve two purposes: Hydroxyls at the end of the head group allow the molecule to form hydrogen bonds to the molecules in the opposing layers, stabilizing the smectic layering. Meanwhile, the hydroxyls on the sides of the head group serve to hold together the neighbor molecules\textsuperscript{31}. But what the exact orientation of lipids molecules in smectic layer is still controversial (Figure 1.9): It was found that the periodicity of glucolipids n-Dodecyl-β,D-glucopyranoside (C\textsubscript{12}G\textsubscript{1}) layer in mixtures with bent-core molecules\textsuperscript{32} is larger than one molecular length but smaller than the length of two fully extended molecules. This may indicate a non-interdigitated tilted deVries-type SmA phase (see Figure 1.9)\textsuperscript{33}. But the phase with chiral lipid molecules tilting in the layer structure is known as SmC* phase, which has spontaneous polarization during switching. However in pure dry lipid form, no electric field induced polarization is observed or reported.
Another possibility is that lipid molecules interdigitate with the molecular tails, i.e. SmA_d. This would also reduce layer thickness of SmA.

In this thesis we studied the theromotropic behavior of six branched-tail glycolipids. Based on their dielectric behavior at low frequencies, typical phase textures and measurements of optical birefringence temperature dependence, we will describe the phase diagram of these glycolipids and compare them with traditional thermotropic liquid crystal properties. A possible model of the lipid molecules orientation in the layer structure will be proposed, which could provide useful information for future study of lipids in cell membrane.

1.3 Liquid Crystals in Colloidal Crystals

Nanometer and micrometer size colloidal particles have a number of applications: They can form photonic band gap materials by self-assembled into periodical crystal structure.34 Attached to the surface with a special protein or gene, colloidal particles could aggregate to form micrometer-sized areas sensitive to one or more genes. Then the micrometer-sized area can be embedded as bio-sensors.35 Lots of methods have been explored to assemble or selectively deposit colloidal particles on different substrates: For example selective deposition could be realized by an external electric field36,37, a light source38,39, mechanic shearing40, controlling temperature gradient in deposition41, adjusting surface properties of colloidal particles42, or by adding surfactant or salt, thus changing the surface tension of solution43,44,45. In most cases, more than one of the methods listed above are combined to guide particles into an arbitrary area. Depending on the final object of deposition and the deposition uniformity needed, different approaches
for deposition are selected: for deposition of colloidal particles on patterned substrates, applying an external electric field is very effective and can achieve deposition of high concentration of particles on surface\textsuperscript{37}. In the method controlling the surface tension of the solution, monolayer colloidal crystal structures formed\textsuperscript{43}. By applying laser light to trap particles in an isotropic or anisotropic media\textsuperscript{38}, it is possible to precisely locate one or several colloidal particles. For a large quantity of closely-packed colloidal particles, mechanic shearing and controlled temperature gradients are successful.

There are a number of methods to achieve single and multilayer colloidal particles packing, such as sedimentation from dilute solution, electric deposition, spin coating, vacuum filling, etc. The simplest method is just placing a droplet of the dilute colloidal particles solution on a plate, and let the water evaporate. Surface roughness is a very important factor contributing to the deposition of colloidal particles\textsuperscript{46}. We are interested in whether it was possible to influence the structure of the deposited particles by surface modification. Rubbed polyimide (PI) thin film, commonly used as alignment layers for liquid crystal displays\textsuperscript{46}, was used as deposition substrates. After rubbed by nylon wrapped roller, nanometer size grooves formed on PI surface along the rubbing direction\textsuperscript{47}. Though widely used, the mechanism of liquid crystal alignment by rubbed PI is still under discussion\textsuperscript{48, 49, 50}: Some scholars proposed the rubbing induced steric interaction\textsuperscript{47} as the main reason for alignment. However, showed proof that after rubbed, the surface polarity was changed and the polar groups of PI extended out of surface\textsuperscript{48}, therefore inducing the liquid crystals aligned along polarity direction. Also alignment by exposure to linear polarized UV gave support to the change of the surface polarity
inducing alignment\textsuperscript{49, 50}. In this study, we deposited 2.6 \( \mu \text{m} \) colloidal particles by the modified evaporation method on six different substrates: on clean glasses with and without Indium Tin Oxide (ITO) coatings, and on four different polyimide-coated plates (no rubbing, rubbing in one direction, rubbing in two orthogonal directions, and in three directions 120 degrees with each other). Sizes along rubbing direction were calculated and compared to domain sizes perpendicular to rubbing direction. Based on that, we verified a liquid crystal alignment mechanism.

We also studied electric field induced translational and rotational movement of colloidal particles in nematic and smectic liquid crystals. By statistically characterizing field-induced rotational and translational movement (speed, direction etc.) of colloidal particles in the liquid crystals, we developed a model to explain those interesting phenomena.

\subsection*{1.4 Dissertation Outline}

The purpose of this dissertation is to report an extensive study of electro-optical and mechanic properties of unconventional liquid crystals systems: glycolipids, bent-core liquid crystals and mixtures (bent-core/bent-core, bent-core /glycolipids), liquid crystals and colloidal crystals system. The organized body of thesis is as follows:

Chapter 2 is the brief introduction of materials studied in thesis including their sources and physical characterization results. The molecular structure of glycolipids and their phase behaviors are summarized and listed in Table 2.1. All bent-core compounds studied in thesis have been divided into two categories: symmetric bent-core molecules
and asymmetric bent-core molecules, the corresponding molecular structures and phase behavior are described.

In Chapter 3 we describe the characterization methods with working principles and experimental set up for studying the phase behaviors and electro-optical properties of liquid crystals. These methods include DSC, dielectric spectra measurements, polarization and switching time measurements. An improved dielectric fitting model and the corresponding Labview program are also described.

Chapter 4 describes the detailed study of the thermotropic liquid crystal phase behaviors of four glucosides and three maltosides lipid including their phase diagrams, textures, DSC measurement results and dielectric properties. We found that hydrogen bondings between glycolipids molecules are the main reasons accounting for the unusual dielectric relaxation behavior of glycolipids at low frequencies.

In Chapter 5 we exhibit our study of 4-CBDB, the newly discovered optically isotropic ferroelectric bent-core mesogens. Additionally two interesting asymmetric bent-core compounds are described: 1). B-Ch, Bent-core compound with chiral cholesterol group attached (B-Ch) forms wide temperature range of blue phase, chiral nematic and SmC* phase; 2) A room temperature switch-able bent-core liquid crystal (B-2F) which experiences synclinic to anticlinic antiferroelectric transformation.

In Chapter 6 two kinds of mixtures are studied: three representative bent-core compounds BS10 (SmCG) , 9-CPOB (nematic) and 4CN-3F-OPIMB (SmAP) mixture with glycolipid C_{12}G_{1} and mixtures of bent-core (B-Ch) with bent-core (B-2F). Binary phase diagram based on the mixtures physical properties are depicted. Models of the
relative orientation of bent-core molecules to glycolipid molecules and bent-core molecules to different bent-core molecules are proposed based on their mixture properties.

Chapter 7 describes the systematic study of the effect of surface conditions on colloidal particles deposition and also alignment of nematic liquid crystals around colloidal particles as in close packing colloidal particles templates. We also studied colloidal particles translational (spherical particles) and rotational movement (cylindrical particles) in liquid crystal media under low frequency AC electric field.
References:

* Pictures were taken from the papers published in *Liquid Crystals* issued by Taylor & Francis Group ([http://www.tandf.co.uk](http://www.tandf.co.uk))
Chapter 2

Materials

Unconventional liquid crystal systems composing of colloidal crystals and liquid crystals system, bent-core liquid crystals, glycolipids--amphiphilic liquid crystals system, and their mixtures were studied. Due to their unusual physical properties, a brief introduction of materials including their sources, chemical nomenclature and physical characterization results is necessary before description of detailed observation on their physical properties. For bent-core liquid crystals, due to their complicated molecular structures, acronyms are always assigned based on molecular structure or material properties.

2.1 Branched Glycolipids-amphophilic liquid crystal systems

Six branched glycolipids were studied; four of them have one sugar heads (glucosides), the other two have two sugar heads (maltosides). They were provided by Dr. Rauzah Hashim, University of Malaysia. We used the notation: $C_{m-n,G_k}$, to name these compounds: where m and n give the number of carbon atoms in the longer and shorter chains of their tails, and k is the number of sugar heads ($k=1$ corresponds to glucosides and $k=2$ denotes the maltosides). The synthesis and purification method of the materials
among other similar branched lipids is published elsewhere\(^1\). As a control material we also have studied dodecyl-\(\beta\)-D-glucopyranoside (C\(_{12}\)G\(_1\)), which was purchased from Sigma Aldrich. It has a single hydrocarbon chain with 12 carbons. All the glycolipids are hygroscopic, and the phase sequences are very sensitive to the humidity. For this reason special care was taken to dry out the materials before measurements. Phase identifications of these lipids are mainly based on the polarizing microscopic studies. DSC and electric conductivity measurements were used only to identify a phase transition. The names, molecular structures and phase sequences above room temperature in both heating and cooling, as determined from the combination of DSC, polarizing microscopy and electric conductivity measurements, are listed in Table 2.1:

### 2.2 Bent-core liquid crystals

Two types of bent-core liquid crystals were studied. One is the symmetric bent-core liquid crystal with two identical arms of molecules connected to the 1,3 positions benzene rings which provides an open angle of \(120^\circ\) - \(140^\circ\). The other type is the asymmetric bent-core liquid crystals with two different arms are connected to the 1,3 position of the benzene ring.

#### 2.2.1 Symmetric bent-core liquid crystal

a. 1,3-phenylene bis[4-(4-decyl thiopheoyl(iminomethyl)) benzoate] (BS10\(^{2,3}\))

1,3-phenylene bis[4-(4-decyl thiopheoyl(iminomethyl)) benzoate] has alkylthio group in the tail of bent-core molecule shown in Figure 2.1. This material was provided
<table>
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<th>Structure</th>
<th>Phase sequence (°C)</th>
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<tr>
<td></td>
<td></td>
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<tr>
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<td></td>
<td></td>
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<tr>
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Table 2.1: Studied lipids and their phase sequences assigned based on DSC, polarizing microscopy and electric conductivity measurements. In the notation, C_{m-n}G_{k}, m and n give the number of carbon atoms in the hydrophobic long and short chains and k is the number of sugar heads. (k=1: glucosides; k=2 maltosides). C_{12}G_{1} has a single hydrocarbon chain with 12 carbon atoms. The phase sequence is given above room temperature.
temperature in heating (upper rows) and in cooling (lower rows) at 2°C/min heating/cooling rates.

Figure 2.1: Molecular structure and phase sequence\(^2\) of 1,3-phenylene bis[4-(4-decyl thiophenoyl(iminomethyl)) benzoate].

by Dr. Gerd Heppke’s group, at Technische Universität Berlin. Based on its chemical structure, BS10 is the acronym for the compound in which ‘B’ means bent-core liquid crystal, ‘S’ refers to the unusual alkylthio group inside this compound, and ‘10’ denotes the number of carbon atom in the alkylthio group. According to previous studies\(^2,3\), BS10 has only one type of switchable B7 phase. We studied physical properties of mixtures formed by BS10 and C\(_{12}\)G\(_1\).

b. 4-chloro-1,3 phenylenebis[4-(4-9-oxyphenyl propenoate) benzoate] (9-CPOB)\(^4\)
Figure 2.2: Molecular structure and phase sequence of 4-chloro-1,3 phenylenebis[4-(4-9-
oxyphenyl propenoate) benzoate].

This compound has a broad range of nematic phase. 9-CPOB was provided by Dr.
Gerd Heppke’s group, at Technische Universität Berlin. Detailed chemical structure and
phase behavior is shown in Figure 2.2. 9-CPOB was selected to make mixtures with
C_{12}G_1 to study if the chirality of C_{12}G_1 can be transferred into nematic and smectic
phases of 9-CPOB.

c. 4-chlororesorcinol bis[4-(4-n-dodecyloxybenzoyloxy)benzoate] (4-CBDB)\textsuperscript{5,6}

Figure 2.3: Molecular structure and phase sequence of 4-CBDB.

This compound was provided by Prof. G. Pelzl and W. Weissflog (Halle,
Germany). It is named as 4-CBDB in which 4 is the position of chlorine atom on the
benzene ring and ‘C’ refer to the chlorine atom. This material has an unusual transition
from a nematic phase to an optically isotropic mesophase (I_m) which is characterized by a
short range (\sim20nm) local smectic structure. Both the nematic and I_m phases are
monotropic with the following phase sequence: (I 95°C N I_m 80°C) Cr 98°C\textsuperscript{5,6}. We
performed detailed electro-optical switching properties and dielectric properties of
optically isotropic mesophase. Based on that we described that how the namometer-sized
localized smectic domains correlated to form optically isotropic phase. In our study we found that the optically isotropic mesophase is ferroelectric. In chapter 5 we propose an isotropic slim cluster model to explain and understand the unusual behavior of the I\textsubscript{m} phase.

d. 4-cyano-1,3-phenylene-bis[4-(3-fluoro-4-octyloxyphenylimino-methyl)benzoate]-4CN-3F-OPIMB\textsuperscript{7}

![Figure 2.4: Molecular structure and phase diagram of 4CN-3F-OPIMB.](image)

Figure 2.4: Molecular structure and phase diagram of 4CN-3F-OPIMB.

4CN-3F-OPIMB was provided by Prof G. Pelzl and W. Weissflog (Halle, Germany). Here ‘4CN’ means the CN group at the fourth position of the benzene ring and ‘3F’ refers to the position of two F atoms at the benzene ring. OPIMB is the initial letters of the chemical nomenclature for the main structure of this molecule. 4CN-3F-OPIMB has been reported\textsuperscript{7} to have a broad range of SmAP phase below the SmA phase. Mixtures of 4CN-3F-OPIMB and C\textsubscript{12}G\textsubscript{1} were studied for the electro-optical properties along with their phase diagram.

### 2.2.2 Asymmetric bent-core liquid crystals

Sixteen asymmetric bent-core liquid crystals were studied. DSC and electric conductivity measurements were used only to identify a phase transition. The phase
assignments were mainly based on the polarizing microscopic studies. The chemical nomenclature, molecular structures and phase sequences above room temperature in both heating and cooling, as determined from the combination of DSC, polarizing microscopy and electric conductivity measurements, are listed in Table 2.2.

The asymmetric bent-core compounds can be divided into two types: Type 1: the molecule has a chiral tail on one side (Table 2.2); Type 2: The molecule is achiral (Table 2.3); These compounds were synthesized and purified by Dr. Uma S. Hiremath and Dr. C. V. Yelamaggad, from Center for Liquid Crystal Research, India during their visit to the Liquid Crystal Institute in 2004. The names for these compounds were given by the chemists who synthesized them. For example SC242 is for the compound with formal chemical nomenclature: 4-((3-(4-(2-hydroxy-4-(5--(cholesteryloxyoxy) pentyloxy) benzylideneamino-benzoyloxy) phenoxy) carbonyl) phenyl 4-(decyloxy)benzoate.

Within these sixteen compounds, SC242, U496 and their mixtures are studied in detail for their electro-optic properties.

<table>
<thead>
<tr>
<th>Type 1: Asymmetric bent-core liquid crystals with chiral tail</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Name</strong></td>
</tr>
<tr>
<td>SC241</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
SC242

\[
\text{C}_{10}\text{H}_{21}\text{O}
\]

4-((3-(4-(2-hydroxy-4-(5-(cholesteryloxycarbonyl)pentyloxy)benzylideneamino-benzoyloxy)phenoxy)carbonyl)phenyl 4-(decyloxy)benzoate

\[
\begin{align*}
I & \quad 174.5 \\
M1 & \quad 138.3 \\
M2 & \quad 52 \\
Tg & \quad 72
\end{align*}
\]

SC243

\[
\text{C}_{10}\text{H}_{21}\text{O}
\]

4-((3-(4-(2-hydroxy-4-(5-(cholesteryloxycarbonyl)butyloxy)benzylideneamino-benzoyloxy)phenoxy)carbonyl)phenyl 4-(decyloxy)benzoate

\[
\begin{align*}
Cr & \quad 141.9 \\
B1 & \quad 149.5 \quad I \\
B1 & \quad 147.7 \quad B1 \quad 75.1
\end{align*}
\]

SC245

\[
\text{C}_{10}\text{H}_{21}\text{O}
\]

4-((3-(4-(2-hydroxy-4-(5-(cholesteryloxycarbonyl)propyloxy)benzylideneamino-benzoyloxy)phenoxy)carbonyl)phenyl 4-(decyloxy)benzoate

\[
\begin{align*}
Cr & \quad 158.0 \\
N* & \quad 186.3 \quad I \\
I & \quad 183.8 \quad N* \quad 164 \quad Mx \quad 50 \quad Tg
\end{align*}
\]

SC255

\[
\text{C}_{10}\text{H}_{21}\text{O}
\]

4-((3-(4-(4-(5-(cholesteryloxycarbonyl)pentyloxy)benzylideneamino-benzoyloxy)phenoxy)carbonyl)phenyl 4-(decyloxy)benzoate

\[
\begin{align*}
Cr & \quad 144.2 \\
N* & \quad 162.8 \quad I \\
I & \quad 162.4 \quad N* \quad 143 \quad B1HT \quad 110 \quad B1LT \quad 104.3 \quad Mx \quad 84.8 \quad (12.6) \quad Cr
\end{align*}
\]
Table 2.2: Molecular structures, chemical nomenclature and phase sequences of the asymmetric bent-core liquid crystals with chiral tails on one side.

<table>
<thead>
<tr>
<th>Name</th>
<th>Molecular structure, chemical nomenclature and phase sequence (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC261</td>
<td><img src="image" alt="Molecular Structure" /> 4-((3-(4-(4-(5--(cholesteryloxycarbonyl)propyloxy)benzylideneamino-benzoyloxy)phenoxy) carbonyl) phenyl 4-(decyloxy)benzoate Cr 145.6 TGB 153 N* 171.5 I I 170.2 N* 124.1 Mx (?) Tg</td>
</tr>
<tr>
<td>SC262</td>
<td><img src="image" alt="Molecular Structure" /> 4-((3-(4-(4-(5--(cholesteryloxycarbonyl)butyloxy)benzylideneamino-benzoyloxy) phenoxy) carbonyl) phenyl 4-(decyloxy)benzoate Cr 120.0 Cr 129.6 B1 137.8 I I 135.5 B1 75.1</td>
</tr>
<tr>
<td>SC268</td>
<td><img src="image" alt="Molecular Structure" /> 4-((3-(4-(4-(5--(cholesteryloxycarbonyl)heptyloxy)benzylideneamino-benzoyloxy) phenoxy) carbonyl)phenyl 4-(decyloxy)benzoate Cr1 120.1 Cr2 122.5 TGB 140 N* 152.6 I I 151.3 N* 137 TGB 114.7 B1 77.7 Cr</td>
</tr>
</tbody>
</table>

Type 2: Asymmetric and achiral bent-core liquid crystal
4-((3-(4-(Decyloxy)benzoyloxy)benzoyloxy)phenylimino)methyl)-3-hydroxyphenyl 4-(decyloxy)-2,3-difluorobenzoate

U497

Ac431

3-(2-Hydroxy-4-(4-(Octadecyloxy)benzoyloxy)benzoyloxy)benzylideneamino)phenyl)- (2-Hydroxy-4-(4-(Octadecyloxy)benzoyloxy)benzoyloxy)benzylideneamino)

Cr115 Cr2 138.2 Cr3 165.5 Bx 195.5 I

I 193.5 Bx 149.9 Cr1 127.6 Cr2 112.5 Cr

U356h

3-(2-Hydroxy-4-(4-(Hexdecyloxy)benzoyloxy)benzoyloxy)benzylideneamino)phenyl)- (2-Hydroxy-4-(4-(Hexdecyloxy)benzoyloxy)benzoyloxy)benzylideneamino)

Cr116 Cr2 130.8 Cr3 167.5 Bx 191.8 I

I 187.5 Bx 143.3 Cr1 122.3 Cr2 114.3 Cr

U356g

3-(2-Hydroxy-4-(4-(Dodecyloxy)benzoyloxy)benzoyloxy)benzylideneamino)phenyl)- (2-Hydroxy-4-(4-(Dodecyloxy)benzoyloxy)benzoyloxy)benzylideneamino)
<table>
<thead>
<tr>
<th></th>
<th>Molecular Structure</th>
<th>Chemical Nomenclature</th>
<th>Phase Sequences</th>
</tr>
</thead>
<tbody>
<tr>
<td>U356f</td>
<td><img src="image1" alt="Molecular Structure" /></td>
<td>3-(2-Hydroxy-4-(4-((Undecyloxy)benzoyloxy)benzoyloxy)benzoyloxy)benzylideneamino)phenyl)- (2-Hydroxy-4-(4-(Undecyloxy)benzoyloxy)benzoyloxy)benzylideneamino)</td>
<td>Cr116.3 Cr2 130.8 Cr3 167.5 Bx 191.8 I 187.5 Bx 143.3 Cr1 122.3 Cr2 114.3 Cr</td>
</tr>
<tr>
<td>U356e</td>
<td><img src="image2" alt="Molecular Structure" /></td>
<td>3-(2-Hydroxy-4-(4-((Decyloxy)benzoyloxy)benzoyloxy)benzoyloxy)benzylideneamino)phenyl)- (2-Hydroxy-4-(4-(Decyloxy)benzoyloxy)benzoyloxy)benzylideneamino)</td>
<td>Cr110.3 Cr1 179.8 Bx 189.4 I 178.6 Bx 148.2 Cr1 99 Cr</td>
</tr>
<tr>
<td>U356d</td>
<td><img src="image3" alt="Molecular Structure" /></td>
<td>3-(2-Hydroxy-4-(4-((Nonyloxy)benzoyloxy)benzoyloxy)benzoyloxy)benzylideneamino)phenyl)- (2-Hydroxy-4-(4-(Nonyloxy)benzoyloxy)benzoyloxy)benzylideneamino)</td>
<td>Cr106.4 Cr1 184.5 Bx 189.7 I 187.3 Bx 157.6 Cr</td>
</tr>
</tbody>
</table>

Table 2.3: Molecular structures, chemical nomenclature and phase sequences of the asymmetric bent-core liquid crystals without chiral tail.
2.3 Polystyrene Colloidal particles

Colloidal particles suspension solution used in the experiments was purchased from Interfacial Dynamic Co. These polystyrene colloidal particles were supplied in the form of suspension in distilled de-ionized water. The particles are hydrophobic with the negative surface charges provided by ionized sulfate groups. The original particles solution is 2wt% and it was diluted to 0.05wt% in the experiments. Two sizes of particles 2.6 μm and 0.3μm were used in the experiments. In our study the colloidal particles are dispersed into two commercially available liquid crystalline (LC) materials: octyl cyano biphenyl (8CB) from Aldrich, and a mixture CS 2003 from Chisso, Inc. 8CB has a smectic A (SmA) phase in temperature range 23 - 33°C characterized by a large positive dielectric anisotropy (Δε=8 at 32°C). CS2003 is a room temperature ferroelectric SmC* mixture with ferroelectric polarization $P_o\sim40nC/cm^2$ and negative dielectric anisotropy (Δε=−0.6 at 50°C). It also has a SmA* phase between 56°C and 64°C, and a chiral nematic (N*) phase between 64°C and 90°C.
References:

Chapter 3

Characterization Methods and Experiment Set Up

3.1 Introduction

Phase diagrams and transition temperatures of materials studied in this thesis are determined by Differential Scanning Calorimeter (DSC) and phase textures are observed under cross-polarized microscope. Electro-optical switching properties of liquid crystal materials are tested on the sample of liquid crystals thin film sealed in the empty cells formed by two ITO coated glass substrates with an anti-parallel rubbed polyimide (PI) treatment. Triangular and rectangular electric fields are applied to the sample. The spontaneous polarizations are obtained from the integration of current appearing above Ohmic baseline under a triangular electric field. Switching time is determined from the peak appearing in the polarization current under the rectangular electric field. In addition, the Diamant-bridge method for measuring polarization as a function of electric field was used to clarify ferroelectric or anti-ferroelectric properties of some bent-core liquid crystals. Dielectric measurements are an important tool used to characterize bent-core liquid crystals. The dielectric permittivities of liquid crystals are frequency dependent, and can be expressed as a complex value: \( \varepsilon^* = \varepsilon' - i\varepsilon'' \). The complex dielectric permittivity
is related to molecular collective activity. Dielectric $\varepsilon(f)$ spectra provide information about molecular dynamics and fluid structure through the changes of the dielectric permittivity which is closely related to the orientation order. The value of the real and imaginary parts of dielectric permittivity are obtained by fitting measured impedances of liquid crystals sandwiched between ITO coated plates with homeotropic or planar alignment.

### 3.2 Empty liquid crystal cells preparation

Characterizations of liquid crystal material are often performed on liquid crystal thin films which are sealed in empty cells formed by two conductive substrates with an alignment layer coating. The Properties of various commercial cells used in my study are presented Table 3.1.

<table>
<thead>
<tr>
<th>Empty cells</th>
<th>EHC Co</th>
<th>Display Tech Inc.</th>
<th>Instec Inc</th>
</tr>
</thead>
<tbody>
<tr>
<td>alignment</td>
<td>planar</td>
<td>vertical</td>
<td>planar</td>
</tr>
<tr>
<td>Cell thickness (μm)</td>
<td>5</td>
<td>2</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 3.1: Parameters of empty liquid crystal cells from different companies.

In addition to these commercial available cells, most of empty liquid crystal cells used in study are constructed in clean room in LCI. Cells coated with either planar or homeotropic alignment layer. The cell gap varies from 2μm to 5μm depending on study purposes. A diagram of the cell fabrication process is shown in Figure 3.1:
The cell thickness can be obtained from interference spectrum of transmitted light through empty cells in visible range. The cell thickness can be calculated according to:

\[ d = \frac{1}{4 \times \text{slope}} \]

where the slope can be obtained from the curve of plotting \( k \) (the arbitrary integer numbers given to count sequences of wavelength corresponding to the maximum and minimum transmittance in the spectrum) against the inverse of the wavelength mentioned above. Liquid crystals are filled into empty cell by capillary forces at their isotropic phase on a Korfle heat bench.

### 3.3 Differential Scanning Calorimeter - DSC

DSC is used to measure the phase transition temperatures of materials and transition enthalpies. The equipment measures heat difference between the sample pan (containing testing sample) and the reference pan at certain heat rate (shown in Figure 3.2). As two pans (the reference pan and the pan with sample) are heated or cooled at same rate, extra heat will release or absorb at sample's pan when there are phase
transitions happen in samples. Thus peaks will appear in the heat flow curve corresponding to the temperatures where phase transitions happen (shown in Figure 3.3). From the peak position the exact phase transition temperatures can be determined.
Integrating the peak above the baseline gives the total heat released or absorbed at the transition.

An example of DSC measurements is given in Figure 3.3 showing heat flows of the heating process of C$_{12}$G$_1$ from 50°C to 150°C at 5°C/min. As we can see, there are two peaks (correspond to a crystal to SmA transition and a SmA to isotropic transition of C$_{12}$G$_1$) in the heating process of C$_{12}$G$_1$ up to 150°C.

### 3.4 Dielectric Spectroscopes

Dielectric measurements are carried out on Indium Tin Oxide (ITO) coated cells, which are transparent to visible light, allowing simultaneous optical observations of the material alignment$^1$. The cells filled with LC has an absorption in the 1-10MHz range due to RC circuit formed by the capacitance of the liquid crystal and the resistance of the ITO, which shifts to lower frequency with decreasing cell thickness. Therefore thin and low-resistive ITO is needed for the test. More precise measurements are possible on gold or copper coated surfaces.

The measuring field strength should be in the linear regime, i.e. the field should not cause observable reorientation in the liquid crystal. In nematics it means voltages below the Freedericks transition, which means $U<1$V for our cells. In every measurement serious care should be taken to verify that the measurements are in the linear regime.

It is advised that the measurements be taken both in heating and in cooling, since in liquid crystals the behavior depends strongly on this condition (for example monotropic phases appear only in cooling from the isotropic phase).
3.4.1 Equivalent circuit of an ideal cell filled with liquid crystals

For simplicity here we first treated a liquid crystal as ‘an isotropic dielectrics’ which can be represented as a capacitor with capacitance $C = \varepsilon_0 \varepsilon \frac{A}{d}$ ($\varepsilon$ is the dielectric constant, $A$ is the area of the film and $d$ is the film thickness) in parallel to the resistance of liquid crystals $R = \rho d / A$ ($\rho$ is the resistivity of the material). A diagram of the circuit for the ideal situation is shown in Figure 3.4:

![Figure 3.4: Equivalent circuit of an ideal cell filled with liquid crystal.](image)

According to Ampere’s law, the current through the circuit with an applied AC field is

$$
\mathbf{j}_T = \mathbf{j}_f + \frac{\partial \mathbf{D}}{\partial t}.
$$

(3.1)

The first term is the current density due to free charges and the second term is the rate of the change of electric displacement $\mathbf{D}$. Assuming the material obeys Ohm’s law to first approximation, then $\mathbf{j}_f = \sigma \mathbf{E}$ in which $\sigma = 1/\rho$ is the electrical conductivity. Substituting this into Eq (3.1) we can get
\[ \mathbf{j}_r = \sigma \mathbf{E} + \frac{\partial \mathbf{D}}{\partial t}. \quad (3.2) \]

In linear isotropic dielectric media we have

\[ \mathbf{D} = \varepsilon_o \mathbf{E} + \mathbf{P}. \quad (3.3) \]

here \( \varepsilon_o \) is the permittivity in free space, \( \mathbf{P} \) is polarization (including contribution from electric polarization, ionic polarization and orientation polarization), So,

\[ \mathbf{j}_r = \sigma \mathbf{E} + \varepsilon_o \frac{\partial \mathbf{E}}{\partial t} + \frac{\partial \mathbf{P}}{\partial t}. \quad (3.4) \]

We can then write the electric field in the following form:

\[ \mathbf{E}(\omega) = \mathbf{E}_o e^{i \omega t}. \quad (3.5) \]

If the applied field is not so strong to cause reorientation of the liquid crystal molecules, we can have

\[ \mathbf{P}(\omega) = \varepsilon_o \chi(\omega) \mathbf{E}_o, \quad (3.6) \]

in which \( \chi \) is the electric susceptibility and is function of frequency. Then

\[ \mathbf{j}_r = \sigma \mathbf{E}(\omega) + i \omega [\varepsilon_o \mathbf{E}(\omega) + \varepsilon_o \chi(\omega) \mathbf{E}(\omega)] \]
\[ = \sigma \mathbf{E}(\omega) + i \omega \varepsilon_o (1 + \chi(\omega)) \mathbf{E}(\omega). \quad (3.7) \]

Since susceptibility is a complex quantity we can write

\[ \chi_e = \chi'_e - i \chi''_e. \quad (3.8) \]
so,

\[
\tilde{j}_r = \sigma \tilde{E}(\omega) + i\omega \varepsilon_0 \left(1 + \chi'_e(\omega) + i\chi''_e(\omega)\right)\tilde{E}(\omega) \\
= \sigma \tilde{E}(\omega) + \omega \varepsilon_0 \chi''_e(\omega)\tilde{E}(\omega) + i\omega \varepsilon_0 (1 + \chi'_e(\omega))\tilde{E}(\omega).
\]  

(3.9)

For a parallel plate capacitor \(\tilde{j} = \frac{\tilde{I}}{A}\) and \(\tilde{E} = \frac{\tilde{V}}{d}\), where \(A\) is the area and \(d\) is the thickness of the capacitor.

\[
\tilde{I}(\omega) = \tilde{j}A = \tilde{V}(\omega)\frac{A}{d} \left[\sigma + \omega \varepsilon_0 \chi''_e(\omega) + i\omega \varepsilon_0 (1 + \chi'_e(\omega))\right].
\]  

(3.10)

In linear isotropic media

\[
\tilde{D}(\omega) = \varepsilon(\omega)\tilde{E}(\omega),
\]

(3.11)

\[
\varepsilon(\omega) = \varepsilon_0 (1 + \chi'_e(\omega)).
\]

(3.12)

where \(\varepsilon\) is the permittivity of the material and is a function of frequency. It is also a complex quantity.

\[
\varepsilon'(\omega) = \varepsilon_0 (1 + \chi'_e(\omega)),
\]

(3.13)

\[
\varepsilon''(\omega) = \varepsilon_0 \chi''_e(\omega)).
\]

So we get

\[
\frac{\tilde{I}(\omega)}{\tilde{V}(\omega)} = \frac{A}{d} \left[\sigma + \omega \varepsilon''_e(\omega) + i\omega \varepsilon'(\omega)\right].
\]

(3.14)

In a complex form, the applied field and current through the circuit could be written as
\[ \tilde{V} = \tilde{V}_o e^{i \omega t}, \quad (3.15) \]

\[ \tilde{I} = \tilde{I}_o e^{i (\sigma + \delta)}, \quad (3.16) \]

The current has the same frequency but out of phase by \( \delta \). \( \tilde{V}_o \) and \( \tilde{I}_o \) are related by

\[ \frac{\tilde{I}_o}{\tilde{V}_o} e^{i \delta} = \frac{1}{|Z|} e^{i \delta}, \quad (3.17) \]

where \( Z \) is the complex impedance of the capacitor filled with dielectric material. So

\[ \frac{I}{V} = \frac{1}{|Z|} e^{i \delta}, \quad (3.18) \]

and

\[ |Z| e^{i \delta} = |Z| (\cos(\delta) + i \sin(\delta)) = \Re(Z) + i \Im(Z). \quad (3.19) \]

Substituting real \( \Re(Z) \) and imaginary part \( \Im(Z) \) of impedance, we can get

\[ \frac{1}{|Z|} e^{i \delta} = \frac{1}{\Re(Z) - i \Im(Z)} = \frac{\Re(Z) + i \Im(Z)}{\Re^2(Z) + \Im^2(Z)}. \quad (3.20) \]

Combining Eq (3.14) and Eq (3.20) we can get

\[ \frac{A}{d} (\sigma + \omega \varepsilon''(\omega)) + i \omega \varepsilon'(\omega)) = \frac{\Re(Z) + i \Im(Z)}{\Re^2(Z) + \Im^2(Z)}. \quad (3.21) \]

Comparing the real and imaginary part of the above two expressions:
\begin{align*}
\frac{A}{d} \omega \varepsilon'(\omega) &= \frac{\text{Im}(Z)}{\text{Re}^2(Z) + \text{Im}^2(Z)}, \\
A \frac{d}{d} (\sigma + \omega \varepsilon''(\omega)) &= \frac{\text{Re}(Z)}{\text{Re}^2(Z) + \text{Im}^2(Z)}.
\end{align*}
\quad (3.22)

i.e.,
\begin{align*}
\varepsilon'(\omega) &= \frac{d}{\omega A} \frac{\text{Im}(Z)}{\text{Re}^2(Z) + \text{Im}^2(Z)}, \\
\varepsilon''(\omega) &= \frac{d}{\omega A} \left( \frac{\text{Re}(Z)}{\text{Re}^2(Z) + \text{Im}^2(Z)} - \sigma \right).
\end{align*}
\quad (3.23)

Capacitance of an empty cell is given by
\begin{align*}
C_o &= \varepsilon_o \frac{A}{d}.
\end{align*}
\quad (3.24)

With Eq.(3.24) can be written as
\begin{align*}
\varepsilon'(\omega) &= \frac{d}{\omega A} \frac{\text{Im}(Z)}{\text{Re}^2(Z) + \text{Im}^2(Z)} = \frac{\varepsilon_o}{\omega C_o} \frac{\text{Im}(Z)}{\text{Re}^2(Z) + \text{Im}^2(Z)}, \\
\varepsilon''(\omega) &= \frac{d}{\omega A} \left( \frac{\text{Re}(Z)}{\text{Re}^2(Z) + \text{Im}^2(Z)} - \sigma \right) = \frac{\varepsilon_o}{\omega C_o} \left( \frac{\text{Re}(Z)}{\text{Re}^2(Z) + \text{Im}^2(Z)} - \sigma \right).
\end{align*}
\quad (3.25)

Often for convenience of calculation, a relative dielectric permittivity---dielectric constant is used
\begin{align*}
\varepsilon_r = \varepsilon/\varepsilon_o,
\end{align*}
\quad (3.26)

so real and imaginary part of dielectric constants are
\[ \varepsilon'_r(\omega) = \frac{1}{\omega \varepsilon_0} \frac{\text{Im}(Z)}{\text{Re}^2(Z) + \text{Im}^2(Z)}, \]

\[ \varepsilon''_r(\omega) = \frac{1}{\omega \varepsilon_0} \left( \frac{\text{Re}(Z)}{\text{Re}^2(Z) + \text{Im}^2(Z)} - \sigma \right). \] (3.27)

In the following equations we omit the subscript ‘\(r\)’ in writing the relative dielectric constants. The real and imaginary parts of impedance can be calculated from the impedance and phases measured by an LCR meter. The imaginary part of the dielectric constant contains a conductivity contribution. It appears as \( \varepsilon'' \propto 1/\omega \) at low frequencies and \( \sigma \) can be obtained by fitting. The effect of conductivity can be neglected at high frequencies i.e. above 1kHz because contribution of conductivity at high frequencies range is very small (<0.001).

To study the dielectric properties of liquid crystals one has to take into account that are anisotropic in most cases with a few exceptions (e.g. cubic liquid crystal phases). The dielectric constant of the liquid crystals therefore will be a tensor, which in the local molecular frame can be given as \( \hat{\varepsilon} = \begin{pmatrix} \varepsilon_1 & 0 & 0 \\ 0 & \varepsilon_2 & 0 \\ 0 & 0 & \varepsilon_3 \end{pmatrix} \). The directions of \( \varepsilon_1, \varepsilon_2 \) and \( \varepsilon_3 \) are shown in Figure 3.5. For uniaxial calamitic liquid crystals molecules \( \varepsilon_1 \) is equal to \( \varepsilon_2 \) and can be written as \( \varepsilon_{\perp} \). The direction of \( \varepsilon_3 \) is parallel to the average molecular long axis so we can write it as \( \varepsilon_{\parallel} \). The value of the measured dielectric constant depends on the orientation of the director with respect to the external electric field. If the director is
along the external electric field, then we measure $\varepsilon_{\parallel}$; when the director is perpendicular to the external electric field, we measure $\varepsilon_{\perp}$.

More complicated situations will appear if the molecular shapes are not rod-like or in case of biaxial smectic phase, such as SmC. In this case one needs to measure the dielectric constants at least in three different orientations.

![Diagram](image.png)

**Figure 3.5** Definition of the dielectric tensor components in the local molecular frame: The directions of $\varepsilon_1, \varepsilon_2, \varepsilon_3$ are perpendicular to each other in which $\varepsilon_3$ being parallel to the average molecular long axis.

In the real liquid crystal cells, the resistance of the electrode, the conducting wire and the capacitance and resistance of the alignment thin layer need to be considered. Taking all these factors into account, the circuit diagram can be described as in Figure 3.6. In this model, the resistance of air is not regarded infinite (it turned out to be in the range of $10^9$-$10^{10}\Omega$).

![Diagram](image.png)

**Figure 3.6**: Equivalent circuit of empty cell with surface treatment.
For simplicity, we consider the only conductivity contributions from the upper and lower electrodes. The impedance of the empty cell is given by the following values. $C_p$ is the effective capacitance of alignment layers, $R_p$, the effective resistance of alignment layer, $C_o$, the capacitance of the air, $R_{air}$, the effective resistance of the air, and $r_{lead}$, the effective sum resistance of the ITO substrates and wires. With the following equations we can fit the curve for the value of $C_p$, $R_p$, $C_o$, $R_{air}$, $r_{lead}$, of the empty cells.

$$Z_{empty-cell} = r_{lead} + \frac{R_p}{1 + (\omega C_p R_p)^2} + \frac{R_{air}}{1 + (\omega C_{o} R_{air})^2} - i\left(\frac{\omega C_p R_p^2}{1 + (\omega C_p R_p)^2} + \frac{\omega C_{o} R_{air}^2}{1 + (\omega C_{o} R_{air})^2}\right),$$  \hspace{1cm} (3.28)

$$\text{Im}(Z_{empty-cell}) = \frac{\omega C_p R_p^2}{1 + (\omega C_p R_p)^2} + \frac{\omega C_{o} R_{air}^2}{1 + (\omega C_{o} R_{air})^2}.$$  \hspace{1cm} (3.29)

$$\text{Re}(Z_{empty-cell}) = r_{lead} + \frac{R_p}{1 + (\omega C_p R_p)^2} + \frac{R_{air}}{1 + (\omega C_{o} R_{air})^2}. \hspace{1cm} (3.30)$$

When the liquid crystals are filled into empty cell, equivalent circuit is shown in Figure 3.7, and expression for impedance of circuit is as following:

$$Z_{lc-cell} = r_{lead} + \frac{R_p}{1 + (\omega C_p R_p)^2} + \frac{R_{lc}}{1 + (\omega C_{lc} R_{lc})^2} - i\left(\frac{\omega C_p R_p^2}{1 + (\omega C_p R_p)^2} + \frac{\omega C_{lc} R_{lc}^2}{1 + (\omega C_{lc} R_{lc})^2}\right),$$  \hspace{1cm} (3.31)

$$\text{Re}(Z_{lc-cell}) = r_{lead} + \frac{R_p}{1 + (\omega C_p R_p)^2} + \frac{R_{lc}}{1 + (\omega C_{lc} R_{lc})^2}, \hspace{1cm} (3.32)$$

$$\text{Im}(Z_{lc-cell}) = \frac{\omega C_p R_p^2}{1 + (\omega C_p R_p)^2} + \frac{\omega C_{lc} R_{lc}^2}{1 + (\omega C_{lc} R_{lc})^2}, \hspace{1cm} (3.33)$$

where $C_{lc}$, and $R_{lc}$ are the effective capacitance and the effective resistance of liquid crystals respectively.
Figure 3.7: Equivalent circuit of an actual cell filled with liquid crystal.

The measured imaginary and real components of the liquid crystal cells are related to those of the liquid crystal by

\[
\text{Re}(Z)_{lc\text{-cell}} = r_{lead} + \frac{R_p}{1 + (\omega C_p R_p)^2} + \frac{R_{lc}}{1 + (\omega C_{lc} R_{lc})^2} = r_{lead} + \frac{R_p}{1 + (\omega C_p R_p)^2} + \text{Re}(Z)_{lc}, \quad (3.34)
\]

\[
\text{Im}(Z)_{lc\text{-cell}} = \frac{\omega C_p R_p^2}{1 + (\omega C_p R_p)^2} + \frac{\omega C_{lc} R_{lc}^2}{1 + (\omega C_{lc} R_{lc})^2} = \frac{\omega C_p R_p^2}{1 + (\omega C_p R_p)^2} + \text{Im}(Z)_{lc}. \quad (3.35)
\]

From the measurement of empty cell we can get \( r_{lead}, C_p, R_p \) and \( C_o \), then the values of \( C_{lc}, R_{lc} \) consequently \( \varepsilon', \varepsilon'' \) of liquid crystal can be calculated.

### 3.4.2 Procedure of the dielectric measurement and tests with liquid crystals

On the basis of above model, we can establish a procedure for dielectric measurements on liquid crystals. It involves three steps:

**Step1:** Measurement of the magnitude of the impedances (\( Z \)) and phases (\( \delta \)) of an empty cell. The empty cell parameters can be obtained by fitting real and imaginary parts of impedance (\( C_p, R_p, C_o, R_{air}, r_{lead} \)).

**Step2:** Filled the empty cell with liquid crystals and measured the impedances and phases for filled cell.
Step3: According to fitting parameters of empty cell, real and imaginary parts are calculated and dielectric constants are obtained with Eq (3.27).

All measurements are carried out with the Qualtech 1920 Precision LCR meter. This instrument has a basic accuracy specification of 0.1% for test results over a wide frequency range, from 20Hz to 1MHz. Preliminary software was provided by QuadTech to run the LCR meter; We modified it to fit our purposes. The modifications include data acquisition, data processing, data storage and addition of frequency scan capabilities. Fitting programs for empty cell fitting and dielectric constant calculations were written in Labview. The details of the entire process are described below and was calibrated by measuring the well-known liquid crystal 5CB.

a) The impedance and phase of an empty cell were measured at room temperature between 100Hz and 1MHz, in which 200 points were obtained. The actual impedance and phase of the empty cell are shown in Figure 3.8.

![Figure 3.8: Impedance and phase of empty cell with function of frequency from 100Hz to 1MHz.](image-url)
$C_p$, $R_p$, $C_o$, $R_{air}$, $r_{lead}$, were fitted by starting with certain initial value of the parameters $C_p \sim 10\text{nF}$, $R_p \sim 10^3\Omega$, $R_{air} \sim 10^9\Omega$, $r_{lead} \sim 10^2\Omega$, $C_o \sim 10\text{pF}$. The fitting program was written in Labview. The actual interface of the fitting program is shown in Figure 3.9.

In this program all the parameters can be manually adjusted to see how well the curves fit the experimental data. The example in Figure 3.9 shows that the resistance of alignment layer is $4.38 \times 10^3\Omega$, the resistance of the ITO and wire is $925\Omega$. The capacitance of alignment layer is $17.5\text{nF}$. The capacitance of the entire cell (air) is $53.6\text{pF}$. The resistance of the air is fitted to be: $4.6\text{G}\Omega$. Knowing $C_o$ from fitting and electrode area ($0.25\text{ cm}^2$) of the empty cell the cell gap can be calculated according to Eqt.(3.24): The cell gap is $4.1\mu\text{m}$.

![Figure 3.9: Labview fitting program interface for $C_p$, $R_p$, $C_o$, $R_{air}$, $r_{lead}$, for empty cell.](image-url)
Figure 3.10: Impedance and phase of cell with 5CB at room temperature at frequency from 100Hz to 1MHz.

Figure 3.11: Real and imaginary part of dielectric constant of 5CB at room temperature at the function of frequency.

b) Measurement of cell with 5CB at room temperature was made also from 100 Hz to 100MHz: The real and imaginary part of 5CB based on the fitted parameters from empty cell are shown in Figure 3.10.
Because the direction of the electric field applied is perpendicular to the average molecular axis of liquid crystals, so the dielectric constant of 5CB we obtained is $\varepsilon_\perp$. The conductivity of 5CB can be fitted from $1/f$ dependence of $\varepsilon''$ in the range of $10^2$-$10^4$ Hz range. In the example of Figure 3.11 we can get $\sigma_{5CB} = 1.78E-12$ S/m.

The values of $\varepsilon_\perp = 5.91$ (at 1.0kHz) is close to published data of 5CB ($\varepsilon_\perp = 6.0$ at 1kHz from Product information of K15 provided by EMD Chemicals), which confirms the validity of the process we used.

3.5 **Switching dynamics and electro-optic measurement of ferroelectric liquid crystals**

3.5.1 **Switching dynamics of ferroelectric liquid crystals**

Switching dynamics of ferroelectric liquid crystals has been described in Lagerwall’s book (Figure 3.12): Considering a smectic liquid crystals thin film with the layers normal to the substrates (bookshelf structure), the spontaneous polarization (Ps) of liquid crystals can be switched when reversing the direction of the electric field. Switching of the spontaneous polarization takes place by variations of azimuthal angle $\varphi$ as rotation of director around the cone shown in Eq(3.36). The response time can be obtained by the following equation:

$$\gamma_\varphi \frac{\partial \varphi}{\partial t} = -P_s E \sin \varphi - \frac{1}{2} \varepsilon_0 \Delta \varepsilon E^2 \sin^2 \theta \sin(2\varphi) - KV^2 \varphi. \quad (3.36)$$
In this equation $\gamma_\varphi$ is the rotation viscosity and $K$ is the relevant twist elastic constant of the liquid crystals. If the rotation is uniform, no gradient of $\varphi$ exists and no elastic deformation of liquid crystal molecules, Eq (3.36) can be written as:

$$\gamma_\varphi \frac{\partial \varphi}{\partial t} = -P_s E \sin \varphi - \frac{1}{2} \varepsilon_o \Delta \varepsilon E^2 \sin^2 \theta \sin(2\varphi).$$ \hfill (3.37)

The solution to (3.37) is given as:

$$t/\tau = \frac{1}{\alpha^2 - 1} \left( \ln \frac{\tan(\varphi / 2)}{\tan(\varphi_o / 2)} + \alpha \ln \frac{(1 + \alpha \cos \varphi) \sin \varphi_o}{(1 + \alpha \cos \varphi_o) \sin \varphi} \right).$$ \hfill (3.38)

where $\tau = \gamma_\varphi / E(p + \alpha), \varphi_o(t = 0)$ and $\alpha = \frac{\Delta \varepsilon E \sin^2 \theta}{P}$.

Figure 3.12: Illustration of switching process of spontaneous polarization of liquid crystal under reserves of electric field.

When $\alpha \ll P$ ($\Delta \varepsilon$ is small) the contribution from the ferroelectric interaction dominates over the quadratic (dielectric) term and the characteristic response time becomes proportional to the inverse of the electric field. In this case the rotational
viscosity can be obtained from the slope of repose time as the function of inverse electric field.

### 3.5.2 Spontaneous polarization of ferroelectric liquid crystals

When a ferroelectric liquid crystal is subjected to external electric fields the current going through the circuit follows Eq. (3.4). The current density contribution from polarization is mainly due to the spontaneous polarization reorientation according to external electric field applied. If the amplitude of electrode area $A$ is multiplied on both sides of the equation, we can get current in the circuit:

$$ I = \frac{V}{R} + C_o \frac{\partial V}{\partial t} + P_s A \sin \theta \frac{\partial \theta}{\partial t}, \quad (3.39) $$

where $C_o = \varepsilon_o \frac{A}{d}$, $V = E \cdot d$, $R = \frac{1}{\sigma A}$, $d$ is the thickness of the capacitor, then

$$ P_s A \sin \theta \frac{\partial \theta}{\partial t} = I_p = I - \left( \frac{\vec{V}}{R} + C_o \frac{\partial \vec{V}}{\partial t} \right) = I - I_R - I_C. \quad (3.40) $$

Here $I_R$ means the current due to the conductivity and $I_C$ is the current due to the capacitance. Integration over both sides one can obtain that

$$ \int_0^\pi P_s A \sin \theta d\theta = \int_0^{T/2} I_p dt. \quad (3.41) $$

the spontaneous polarization direction changes from $180^\circ$ to $0^\circ$ (from antiparallel to electric field to parallel to electric field) when electric field change sign in half period.

After integration one obtains
\[ P_s = \frac{\int_0^{T/2} I_p dt}{2A}. \] (3.42)

In real measurements, voltages drop on a resistor connected in series to sample is measured, rather than current. So the polarization can be expressed as:

\[ P_s = \frac{\int_0^{T/2} V dt}{2A \cdot R_s}. \] (3.43)

### 3.5.3 Block diagram of the experimental setup

The experimental setup for studying the electro-optical switching properties of the liquid crystals is shown in Figure 3.13. Liquid crystals are filled between two ITO substrates coated with alignment layer. Then the liquid crystal cell is placed into the HS400 heat stage (from -60°C to 400°C) made from *Instec Research Instrumentation Technology Inc.* In the heat stage there is a circular view window for optical microscope observation. The temperature of sample is changed by a temperature controller STC200 (*Instec Inc*) and the texture of sample is observed through Olympus microscope BX60 with cross polarizers. A CCD camera is attached to microscope and through a computer the textures of sample can be recorded in the form of still images or digital movies files obtained by a DVD or a VCR recorder. A photodiode is placed to the eyepiece of the microscope to monitor changes of the transmittance and the reflectance of the sample. Optical signals recorded by the photodiode are measured by the HP34401A multimeter where the testing data are recorded and stored. In addition to the direct measurement of
DC and AC conductivity, DSC, microscope texture observations, measuring changes of the transmittance of liquid crystal samples at ramping temperatures become very important methods to study the phase transition phenomena of liquid crystals.

The DC pulse or AC fields with various frequencies applied to the liquid crystal cell are generated by the HP 33210A function generator and the magnitudes of the electric fields are amplified 20 times through linear amplifier F20AD made by FLC Electronic Inc. Voltage signals from the photodiode, function generator and response of sample to the external fields are read and stored through the HP 54600 oscilloscope.

Figure 3.13: Block diagram of experiment setup for electro-optical properties study of bent-core liquid crystals.

With the set up shown in Figure 3.13, textures of the liquid crystals with function of external electric fields and temperatures could be recorded. In addition to spontaneous polarization, switching time and tilt angle could be studied with externally applied fields. As mentioned in the previous section, the spontaneous polarization could be obtained
from the time integration of the voltage drop across the resistor connected in series to the sample (shown in Figure 3.14).

Often triangular electric fields are applied to the sample cells, which provide easy deduction of the linear base line (see in Figure 3.14 (a)); Switching time can be obtained by reading time values corresponding to the peak of the polarization current (Figure 3.14 b).

The general method of determining the ferroelectricity or antiferroelectricity of the liquid crystals is by counting how many polarization peaks appear in the polarization current under triangular electric fields. For example, the Figure 3.14(a) showed a ferroelectric type switching curve because there is one major peak appeared in half period polarization current curve. Two peaks often appear in the antiferroelectric switching and they are symmetric along time axis. But when high frequency electric field applied, the liquid crystal molecules have no time to experience the transition from one ferroelectric state to antiferroelectric state, thus only one peak appears in the polarization current. Therefore it is not totally true to determine the ferroelectricity/antiferroelectricity of the liquid crystals by just counting numbers of peaks in the polarization current. The Diamant-bridge method (electric circuit is shown in Figure 3.15) for measuring polarization hysteresis is another method to determine ferroelectricity. It directly measures polarization values as a function of electric field.

An example of the hysteresis loop of a ferroelectric liquid crystal is shown in Figure 3.16. From the shape of the hysteresis loop ferroelectricity/antiferroelectricity of liquid crystals can be easily determined. The hysteresis loop does not pass the original
point if the ferroelectric polarization is tested while it does pass for antiferroelectric polarization (shown in Figure 3.16).

![Graph showing current through resistor and voltage applied over time](image)

Figure 3.14: 4-chlororesorcinol bis[4-(4-n-dodecyloxybenzoyloxy)benzoate] at 124°C, polarization current with function of time as electric field applied: a) triangular electric field $f=12$ Hz, $E=18$ V/µm, $P_s=115$ nC/cm$^2$; b) rectangular electric field $f=12$ Hz, $E=20$ V/µm, switching time $\tau=6.9$ µs.
Figure 3.15: Sketch of the circuit of Diamant-bridge method.

Figure 3.16: The field dependence of the polarization of 4-chlororesorcinol bis[4-(4-n-dodecyloxybenzoyloxy)benzoate] at 77°C (insert shows the hysteresis loop measured by Diamant bridge method).
References:

1 Metals become transparent at the plasma frequency $\omega_p$, which depends on the carrier density of the conductor. Most metals are opaque for visible light but ITO has a carrier density ~1% and $\omega_p$ is in the near infrared range, thus is transparent in the visible range. (see J.D. Livingston, “Electronic properties of engineering materials”, Wiley, MIT Series in Materials Science & Engineering (1999)


Chapter 4

Thermotropic Liquid Crystalline Properties of Amphiphilic Branched Glycolipids

Glycolipid is one of the three lipids found in the biological cell membranes. They contain polar (hydrophilic) sugar head groups and apolar (hydrophobic) alkyl chains. Glycolipids can be isolated from living materials, such as marine sponges\textsuperscript{1}, or they can be synthesized chemically or enzymatically.\textsuperscript{2} Some of them have immune-stimulating activity, which make them candidates for anti-cancer drugs\textsuperscript{3}, they play a role in cell fusion processes\textsuperscript{4,5} and membrane traffic in the course of an infection\textsuperscript{6,7}, and they are involved in cell surface recognition processes.\textsuperscript{8}

Lyotropic properties of synthetic glycolipids have been extensively studied in the last decade but studies of their thermotropic states are scarce.\textsuperscript{9,10} Their thermotropic mesophases are stabilized by the hydrogen-bond forming ability of the polar moiety\textsuperscript{11}, which is highly sensitive to temperature. In their thermotropic form they often exhibit smectic A\textsuperscript{12} phase with fluid bilayers, where the double layer spacing is consistently found to be smaller than two molecular length.\textsuperscript{13} These observations lead to the now widely accepted structure\textsuperscript{14} in which the alkyl chains partially overlap to form
interdigitated smectic A\textsubscript{d} bilayers. However the layer periodicity can also be explained by a locally tilted layer structure, where the tilt direction of the different layers is uncorrelated, resulting in the orthogonal smectic appearance, similar to the de Vries smectic A\textsuperscript{15} phase of thermotropic liquid crystals with aromatic cores.

Other than their phase structures, very little is known about their macroscopic physical properties, which justify our work in which we have studied their optical and dielectric properties in sandwich cell geometries. We compare their observed physical properties to typical thermotropic liquid crystals with aromatic cores and make efforts to explain their structure and phase properties.

4.1 Experimental Results

Molecular structures of glycolipids and their chemical nomenclature, phase sequence were listed in Table 2.1 of Chapter 2.

4.1.1 Structure and Properties

All branched tail materials had very wide mesophase ranges from below room temperature to over 100\textdegree{}C with clearing temperatures increasing with increasing molecular weight. The materials with the shortest branched chains (C\textsubscript{8-4}G\textsubscript{1} and C\textsubscript{6-2}G\textsubscript{2}), and the single chain C\textsubscript{12}G\textsubscript{1} exhibit only one broad smectic phase, whereas those with longer branched chains show transitions between columnar and smectic phases. The textures on cooling typically consist of much larger domains than on heating, thus enabling us to do better phase assignment. We found that at the transition to the mesophase sword-like domains form, and the fully developed textures typically consist of
leaf type fan shape domains resembling to thermotropic columnar phases. This texture is obviously different from that found in the single chain $C_{12}G_1$, which form the classical fans typical for SmA and SmC materials. The lower temperature phases of the first 4 materials resemble to smectic A phase.

The textures of $C_{14-10}G_2$ and $C_{14-10}G_1$ appeared optically isotropic in the temperature ranges between 85°C to 135°C (for $C_{14-10}G_2$) and 69°C to 91°C (for $C_{14-10}G_1$) between crossed polarizers in the heating process. This optically isotropic phase can be identified as a cubic phase.\(^\text{10}\) This is another unusual feature of these materials, since other thermotropic liquid crystals there are always fewer phases in heating than in cooling. The cubic phase is kinetically hindered and often do not show up at all. In $C_{12-8}G_2$, the cubic phase appears right below the fluid isotropic phase (see Figure 4.2/e and f). In this case the transition to the isotropic fluid phase is not visible in polarizing microscopy, but the transition is clearly seen by DSC and by the sudden change in the fluidity.

From the color of the films placed between crossed polarizers (in comparison to the Michael -Levi color chart), we deduce that all of the studied glycolipids have a birefringence smaller than 0.05, which is several times smaller than usual for calamitic materials. Due to the weak birefringence, in addition to the thin films of thickness between 5\(\mu\)m and 20\(\mu\)m, we have studied the materials in rectangular capillaries of 0.5 mm internal thickness, too. We observed that the birefringences are particularly small for the molecules with longer tails, indicating more disorder of the hydrophobic chains than
of the polar heads. Partially due to the lack of the nematic phase, these materials typically do not form aligned textures between rubbed polymer surfaces (see example in Figure 4.2)

![Figure 4.1: Transmittance vs. temperature of C_{14-10}G_2 in 0.5mm thick rectangle shape capillary.](image)

a, b and e) indicating the weak influence of the surface alignment layer on the material. This is probably due to the hydrophobic nature of the polymer coating, which leads to preferred contact with the more disordered hydrophobic tails. This argument could also explain that C_{8-4}G_1, which has a short branched tail, becomes aligned in rubbed polyimide surfaces (see Figure 4.2/c and d).
4.1.2 Dielectric Properties

Dielectric measurements were carried out in 5μm cells with polyimide substrates on all the materials listed in Table 2.1, except on C_{14-2}G_2, which we could not fill into the cells without formation of air bubbles.
All the studied materials exhibit much larger static dielectric susceptibilities than typical calamitic dielectric liquid crystalline materials. The susceptibilities are correlated to the number of sugar head groups: the dielectric susceptibilities of glucosides (one sugar head) are about 55-60, whereas of the maltose compounds (2 sugar heads) are in the range of 90-110.

Figure 4.3: Dielectric dispersions of the studied glycolipids at 30°C below their clearing points. The insert shows the corresponding Cole-Cole plots. In the Cole-Cole plots 1 is for the $C_{6-2}G_2$, 2 for the $C_{10-6}G_2$, 3 for the $C_{12-8}G_2$, 4 is for the $C_{8-4}G_1$, 5 is for the $C_{14-10}G_1$ and 6 is for the $C_{12}G_1$.

In Figure 4.3 we have plotted the frequency dependence of the real part of the dielectric permittivities 30°C below their clearing points for all the studied materials. The static dielectric constants are around 110 for maltoside lipids (two sugar heads) and 60
for glucoside lipids (one sugar head). These results show that the static susceptibility is primarily determined by the number of sugar head groups, although the effect of the chains is also noticeable.

Representative dispersion curves for a glucoside and a maltoside compound are shown in Figure 4.4. The relaxation processes in the glucosides become more distributed at lower temperatures, whereas for the maltosides the height and the width of the peaks are almost temperature independent.

![Figure 4.4: Dielectric spectra of C_{14-16}G_{1}(a), and of C_{12-8}G_{2} (b). The data were taken in the heating process.](image)

The temperature dependences of the relaxation frequencies are plotted in Figure 4.5. The relaxation frequencies strongly depend on the temperature, and on the structure of the phase. Typically maltosides have an order of magnitude lower relaxation frequency than of glucosides. Comparing the activation energies in the columnar phases shown in Figure 4.5, we see that they are about 2kcal/mol in glucosides and about 5kcal/mol in maltosides. This again correlates to the number of sugar heads. However, in the smectic
phases they are about 10 kcal/mol (except for $C_{14,10}G_1$, where it is 17 kcal/mol) independent of the number of heads, or branching. The activation energy is smallest in the isotropic phase, larger in the columnar phase and the largest in the smectic mesophase. In a given phase the activation energy decreases with increasing chain length, and it seems to be smaller in the branched chains than in the single chain substance (compare $C_{12}G_1$ with $C_{12,8}G_1$).

![Figure 4.5: Relaxation frequency in logarithmic scale of glycolipids as the function of $1/T$. Linear slopes correspond to Arrhenius behavior $f = Ce^{-E_a/k_BT}$. Vertical bars indicate the isotropic to meso-phase transition (clearing point). The numbers above the lines give the corresponding activation energy $\gamma$, which is determined by the slope of the relaxation frequency in logarithmic scale as the function of inverse absolute temperature, in kcal/mol units.](image_url)
4.2 Discussion

The thermotropic liquid crystalline properties of the amphiphilic sugar lipids differ in a number of respects from the properties of conventional thermotropic liquid crystals. They have lower birefringence and they show a tendency to align homeotropically on rubbed polymer surfaces, which for conventional thermotropics, rather promote planar alignment. This is due to the amphiphilic nature of the sugar lipids, where the polar heads tend to avoid contact with the hydrophobic polymer surface. The sugar lipids with branched tails have very wide mesophase range, with a tendency to form a columnar phase at higher, and a smectic A phase at lower temperatures. Note that in contrast to normal calamitics thermotropic liquid crystals. This is due to the random orientation of the tail groups at higher temperatures, which occupy larger space, thus stabilizing the columnar phase.

The appearance of the quasi isotropic textures in heating of the C_{14-10}G_2 and C_{14-10}G_1 materials is due to a cubic structure, which is quite common in lyotropic materials, but rather unusual from thermotropic liquid crystals.

The dielectric susceptibility of amphiphilic sugar lipids is much higher than of thermotropic dielectric smectic and columnar liquid crystals of aromatic cores. The strong correlation between the number of sugar heads and the magnitude of susceptibility reveals that polar head groups are very important for the field-induced polarization. This relation is only slightly modified by the non-polar hydrocarbon chains. We note that such high susceptibilities are observed only in connection with the so-called Goldstone mode of helical ferroelectric SmC* liquid crystals\textsuperscript{21}, suggesting that these materials may also
have tilted chiral smectic structures instead of the orthogonal smectic or columnar phases. (Indeed our previous studies\textsuperscript{22} suggested that the C\textsubscript{12}G\textsubscript{1} may have a locally tilted smectic structure, where the tilt direction of the different layers is not correlated.) The observation that in these materials the magnitude of the quasi-static dielectric constant is basically independent of the phase transitions and persists even in their isotropic phase, however shows that they are related to the molecular properties rather than to their phase structures. The temperature dependence of their relaxation times also differ from that of the Goldstone modes in SmC* materials: there they are almost temperature independent; here they show strong temperature dependences that can be described by the Arrhenius behavior (see Figure 4.5\textsuperscript{6} ). The strongly temperature dependent low relaxation frequencies are due to the hydrogen bonds between the head groups. Among the branched tail materials the relaxation frequencies are larger for the glucosides, indicating that the size of the hydrogen bonds is smaller than for the maltosides. This is understandable, since the maltosides have twice as many bonds where they can be linked to other heads. Concerning the activation energy, it is in general increasing as the order increasing. As for sugar lipids the smectic phase is more ordered than the columnar, we expect that the activation energy is increasing and the relaxation frequency is decreasing through the transitions from the isotropic to the columnar, and then to the smectic phase. This is indeed seen in Figure 4.5\textsuperscript{a} .
References:

6 D. P. Siegel et al, Biochem., 28, 3703 (1989)
Chapter 5

Characterization of novel bent-core liquid crystals

5.1 An optically isotropic bent-core liquid crystal

The discovery of the mesogenic properties of bent-core molecules has opened up a major new and exciting direction in the science of thermotropic liquid crystals (LCs). Seminal findings – with broad implications for the general field of soft condensed matter – include the observation of (anti)ferroelectricity and spontaneous chiral symmetry breaking in phases that are solid-like in one-dimension (smectic phases) but are composed of molecules that are not intrinsically chiral themselves.\(^{1,2,3,4}\) To date, most of the research effort has focused on bent-core smectics\(^5\), mainly since nematic phases are rather uncommon in bent-core compounds. This is because the translational freedom required for a nematic phase is typically favored when the molecules can rotate relatively freely around their long axis, a property that is not readily compatible with bent-shape molecules. Indeed, the viscosities associated with both director rotations and flow in the optically uniaxial nematic phase of bent shape molecules\(^6,7,8,9\) are unusually high, a feature that has led to the suggestion of a structure consisting of smectic “cybotactic” groups even far away from a smectic phase.\(^{10,11}\) Since the cybotactic groups are
uncorrelated and perpetually changing, we do not expect macroscopic polarization in the nematic phase, but only in polar smectic phase below the nematic. A few examples found recently include N-SmA-SmC-SmCP\textsuperscript{7,12} and N-SmCP\textsuperscript{8,13,14} polymorphisms. In these cases the SmCP phases were antiferroelectric and birefringent.

Recently Pelzl et al.\textsuperscript{15} and Weissflog et al.\textsuperscript{16} have reported a material 4-chlororesorcinol bis[4-(4-n-dodecyloxybenzoyloxy)benzoate] (4-CBDB) with an unusual transition from a nematic phase to an optically isotropic mesophase (I\textsubscript{M}) with local smectic structure. Both the nematic and I\textsubscript{M} phases are monotropic with the following phase sequence: (I \(95^\circ\text{C} \rightarrow\text{N} \rightarrow I\textsubscript{M} \rightarrow 80^\circ\text{C} \rightarrow \text{Cr}) \rightarrow 98^\circ\text{C}. By X-ray measurements the presence of cybotactic smectic groups was observed over the entire nematic range. In the I\textsubscript{M} phase a short range smectic structure with layer correlation length only about 22 nm was detected. The director tilt angle was found to be about 45\(^\circ\) both in the smectic phase and in the cybotactic groups, whereas the angle between the molecular arms (opening angle) was estimated to be 140\(^\circ\) in the nematic phase. It was also pointed out that in several aspects (weak birefringence, short layer correlation length) the I\textsubscript{M} phase is similar to the so-called smectic blue phases\textsuperscript{17}, although there are also a number of profound differences. First of all, the Smectic blue phases appear below the isotropic and above a TGB phase, whereas the I\textsubscript{M} lies below the nematic and above a crystal phase. Second, the X-ray profiles of Sm blue phases show definite peaks, whereas in the I\textsubscript{M} phase of 4-CBDB only uniform ring was observed, which points to random layer orientations similar, for example, to the sponge phase of lyotropic systems.\textsuperscript{18}
The aim of the present study is to determine more completely the properties of the IM phase, through a range of experimental techniques, and to thereby develop a more definite model for its structure. We will show in particular that the IM phase is ferroelectric, which, to our best knowledge, is the first account of an isotropic ferroelectric liquid crystal mesophase. Our measurements lead us to conclude that the IM phase consists of randomly aligned, roughly 20 nm size orthoconic anticlinic racemic smectic (SmC_{a}P_{F}) granules. We conducted polarizing microscopic, electric current, dielectric, and dynamic light scattering measurements on samples of 4-CBDB. Our measurements were complimented by dynamic light scattering measurement carried out in Prof. S. Sprunt laboratory.

- **Textural (polarizing microscopic) observations**

Samples of 4-CBDB were loaded into standard electro-optic cells treated with rubbed alignment layers for homogeneous alignment of the nematic director. In fresh cells, after cycling through the isotropic liquid, we observed uniform nematic alignment, with the optical axis oriented along the rubbing direction, over the entire nematic range (Figure 5.1/a). On cooling from the nematic phase there is a 1-2°C range starting at 80°C, in which the optically isotropic areas are decorated with birefringent filaments (Figure 5.1/c). This range indicates a coexistence of the N and IM phases. In addition, we observed that the pattern during the formation of the IM phase on cooling from the nematic reveals the features of the surface rubbing: the IM phase appears first in stripes along the rubbing direction (see Figure 5.1/c). On further cooling, or after applying
Figure 5.1: Typical textures of homogeneously aligned 4μm thick sample of 4-CBDB between crossed polarizers that are set along the edges of the pictures (320μm x 240μm areas). Upper row: textures at zero field. (a): fresh cell at 90°C; (b): texture after 5 heating-cooling cycles at 90°C; (c): texture at the N - IM phase transition at T=80°C (arrow indicates surface rubbing direction); Lower row: textures under electric fields. (d): T=79°C, electrode and non-electrode area under E=12.5V/μm, f=12Hz square wave field applied for 10 seconds; (e): T=77°C under 20V/μm 4Hz rectangular electric fields; (f) T=77°C under 20V/μm 345Hz rectangular electric fields.
electric fields of $E > 10\text{V/}\mu\text{m}$ for a few seconds, the texture becomes completely black between crossed polarizers (Figure 5.1/d). After a number ($>3\text{-}5$) of heating – cooling cycles we observed that the texture in the nematic phase becomes non-uniform (Figure 5.1/b) with left and right-handed domains similar to those reported previously$^{19}$.

- **Polarization measurements**

  Electric current measurements were performed on the samples described above first by the triangular voltage method. For E-fields above $\sim10\text{V/}\mu\text{m}$, we observed the appearance of single peaks in the current in each half period, which is a clear indication for ferroelectric - type polarization switching. The temperature and electric field dependences of the electric currents are shown in Figure 5.2/a and b, respectively. The peaks completely disappear in the nematic phase, which rules out the influence of ionic effects and assures the ferroelectric origin of the observations. We note, that in some cases one can observe only one peak even in antiferroelectric materials if the period of the applied triangular voltage is short compared to the ferroelectric - antiferroelectric relaxation time. To clarify this, we also have measured the polarization by the Diamant - Bridge method$^{20}$ (see insert of Figure 5.2/c) and observed only single hysteresis loop, again indicating ferroelectric type switching, down to the lowest frequency (1Hz) available in the measurement.

  The electric field dependence of the polarization determined from the hysteresis loop was found to depend on the history of the applied field. When the polarization is measured in decreasing fields, i.e. after a high field is applied, its value decreases slower
Figure 5.2: Summary of the electric current measurements on a 4μm thick sample of 4-CBDB in the IM phase. (a) Time dependent response under triangular voltages (E=25V/μm) at different temperatures; (b) Time dependent response at T=77°C under triangular voltages of different amplitudes; (c) The field dependence of the polarization at 77°C (insert shows the hysteresis loop measured by Diamant bridge method); (d) The field dependence of the switching time as determined by the current peak position under square wave fields at 77°C.
than it increases in increasing fields (Figure 5.2/c). The difference between the measured polarization in increasing and decreasing fields also depends on the time interval between the data collections, and shows memory fading over several hours.

The electric field dependence of the magnitude of the polarization at $T=77^oC$ is plotted Figure 5.2/c. The apparent polarization increases up to about $500nC/cm^2$ at $40V/\mu m$, which is the highest field we could reach without electric breakdown. At lower temperatures the polarization, measured at a fixed $40V/\mu m$ field decreases, but is still measurable down to $64^oC$. The apparent decrease is due to a continuous shift to higher switching threshold with decreasing temperatures. The reversible switching of the polarization occurred without any observable electro-optical response when the applied frequency was much lower (1-20Hz) than the inverse of the switching time ($1/\tau$=1kHz) (see Figure 5.1/e). However during switching at frequencies closer to the inverse switching time (200-800Hz), we observed brightening the texture in some isolated spots (see Figure 5.1/f).

- **Dielectric measurements**

  We measured the dielectric properties of a 5$\mu m$ film in the same type of electro-optical cell (with antiparallel rubbed polyimide alignment layers) over a 20Hz -1 MHz frequency range by a precision LCR meter (Quadtech, model 1920). Figure 3 displays the temperature dependence of the dielectric constants at two fixed frequencies (2kHz and 100 kHz). The data reveal the existence of a low frequency mode that relaxes above 2kHz. At 100 kHz the dielectric constant is smaller in the I$_M$ than in the homogeneously-
Figure 5.3: Summary of dielectric measurements of 4-CBDB. (a) Temperature dependence of the dielectric constant measured at 2kHz and 100kHz, and (in the inset) the relaxation of the dielectric constant at 2 kHz after a 16.5V/μm 27Hz triangular field was applied for 30 min; (b) Frequency dependences of real and imaginary parts of the dielectric constants before and after 5 and 30 min applications of the field.
aligned nematic phase indicating that the rotation around the average molecular long axis is much more suppressed in the $I_M$ phase.

The frequency dependences of the real and imaginary parts of the dielectric constants in the $I_M$ phase are also shown in Figure 5.3. The different curves correspond to the same sample right after it was cooled from the nematic phase and with no prior exposure to an electric field ("virgin" sample). The other two curves were measured after a 16.5V/μm 27Hz triangular field was applied for 5 minutes and 30 minutes, respectively. In all samples there is a higher frequency relaxation mode at around 450 kHz, which does not depend much on the field treatment applied prior to the dielectric measurement. There is another mode at around 7 kHz, which is weak in the virgin (or relaxed) sample, but strengthened substantially after field treatment. Its amplitude saturates after about 15 minutes of field treatment (or faster if higher fields are applied). At the saturated stage the strength of the susceptibility related to this mode is about 5. This low frequency mode decays slowly in time following an inverse logarithmic law (see inset of Figure 5.3/a), which implies a continuously slowing relaxation process at increasing time scales.

**Discussion**

One could explain the optical isotropy characteristic of the $I_M$ phase by assuming large single smectic domains with anticlinic tilt order, a 45° tilt angle and a nearly 109.5° opening angle of the bent cores. This situation indeed has been observed experimentally for an antiferroelectric anticlinic bent-core smectic with long-range layer correlations. However, in the presently studied 4-CBDB, the opening angle, at least in
the nematic phase, is far from the tetrahedratic \((109.5^\circ)\) angle, and the layer correlation length is short (~22nm). In this case, one can produce an optically isotropic structure by assuming that the short-range smectic order arises due to a collection of nanoscopic smectic granules, with an uncorrelated layer orientation between granules. Although the individual granules may be birefringent, the material would still appear optically isotropic, because the optical axis is randomly oriented in a length scale much smaller than the wavelength of visible light. A similar model was suggested recently by Huang et al\(^{25}\) and Ortega et al.\(^{26}\) without, however, any observation of ferroelectric switching. We note that the optical isotropy would be true for either anticlinic or synclinic director structure in the granules, although the anticlinic arrangement (with a \(~45^\circ\) tilt angle) would be much less sensitive texturally to small-scale deviations from the arbitrary orientation. The observation of local bright (birefringent) domains appearing in the texture (Figure 5.1/f) in square-wave fields where the time spent in each of the oppositely polarized states (corresponding to \(+E\) or \(-E\)) is comparable to the switching time of the polarization indicates that during switching from one ferroelectric state to the other the local birefringence increases. More sensitive measurements by light scattering (reveal that a very weak, locally induced anisotropy can occur in fields as low as several \(V/\mu m\). As illustrated in Figure 5.4, an increase in birefringence during switching happens only in the case of anticlinic arrangement when the switching takes place by rotation around the tilt cone. In all other cases (anticlinic with switching by rotation around the long axes and in both synclinic situations) the local birefringence would decrease during
Figure 5.4: Illustration of the variation of the local birefringence in case of different structures and switching processes. The local birefringence is indicated by ellipses. The closer the ellipse is to circle, the smaller is the birefringence. Gradient shading of the molecules indicates the direction of molecular kink (lighter areas indicate parts closer to the observer). Upper (lower) parts of both synclinic and anticlinic arrangements indicate switching the director around the tilt cone (around the long axis), respectively.
switching. The model about switching by rotation around the director cone is consistent with the study by Weissflog et al.\textsuperscript{16}, who suggested that the high frequency dielectric mode at \( \sim 500\text{kHz} \) is due to rotation around the long axis.

The proposed anticlinic structure is also compatible with the observations in the \( N-I_M \) coexistence region, illustrated in Figure 5.1/c and d. If the structure were synclinic, the surface anchoring would not influence the phase transition temperature, since this structure would be compatible with the uniform rubbing direction at the cell substrates. However in case of an anticlinic structure, especially for the 45\(^\circ\) tilt angle, in every other layer the director would need to be perpendicular to the rubbing, which would depress the transition at the surface regions. This is consistent with the observed pattern at the phase transition, and with 1-2\(^\circ\)C coexistence region characterized by a weakly birefringent pattern coming from the surface region. It also explains the observation that a strong electric field, which can break the surface anchoring (and thus switch the synclinic structure to anticlinic), can induce complete optical isotropy in this coexistence region. These considerations further imply that the structure is anticlinic both at zero applied fields and when strong fields are applied. This is consistent with the observed polarization current curves shown in Figure 5.2/a and b, and with the one loop hysteresis curve (Figure 5.2/c), indicating local ferroelectric order. Finally, the ferroelectric order also explains the low frequency dielectric mode that becomes stronger after poling the film by strong electric fields (see Figure 5.3/a).

The observation that the relaxation from the poled structure to the un-poled one follows an inverse logarithmic rule (see inset of Figure 5.3/a) is very similar to the nature
of the magnetization relaxation in spin glasses\textsuperscript{27} with a polydisperse size distribution of the magnetic granules.\textsuperscript{28} The stress relaxation from the randomly oriented state toward uniformly aligned liquid crystalline elastomers follows this behavior, too\textsuperscript{29}, as does the relaxation of granular materials from their lower density structure to the higher density final steady state\textsuperscript{30}. In all these examples, the relaxation follows a logarithmic rule, because as time goes on, it becomes more difficult for the granules to find the equilibrium, since most neighbors have already found their equilibrium orientation.

In the $I_M$ phase of 4-CBDB, due to the random distribution of the layer normals among the granules, the external electric field exerts a ferroelectric torque on the layers of the grains and (at sufficiently high field) eventually distorts the layers toward the electric field. This poling is more efficient when the field is applied just below the nematic phase, and saturation of the polarization could be observed. It is important to note that in the plane normal to the field the layers orientation would be still arbitrary, thus maintaining the optical isotropy for normal light incidence. The gradual relaxation towards the randomly oriented steady state indicates that the packing in the poled state is unfavorable. At lower temperatures, field-induced realignment of the granules is only weakly effective. In fact, one important difference between our model for the $I_M$ phase and the magnetic spin glass is that in our case the polarization can be switched within granules \textit{without} reorientation of the granules themselves. The dramatically reduced dynamic light scattering found in the fully developed $I_M$ phase shows that the granules are probably weakly bonded into local networks, similar to the structure of the lyotropic sponge phase\textsuperscript{18}.
Our proposed granular model for the ferroelectric I\(_M\) phase is summarized in Figure 5.5. Two quantitative checks of its self-consistency can be obtained from the polarization and dielectric data. First we may compare an estimated average wavenumber for relaxation of the poled state (\(q_{\text{ave}}\)) with the cut-off (\(q_{\text{max}}\)) determined by the grain size inferred from the X-ray measurements of the smectic coherence length (\(\xi\)). Soon after field removal, the net polarization, due to polarization self-interaction, will be averaged out. This can happen via a random distribution between the individual grains characterized by different coexisting periodicities with \(q_{\text{ave}} < q_{\text{max}} \sim 2\pi/\xi\) (where \(\xi \sim 22\text{nm}\)) \(^{19}\). In electric fields applied along the layers this random polarization becomes distorted leading to an induced polarization \(P_{\text{in}}\), which determines the static dielectric susceptibility as \(^{31}\)

\[
\chi = \frac{P_{\text{in}}}{E} = \frac{1}{2\varepsilon_0 K} \left( \frac{P}{q\theta} \right)^2
\]

(5.1)

In this expression \(K\sim10^{-11}N\) is the Frank elastic constant for azimuthal rotation of the tiled director, \(P\sim500\text{nC/cm}^2\) is the ferroelectric polarization, \(\theta\sim\pi/4\) rad (45\(^\circ\)) is the director tilt angle. The measurements gave \(\chi\sim5\), which provides \(q_{\text{ave}}\sim2x10^8\text{m}^{-1}\), corresponding to an average periodicity of about 30nm, which is well above the cut-off established by the estimated grain size. As a second check on consistency, the dielectric relaxation frequency of the switching process, involving rotation around the tilt cone, can be related to the rotational viscosity \(\gamma\) as

\[
f_r = \frac{Kq_{\text{ave}}^2}{\gamma}
\]

(5.2)
Taking into account that the measured relaxation frequency is 7kHz, Eq.(5.2) gives \(\gamma \sim 60\text{Pas}\). To see if this is a reasonable value, we utilize that the rotational viscosity can also be estimated from the switching time, measured at high fields, through the well-known formula\(^{32}\)

\[
\tau \sim \frac{\gamma}{P \cdot E}
\]

(5.3)

From Figure 5.2/d we see for example that at \(E=2 \times 10^7 V/\mu m\) \(\tau \sim 0.55\text{ms}\), which gives \(\gamma \sim 55\text{Pas}\), in complete agreement with the dielectric relaxation measurements.

![Figure 5.5: Sketch of the model of the optically isotropic ferroelectric phase of 4-CBDB.](image)

Lines within the smectic granules indicate the layer planes. Enlarged we show the local director structure and molecular polarization direction within the smectic layers. At high fields (\(E>30V/\mu m\)), and close to the nematic phase, the majority of the layers turn parallel to the field, but the layers between granules remain randomly oriented in the plane of the cell.

In principle, the optical properties during switching can also be explained by a different model proposed by Folcia et al.\(^{33}\), where a racemic structure is produced by a
mixture of anticlinic antiferroelectric nanodomains of opposite chiralities. To explain the low frequency dielectric mode in terms of this model, however, we would need to assume that the slow decay of this mode is related to the ferroelectric – antiferroelectric relaxation. It is hard to imagine that such a relaxation would follow the observed inverse logarithmic rule. A relaxation with an inverse logarithmic represents a cooperative process, where exponentially increasing time scales are associated with the motion toward the steady state: the more units found the equilibrium, the longer will it take for the rest to find the steady state. This is very different from the ferroelectric to antiferroelectric relaxation process, which is related to the interaction between neighbor correlated layers, and should not be influenced by the relaxation state of the ferroelectric order in the other granules, because the layers do not correlated in between the different granules.

Finally we note that the proposed anticlinic ferroelectric layer arrangement means that the chirality associated with the director tilt ("layer – chirality") alternates in subsequent layers (so called “racemic” structure\(^3\)). The optical activity observed in this material (after repeated cycling through the low temperature crystal and high temperature isotropic phases) (Figure 5.1/b and refs.\(^{1,5,16}\)) therefore occurs without macroscopic layer chirality, similar to that observed in the non-tilted solid B\(_4\) phase.\(^{34}\) In fact in a material with direct transition from the B\(_4\) to the B\(_2\) phase it was found\(^{35}\) that the conformational chirality induces eventually a layer chirality, however in a B\(_2\) material with no B\(_4\) phase it was found that both layer and conformational chirality coexisted, but they are not correlated.
In summary, we described the first optically isotropic ferroelectric liquid crystal phase, and proposed a structural model that accounts for all the experimental observations in the $I_M$ phase of 4-CBDB. Ferroelectricity in optically isotropic liquid crystals is not only a unique phenomenon, which has academic interest, but also may present new practical applications, where it is desired that the electronic information set by the polarization be decoupled from optical information.

### 5.2 A chiral asymmetric bent-core material

Liquid crystals of rod-shape molecules show mesoscopic chirality when they contain chiral molecules, such as cholesteryl derivatives, that usually form chiral nematic ($N^*$) phase. $N^*$ posses helical structures with pitch ranging from submicrometer to hundreds of micrometers, representing the transfer of chirality from molecular to mesoscopic scales. In addition to the nematic phase, chiral molecules may form smectic phases, too. Those materials form helical structures only if the director is tilted with respect to the smectic layers ($SmC^*$). Importantly in this latter case the simultaneous molecular chirality and director tilt may lead to the appearance of macroscopic polarization\(^3\), which can be switched with electric fields, thus showing ferroelectricity. The research during the last decade revealed that tilted smectic phases of bent-core molecules\(^1\) posses’ mesoscopic layer chirality\(^3\) even when the molecules do not contain chiral centers. This is the result of the polar packing of the bent-cores and the simultaneous tilt of the molecular plane with respect to the layer normal.

Recently it was shown that when one or more chiral carbons are incorporated in the molecules, for example in the hydrocarbon terminal chains, or by addition of chiral
dopants, two kinds of polarizations $P_b$ (due to the closed packing of the bent-shape molecules), and $P_c$ (due to the chiral and tilted molecular structure), can coexist. In this paper we describe studies on a chiral bent-core substance, which is terminated by an achiral alkyl side chain at one end and by chiral cholesteryl at the other end. This molecule combines the achiral bent-core unit with a chiral end chain, and also introduces asymmetry, since one end is rigid and bulky, whereas the other one is flexible and much smaller. In a smectic phase the first property may result in interplay between the polarization $P_c$ due to the chiral unit, and a polarization $P_b$ due to the polar packing of the bent-cores, such as observed recently by Binet et al. In addition the molecular asymmetry might result in nano-separation of the structure i.e. the cholesterol group would position in the same direction within one layer, thus leading to a longitudinal polarization $P_l$ along the layers. Due to the pear shape of these molecules, however such an order would be spontaneously splayed, which may destroy the polar packing thus leaving only a $P_c$. Our observations will show that the second scenario is realized and the material posses only a polarization due to the tilt and chirality introduced by the cholesteryl units.

- **Experiments**

The chemical structure of the studied material 4-((3-(4-(2-hydroxy-4-(5-(cholesteryloxycarbonyl) pentyloxy)benzylideneamino benzoxyloxy) phenoxy) carbonyl) phenyl 4-(decyloxy)benzoate is shown in Chapter 2 Table 2.2. The synthesis of this and similar substances with their phase sequences will be published separately. To express
the simultaneous presence of the bent core (B) and the chiral cholesterol unit (Ch) we shall call this material as B-Ch.

We have carried out DSC, dielectric spectroscopy, polarization current, polarizing microscopy, conductivity and electro-optical measurements to characterize the phases, the polarity and chirality properties of this material.

1) DSC measurements

DSC measurements indicate only one mesophase ($M_1$) in heating and two mesophases ($M_1$ and $M_2$) in cooling. The phase sequences were found to be:

In heating: $C_r$ 151.1°C (33.4J/g) $M_1$ 175.5°C (0.8J/g) $I$

In cooling: $I$ 174.5°C (0.8J/G) $M_1$ 138.3°C (10.5J/g) $M_2$ 52 Tg

X-ray measurements (carried out by Dr. K. Prasad in Centre for Liquid Crystal Research, Jalahalli, Bangalore, India) indicate a fluid state (diffuse peaks at wide angle) in the temperature range corresponding to the $M_1$ range of the DSC measurements, and a smectic phase in the $M_2$ range. From the small angle diffraction peak we conclude that the tilt angle is about 45°. At wide angles there is only diffuse peak centered at indicating fluid in layer structure, i.e. SmC phase.

2) Optical transmission, resistance and dielectric constant measurement

The temperature dependences of the integrated optical intensity between crossed polarizers on cooling indicate a phase transition in the $M_1$ range at 152°C that was not observable by DSC and X-ay measurements. Tentatively we will label the phase in the higher temperature range as $M_{1a}$ and the one at lower temperature range as $M_{1b}$. In thin (d<10μm) cells with planar anchoring the birefringence increases abruptly from zero in
the $M_{1a}$ to a value in the $M_{1b}$, which is about one third of the transmittance observed in the tilted smectic $M_2$ phase. The electric conductivity of the same cell measured at 100 kHz increases monotonously starting at $152^\circ C$ and reaches maximum upon the transition to the smectic phase (see Figure 5.6).

![Graph showing temperature dependence of optical transmission and electric conductivity.](image)

Figure 5.6: Temperature dependences of the optical transmission (integrated area: ~1mm$^2$) and the electric conductivity measured at 100kHz of a 5μm sample of B-Ch with planar boundary conditions.

Polarizing microscopic textures of the planar cells at selected representative temperatures are shown in Figure 5.7. The blue - fog type texture observed in the $M_{1a}$ phase resembles to the amorphous BPIII phase. The texture in the $M_{1b}$ phase is the oily streak texture typical of cholesteric liquid crystals.
Figure 5.7: Textures in the $M_{1a}$ and $M_{1b}$ phases of B-Ch. (a) ‘Blue fog’-type texture of 50μm thick film at 168°C, the black bar represents 100μm length. (b): Textures of B-Ch at T=145°C. The black bar represents 50μm length.

To measure the pitch in the $M_{1b}$ ($N^*$) phase we have made Cano-wedge cells (wedge angle is $2\cdot10^{-3}$). The pitch of the helix was determined by the periodicity of the Cano lines (an example is seen at 150°C in Figure 5.8/a). The pitch is basically linearly increasing at lower temperatures from 0.26μm at 151°C to 0.31μm at 140°C.

Figure 5.8: The variation of the pitch of B-Ch as the function of temperature in cooling.
The temperature dependence of the pitch indicates that the pitch of the double helix in the higher temperature BPIII phase is below 0.25μm.

Typical textures in the M₂ (SmC*) phase in planar anchoring conditions are shown in Figure 5.9. The textures are not typical for smectics with planar anchoring, where either fan-shape or focal-conic domains are usually observable. This texture rather looks like Schlieren-type textures decorated by chiral pattern. Especially interesting is the square-shape pattern as shown in Figure 5.9/c.

In cells with homeotropic anchoring the textures are dark both in the M₁a and M₁b phases. As M₁a was dark in case of the planar anchoring as well, this mean that M₁a is optically isotropic thus further assuring our previous assignment that M₁a is a blue phase (most probably BPIII). The quasi isotropic texture of the cholesteric (M₁b) phase is due to the short pitch of the material. The texture of the smectic phase looks very similar to that with planar anchoring (no sign of fan-shape or focal conic domains).
Figure 5.10: Texture (400μm × 300μm area) of the B-Ch in 2μm cell with homeotropic coating. (a): 164°C; (b): 145°C; (c): 130°C.

The dielectric constants were measured both in cells of planar and homeotropic anchoring between 100Hz and 1 MHz range. No relaxation is observable in this range. The temperature dependences of the dielectric constant measured at constant 100 kHz also indicate the M$_{1a}$-M$_{1b}$ transition at 152°C (see Figure 5.11). Interestingly the dielectric constants are very small in all phases and in both alignments. In addition, the anisotropy is very small, basically is within the measurement error, indicating that the director structures in the bulk are basically independent of the surface alignment.

Polarizing microscopic observations and electric current measurements show that the smectic M$_2$ phase is polar: the textures show linear electro-optical signals basically without any threshold and the time dependence of the polarization current show a ferroelectric peak, which disappears upon heating to the cholesteric phase, thus ruling out the ionic origin of the peak. The time dependence of the electric current under triangular wave voltages is shown in Figure 5.12 both in the smectic and cholesteric phases. From the area of the current peak above a linear slope corresponding to the ohmic current
indicates that the magnitude of the ferroelectric polarization is $30 \text{nC/cm}^2$. This value is much smaller than typical for bent-core smectics.

Figure 5.11: Temperature dependences of the dielectric constant in different samples of B-Ch with planar and homeotropic anchoring surfaces. The thickness of the samples with planar and homeotropic anchoring are 5 $\mu$m and 2 $\mu$m, respectively.

Figure 5.12: Time dependence of the polarization currents in the Mx phase (120$^\circ$C) and in the cholesteric phase of B-Ch (140$^\circ$C).
The linear electro-optical switching can be observed practically without any threshold. The Malthese crosses distort and rotate with the frequency of the electric field with angles that are proportional to the voltage applied. For relatively small fields ($E<10V/\mu m$) the switching and the texture are reversible: after field removal the original texture shown in Figure 5.9 reforms. However after switching the material with low frequency fields of amplitude $E>12V/\mu m$ a gradual change of the texture is observed. Focal-conic type defects appear which then remain stable even after field removal. For the thicker cells ($d>5\mu m$) stripes separated by about 1-3$\mu m$ distances appear indicating the presence of a helical structure with pitch of a few microns. The pitch decreases at lower temperatures. At increasing fields the helix disappears above a temperature dependent threshold (about 2$V/\mu m$ at 136°C and about 20$V/\mu m$ at 100°C). After helix unwinding the switching angle is about 90 degrees, and the rotation of the optical axis can be seen only by inserting a wave-plate between the sample and analyzer (see Figure 5.13).

In the higher temperature range ($>100^\circ C$) of the $M_2$ phase, where helical pitch is over 2 $\mu m$, we could make surface stabilized cells, where the helix becomes unwound by the surfaces. The textures in such state have relatively large birefringence. At lower temperatures, where the helical pitch becomes less than 2$\mu m$, the helix gradually reforms and the overall birefringence decreases, as it can be seen in Figure 5.14 (b and c). To test the dielectric anisotropy of the material, we have measured the dielectric constant both before and after applying 16$V/\mu m$ rectangular fields of 23Hz for 10 minutes at 122°C. This measurement was done in heating, where the transition to the $M_{1b}$ to $M_{1a}$ phase
Figure 5.13: Textures of B-Ch in a 5μm cell with planar anchoring at 105°C. Pictures represent 200μm × 150μm areas. Upper row: the cell is between crossed polarizers; bottom row: a waveplate is inserted between the sample and the analyzer by 45 degrees with respect to the analyzer. (a, a'): E=+20V/μm; (b, b'): E= 0V; (c, c'): E=-20V/μm.

Figure 5.14: Textures of B-Ch after 16V/μm rectangular fields of 23Hz applied for 10 minutes. (a) 107°C, (b) 89°C, (c): 72°C. Pictures represent 200μm × 150μm areas. occurred only at 166°C. It can be seen that in the M_2 phase the dielectric constant is smaller in the virgin cell characterized with the helical patterns of Figure 5.9 than in the
treated state with textures of Figure 5.13. There is basically no difference in the $M_{1a}$ phase, indicating again that it is a macroscopically isotropic structure.

![Graph showing temperature dependences of dielectric constants](image)

Figure 5.15: Temperature dependences of the dielectric constants of B-Ch measured in 2μm cells with substrates preferring homeotropic anchoring for rod-shape molecules. In the virgin cell no electric field was applied previously. In the treated cell the data were taken after 16V/μm, f=23Hz triangular field was applied for 10 minutes at 122°C.

- **Discussion**

  **$M_{1a}$ phase**: Our studies convincingly show that it is an optically and dielectrically isotropic phase. The textures strongly indicate that it is equivalent to the amorphous BPIII* phase (double twist cylinders with arbitrary orientation). Interestingly the blue
phase range is much more stable than observed usually. We note that in some respect this situation is similar to the blue phase induced by doping chiral nematic liquid crystal with non-chiral bent-core molecules\textsuperscript{40}, where the bent-core molecules assumed asymmetric configuration thereby acted as chiral dopants. In our case, instead of the bent-core dopant we have bent-core units chemically attached to the chiral cholesterol unit.

$M_{1b}$ phase: This is clearly a cholesteric phase with a short pitch in the range of 0.3\(\mu\)m.

$M_2$ phase: In case of closed packing of the bent-cores of B-Ch, the polarization of the tilted smectic phase would be expected to be well over 100nC/cm\(^2\), furthermore the switch of polarization would require well pronounced thresholds of about 3V/\(\mu\)m or larger, as usual for bent-core smectics. However in our case the spontaneous polarization is relatively small (about 30nC/cm\(^2\)), and the switching occurs basically without any threshold in conjunction with the disappearance of a helical structure. These observations and the X-ray results, that show tilted smectic structure, indicate that the $M_2$ phase is a chiral smectic C\(^*\) (SmC\(^*\)) phase. The spontaneous polarization therefore is solely due to the chirality and tilt, and not the polar packing of the bent-cores. This means that the head-tail symmetry is conserved in the smectic phase, which prohibits the close packing of the bent-core unit. This probably is due to the cholesterol units, which are much bulkier than of the alkyl chains, so the have to alternate to avoid splay of the director or bend of the layers, which costs high energy.

The 45\(^\circ\) tilt angle observed by the electro-optical and X-ray studies is usual for SmC\(^*\) materials with direct N\(^*\)-SmC\(^*\) transitions.
The similarities between the virgin cells between homeotropic and planar surface anchoring conditions can be explained by assuming that in both cases the layers are inclined by $45^\circ$ with respect to the substrates. Due to the small pitch therefore in both cases the bulk alignment are basically the same (see Figure 5.16), explaining the similarities between the measured dielectric constants on both types of the cells. It is also possible that the presence of the cholesterol unit induces homeotropic molecular alignment at the substrates independent of the surface conditions (as seen on the lower part of Figure 5.16 (a), which – due to the $45^\circ$ tilt angle - leads to the tilted layer structure. In this case, due to the helix, inside the director would vary between vertical and horizontal positions, i.e., the effective dielectric constant is $\varepsilon_{\text{virgin}} = (\varepsilon_{\parallel} + \varepsilon_{\perp})/2$.

The observation that at high fields the focal conic textures appeared and the measured dielectric constant changed compared to that of the virgin samples point to a permanent realignment of the layers to a bookshelf structure. The ferroelectric polarization peak appears only in this state and the switching angle is $2 \times 45^\circ$ after helix unwinding. The textures in this bookshelf geometry together with the projection of the effective optical index to the substrates are illustrated in Figure 5.16/b. In a fully reformed helical structure (at lower temperatures where $p < d$) the effective dielectric constant is $\varepsilon_{\text{hel}} = \frac{\varepsilon_{\perp} + \varepsilon_{\parallel}}{2} = \frac{3\varepsilon_{\perp} + \varepsilon_{\parallel}}{4}$. Accordingly $\varepsilon_{\text{hel}} - \varepsilon_{\text{virgin}} = \frac{\varepsilon_{\perp} - \varepsilon_{\parallel}}{4}$. Comparing this to the measurements shown in Figure 5.15, we can see that the material has a negative dielectric anisotropy of $\varepsilon_{a} = \varepsilon_{\parallel} - \varepsilon_{\perp} \approx -4 \times 0.3 = -1.2$. 
Figure 5.16: Proposed layer and director structures of the virgin and realigned samples of B-Ch. The head of the nails indicate tilting of the molecules toward the plane of the drawing. The symbols (↑, ↓, ⊙, ◯) indicate the electric polarization pointing (UP, DOWN, inside and outside), respectively.

(a): Virgin cells with planar and homeotropic surface anchoring conditions.

(b): Layer and director structures in the realigned bookshelf geometries under electric fields in different polarities (upper two cells) and at zero electric fields (bottom cell). The ellipses above the cells indicate the projection of the optical indicatrix to the substrates. In the two unwound states the optical axes make ±45° with respect to the polarizers and in the fully formed helical structures the texture is almost quasi isotropic.
In summary, we have studied the effect of the combination of the achiral bent-core unit with the chiral cholesteryl on the phase sequence and physical properties of the material. We find that the presence of the bent-core units induces a wide range of blue phase between the isotropic and cholesteric phase. We also have found a ferroelectric SmC* phase, where the bent-core unit does not seem to form a polar closed packing.

5.3 Asymmetrically fluorinated achiral bent-core material

The asymmetric bent-core liquid crystal material studied here is 4-((3-(4-(4-(Decyloxy)benzoyloxy)benzoyloxy)phenylimino)methyl)-3-hydroxyphenyl4-(decyloxy)-2,3-difluorobenzoate (molecular structure please refer to Chapter 2 Table 2.3, the original name was assigned to this compound is U496), which here we call B-2F expressing that it differs from the bent-core of the B-Ch by the two fluor atoms attached to one of the benzene ring of the bent-core. Note that it has the same hydrocarbon units as the one attached to the one end of B-Ch.

- Experiment

We have carried out DSC, dielectric spectroscopy, polarization current, polarizing microscopy, conductivity and electro-optical measurements to characterize the phases, the polarity and chirality properties of this material.

1) DSC measurements
DSC measurements indicate two mesophase ($M_1, M_2$) in heating and cooling. Also around 78°C glass transition was found in heating. The phase sequences were found to be:

In heating: $T_g\ 74.3\ ^oC\ M_2\ 115.2\ ^oC\ M_1\ 143.4\ ^oC\ I$

In cooling: $I\ 143.3\ ^oC\ M_1\ 114.5\ ^oC\ M_2$

2) Optical transmission, resistance and dielectric constant measurement

The phase behavior of B-2F under microscopy is determined by integrated transmitted light intensity between crossed polarizers, resistance and dielectric constant measurements. curves of transmitted light intensity, resistance at the function of temperature.

Figure 5.17: Temperature dependences of the optical transmission (integrated area: ~1mm$^2$) and the electric conductivity of B-2F measured at 100kHz of a 5µm sample with planar boundary conditions.
Figure 5.18: Different textures of B-2F (400µm x 300µm area) formed in high temperature range phase $M_1$ of B-2F a) 138.1°C b) 124.3°C c) 123°C.

Figure 5.19: Microscopic textures (160µm x 120µm area) of B-2F at a) 140.4 °C b) 133 °C c) 113 °C d) 110 °C.
temperatures showed the isotropic to M₁ transition at 140°C. Also there was another transition at around 115°C (Figure 5.17) in accordance to DSC results. When cooling from isotropic, several kinds of textures coexisted in M₁:

Dielectric relaxation spectrum was tested on 4.5μm planar aligned B-2F thin film. It showed high temperature range of B-2F had strong dielectric relaxation mode at 200 kHz. With transition happened at 115°C, dielectric relaxation at around 200 kHz disappeared and followed by another type of relaxation process. From curves of the imaginary dielectric constant with function of frequency, dielectric relaxation behavior is hardly observed. However weak dielectric relaxation process could be discovered by plotting ε'' in logarithm value (Figure 5.20). Quasi-static dielectric constant of B-2F in M₂ is much smaller than in M₁. As shown in Figure 5.20, quasi-static dielectric constant is around 35 in the M₁ phase. It went down to 4-10 in M₂ phase.

3) Switching Properties:

In M₁ phase no polarization and optical birefringence change are found at the field less than 6V/μm. After field removal, textures relaxed back to their original state. As field applied is larger than 6V/μm, antiferroelectric type of polarization peak appears, birefringence of domains decreased and showed racemic type of switching, i.e. optic axis of domain did not change with polarity of electric field applied. After strong rectangular electric fields applied for a few minutes, the racemic type switching turned into chiral switching (optic axis of domain rotates with polarity of electric field applied) as shown in Figure 5.21, Figure 5.22. After field removed, a low birefringent fan structures appear and after some time high birefringent stripes grow. Continued increasing field to as
Figure 5.20: Dielectric spectra of B-2F in $M_1$ at 125°C (a), $M_2$ range at 75°C (b), and relaxation frequency at the function of inverse temperature at whole temperature range (c).
much as 22.2V/μm, switching domains break into small fragments and became low birefringent under cross-polarized microscope. Rotating polarizer it can be found that optically isotropic domains break into two domains with brightness exchange when rotation angle of polarizer is opposite shown in Figure 5.21. This indicates rotation of polarized light in opposite direction in different domains.

Figure 5.21: Textures of B-2F M₁ phase in 4.5μm planar cell at rectangular field 0.1Hz, 137°C a) +17.7 V/μm b) – 17.7 V/μm c) high birefringent stripes grows in low birefringent fan domains formed immediately after 17.7V/μm removed. Under 22V/μm fields applied with analyzer uncrossed by +20° (d) crossed (f) -20° (pictures represent area of 400μm*300μm)
Figure 5.22: Time dependence of polarization current of B-2F at 125°C under 28 Hz triangular electric field at different amplitudes.

Figure 5.23: Reddish fan structure of B-2F in 4.5μm planar cell under 22.2V/μm 23Hz rectangular electric field at a) 133°C, b) 125°C c) 113°C d) 109°C, e) 105°C e) 89.4°C f) 84.5°C. Pictures represent 400μm x 300μm area.
Cooling under 22.2V/μm rectangular electric field, reddish fan domains began to grow in the region of grainy domains formed in M₁ phase as temperature decreases into M₂ phase. The switching in the M₂ appeared to be of chiral type switching. Interestingly at same time a lot of air-bubbles channel forms along smectic layers (Figure 5.23). In M₂ phase birefringence of domains decrease dramatically.

Magnitude of polarization is based on integration area of peak area above linear slope corresponding ohmic current. Antiferroelectric type polarization peaks disappeared in M₂ phase during polarization test under triangular electric field with same amplitude as applied in M₁ phase. Magnitude of polarization with function of temperature showed maxim of polarization reached to 900nC/cm² (Figure 5.24).

![Figure 5.24: Temperature dependence of B-2F polarization under 22.2V/μm, 13Hz triangular electric field.](image-url)
Testing polarization current under 22.2V/μm rectangular electric fields, we could measure switching time between two ferroelectric states. The results of switching time at the function of inverse temperature are shown in Figure 5.25:

![Switching Time vs 1/T(K⁻¹)](image)

**Figure 5.25:** Switching time of B-2F under rectangular electric field 22.2 V/μm, 23Hz at function of inverse temperature.

**Discussion**

- **M₁:** High temperature M₁ phase has antiferroelectric polarization with racemic type of switching, which is characteristic to the syntilinic antiferroelectric B₂ phase, SmCₜPₐ (‘s’ refers to syntilinic and ‘A’ means antiferroelectric). The result is large birefringence in the racemic state. When the antiferroelectric SmCₜPₐ is switched to ferroelectric state under rule of chirality conservation³, it became anticalinic SmCₜPₐ which explains the observed lower birefringence. However long time of electric field applied would induce chiral transformation⁴. Figure 5.21/a,b. Immediately after field is removed, the textures are in SmCₜPₐ meta stable structure. Longer time provided, textures relax back to ground
SmC$_s$P$_A$ state as shown in Figure 5.21/c. Observing darker and brighter domains (Figure 5.21/ d,e,f ) between slightly uncrossed polarizers indicates optical activity maybe due to reported conformational chirality (CT$^{22,41}$. Conformational chirality is assumed to be due to a propeller – type helical twisted configuration characteristic of the particular type of bent-shape molecules. The twisted conformation of B-2F is due to ester linkages connecting benzene rings at an angle with respect to each other. We noted that previously optically active domains with clear boundaries were observed both in antiferroelectric and ferroelectric states in an all-ester banana-shaped substance$^{22}$. Importantly, the domain boundaries did not correlate to those of different twist-chirality, indicating that the optical activity has a distinct origin from the layer chirality. Large static dielectric constant in M$_1$ phase indicates large polar contribution to dielectric constant. Relaxation behavior around 200 kHz may be due to bent-core molecules’ rotation around their long molecular axis$^{42}$. 

The M$_2$ has low birefringence anticlinic structures at zero field (Figure 5.19). Comparing this with antiferroelectric synclinic we get M$_2$ is anticlinic antiferroelectric (SmC$_a$P$_A$) ground state and can be switched to synclinic ferroelectric (SmC$_s$P$_F$). Also smaller static dielectric constant compared with that in M$_1$ phase indicates contribution from dipole moment of the bent-core molecules largely decreased, which is due to cancellation of dipole moment effect from anticlinic structure.

As a summary we see a transition between racemic to chiral antiferroelectric S$_m$CP phases. This transition could be induced either by temperature variation or by electric fields.
References:

Chapter 6

Liquid Crystal Mixtures

6.1 Bent-core liquid crystals mixed with a glycolipid

6.1.1 Introduction

Smectic liquid crystals of bent-core molecules recently attracted a lot of research interests because they can have ferroelectric or antiferroelectric properties without molecular chirality. Liquid crystals mixtures formed by bent-core molecules with rod-like molecules have been studied to understand the effects of molecular structure on the formation of smectic ordering\textsuperscript{1}. The study\textsuperscript{1} shows that in the binary mixture of bent-core molecules and rod-like molecules calamitic molecular structures play an important role in determining what kind of smectic phase forms in the phase diagram of mixtures. It is observed\textsuperscript{1} that biaxial SmA forms to fill the ‘gap’ between nematic and smectic in the mixture of nematic liquid crystal with double-swallow-tail type molecular structure and bent-core smectic liquid crystal. Meanwhile phase separation happened to mixtures of nematic liquid crystal with zig-zag molecular shape and bent-core smectic liquid crystals\textsuperscript{1}. Additionally organic solvents of low molecular weight had been mixed with bent-core liquid crystals to lower isotropic transition temperatures of the mixtures\textsuperscript{2,3}. It shows that\textsuperscript{2,3} polar solvent (xylene) can mix well with bent-core compound by solvent molecules
sitting between two bent-core molecules. The non-polar solvent, hexane, can mix with bent-core compounds by forming nano-separated layer of solvent molecules between of smectic layers of bent-core molecules.

A simple well known glycolipid dodecyl-\(\beta\)-D-glucopyranoside \(^4\) \((C_{12}G_1)\) (molecular structure shown in Tab 2.1), has a polar sugar head and a single alkyl chain. The pure \(C_{12}G_1\) has wide temperature range of smectic A phase, while in aqueous solution a number of mesophases appear\(^4\).

Bent-core compounds with hydrocarbon tails could also be regarded as weakly amphiphilic. Benzene rings and some polar linkage group such as \(\text{OCO}^-\), are hydrophilic part and hydrocarbon tail is a relatively hydrophobic part, which is proven by studying orientation of bent-core molecules on water surface as they formed monolayer films on water surfaces\(^5\). Therefore it can be very interesting to know the orientation of bent-core molecules in the mixtures with amphiphilic glycolipids. Inspired by a recent study showing that \(\text{C}_{12}\text{G}_1\) molecules can self-assemble into pairs of tilted and anti-ferroelectric double layers sandwiched between layers of bent-core molecules\(^6\), we have also studied mixtures of \(\text{C}_{12}\text{G}_1\) and several bent-core molecules that form various mesophases. Electro-optical, electric current and DSC studies were implemented to understand the interactions between the bent-core and lipid molecules. We find very limited miscibility of the lipid with bent-core molecules that form only nematic phase and wide range miscibility with smectogenic bent-core materials. Other features of the mixtures are more specific to the actual phase of the bent core liquid crystals (non-tilted, single or double tilted), and on their molecular structures.
6.1.2 Experimental Results

Three kinds of bent-core compounds BS10 (Fig 2.1), 9-CPOB (Fig 2.2), 4CN-3F-OPIMB (Fig 2.4) were mixed with C\textsubscript{12}G\textsubscript{1}. In the following section we discuss physical properties of those mixtures as a function of concentration (note: concentrations of mixtures, unless otherwise specified, are weight concentrations of bent-core compounds in mixture):

a. BS10 and C\textsubscript{12}G\textsubscript{1}

- **Phase behavior**

Mixtures with concentrations varying from 0 to 100% of BS10 were prepared at the isotropic temperature of the mixtures. Limited solubility with each other was found. Uniform mixtures were obtained for concentrations of 95%, 87%, 77%, 15% and 8%.

Based on our study we found that BS10 has a B7 phase of ferroelectric at high temperature and antiferroelectric at low temperature. Our discovery is different from previous observations\textsuperscript{7,8} which state that BS10 has only antiferroelectric B7 phase. Here we used B7 (FE) and B7 (AFE) to denote ferroelectric B7 and antiferroelectric B7 phase of BS10. Based on microscope textures between cross-polarizers and polarization measurements of mixtures, the binary phase diagram is shown in Figure 6.1.

The isotropic to B7 transition temperature decreased from 140°C to 133°C when 23% (wt) lipid was in the mixtures. But the B7 (FE) to B7 (AFE) transition temperature did not change very much. Also the B7 (AFE) to B3 transition temperature remained same. Therefore the B7 (FE) range was shortened but the B7 (AFE) range was unchanged.
Textures in B7 (FE) change from helical filaments which is the hallmark of B7 phase, to smaller leaf-like domains. As concentration reached 77%, a very low birefringence texture appeared as mixture cooling from the isotropic phase.

![Texture images](image1.jpg)

**Figure 6.1**: Binary phase diagram of BS10 and C\(_{12}\)G\(_{1}\) and related typical texture under crossed polarized microscope. The black bars in pictures represent 50\(\mu\)m length. The white bars in pictures represent 20\(\mu\)m length.

For mixtures with high C\(_{12}\)G\(_{1}\) concentration, isotropic to SmA transition temperatures decreased from 140\(^\circ\)C (pure lipid) to 129\(^\circ\)C as concentration of BS10 is 15% in the mixture. But the SmA to crystal transition temperatures increased. The needle like focal conic domains formed in SmA phase did not change as BS10 added. But
golden yellow stripes appeared in the textures of 15% mixtures below SmA to crystal transition. (shown in Figure 6.1).

- **Switching Properties:**

  Pure BS10 can be polar switched\textsuperscript{7,8}. Ferroelectric (FE) type switching at the high temperature range and was followed by anti-ferroelectric (AFE) switching at lower temperatures range is determined by the time dependence of the polarization current under triangular electric field as shown in Figure 6.2; The temperature dependence of polarization amplitude of BS10 is shown in Figure 6.3.

  The linear optical switching of B7 (FE) (rotation of optic axis as the polarity of electric field is reversed) under rectangular electric fields at low frequency indicates B7 (FE) is chiral ferroelectric. Under applied rectangular electric fields, no broke of switching domains indicates there is no layer tilting during switching. Therefore no out-of-plane polarization at B7 (FE) ground state. Based on information presented above, orientation of molecules in layer in B7 (FE) can be assigned as SC&AL (synclinic and antileaning)\textsuperscript{9}, which means bent-core molecular plane was tilted with respect to layer normal in the same direction for two adjacent layers. At same time directors of the molecules (average direction of the line connecting the ends of molecules) tilted at different directions with respect to layer normal. Therefore in-plane layer polarization pointed in the same direction. In the B7 (AFE) phases, the optic axis of the domains did not change under electric field reversal and also no layer tilting was observed (Figure 6.4). This indicates the B7 (AFE) orientation of bent-core molecules in the layers is still SC&AL\textsuperscript{9}. The synclinic-antileaning configuration in the antiferroelectric state can be
transformed to anticlinic-antileaning configuration under a rectangular electric field. But

![Graph](image)

Figure 6.2: Pure BS10 polarization current at the function of time at 136°C and 128°C under triangular electric field $E=25\text{V/μm}$ $f=23\text{Hz}$.

![Graph](image)

Figure 6.3: Temperature dependence of polarizations of pure BS10 under triangular electric field $E=25\text{V/μm}$ and $f=29\text{Hz}$, fit with $P=P_o*(1-T/T_c)^{0.28}$, $P_o=380$, $T_c=143$.

directions of in-plane polarizations in adjacent layers are opposite, so net polarization cancelled out at the ground state. Mixed with up 23% of $C_{12}G_1$, the mixtures still can be switched. Due to the large ionic effect (Figure 6.5), it was difficult to isolate a
spontaneous polarization peak from the ionic peak in polarization current close to the isotropic transition temperature. In Figure 6.6, we compare the polarization of the B7 (AFE) part when considering polarization of the mixture for different concentrations.

Figure 6.4: Switching textures of BS10 under 16V/μm, 0.1Hz rectangular electric field, a) 136°C positive pulse, b) 136°C, negative pulse; c) 128°C positive pulse; d) 128°C, negative pulse, pictures represent 160*120μm².
Figure 6.5: At 150°C (isotropic) time dependent of polarization current of BS10 under triangular electric field E=25V/μm f=23Hz.

Figure 6.6: Polarizations of BS10 and C12G1 mixtures in AFE at the function of relative temperature of B7(FE) to B7(AFE) transition under triangular electric field E=25V/μm.
A sharp decrease of the polarization of mixture was observed when 5% wt (12% mole concentration) \( C_{12}G_1 \) was added to the mixture (see in Figure 6.6). The amplitude of polarization decreased from 210nC/cm\(^2\) in pure BS10 to 163nC/cm\(^2\) in 95% mixture. This trend continued until at 77% concentration.

Switching time of the mixtures were plotted against the relative temperature with respect to B7 (FE) to B7 (AFE) transition is shown in Figure 6.7. Switching time first decreased as concentration of mixture decreased to 95% then increased when concentration continued decreasing. For 77%, due to the ionic effect in mixture, we can only obtain switching time value as temperature close to B7 (AFE) to B3 transition (shown in Figure 6.7). The rotational viscosity of the mixtures can be obtained from the slope of the switching time plotting as a function of 1/E (shown in Figure 6.8). Based on the slopes, the rotational viscosities of mixtures are: \( \gamma_{100\%}=0.228 \) (Pa.s), \( \gamma_{95\%}=0.122 \) (Pa.s) \( \gamma_{85\%}=0.08 \) (Pa.s):

Threshold electric fields remain constant in FE region and almost linearly decrease with temperature in the B7 (AFE) phase range in pure BS10 (in Figure 6.9). Comparing threshold electric field of mixtures in B7 (AFE) (shown in Figure 6.10), it is found that threshold electric fields decreased when concentration decreased. At the AFE to B3 transition temperature, all the threshold fields became 3V/\( \mu \)m.

Pure \( C_{12}G_1 \) is dielectric, so does not show polar switching. With 8% of BS10 mixed with \( C_{12}G_1 \), we found antiferroelectric type switching at 123\(^\circ\)C, but the switching quickly ceased and phase separation happened. At temperatures lower than 123\(^\circ\)C, polarization disappeared totally. For the 15% mixtures, Smectic domains motion under an applied
electric field was observed but no polarization was found. The switching process of 15% was also very interesting: After an electric field was applied to sample for several minutes we found SmA domains were realigned by the electric field (Figure 6.11).

b. 9-CPOB and C\textsubscript{12}G\textsubscript{1}

C\textsubscript{12}G\textsubscript{1} has very limited miscibility in 9-CPOB, however it is interesting to find that using C\textsubscript{12}G\textsubscript{1} as a chiral dopant, the nematic phase of 9-CPOB turns into a chiral nematic phase (in Figure 6.12). When an electric field was applied to the mixture, no spontaneous polarization was found.

Figure 6.7: Switching time of BS10 and C\textsubscript{12}G\textsubscript{1} mixtures changed at the function of relative temperature with respect to B7 (FE) to B7 (AFE) transition under rectangular electric field of E=25V/\mu m.
Figure 6.8: Switching time at the function of inverse electric field of BS10 and C_{12}G_{1} mixtures at same relative temperature respecting to T_{FE-AFE}.

Figure 6.9: Threshold electric fields at the function of temperature for pure BS10.
Figure 6.10: Threshold electric field of BS10 and C\textsubscript{12}G\textsubscript{1} mixtures at the function of relative temperatures to T\textsubscript{FE-AFE}.

Figure 6.11: 15% BS10 and C\textsubscript{12}G\textsubscript{1} mixtures SmA domains were realigned (left is before electric field applied and the right one is after field applied) under triangular electric field $E=18\text{V}/\mu\text{m}$ $f=0.5\text{Hz}$ for about 10 mins at 118$^\circ\text{C}$, pictures represent 480*320$\mu\text{m}^2$ region.
Figure 6.12: a) N* phase of 9-CPOB and C_{12}G_1 at 71.8°C (finger-print structure, typical to cholesterics) and b) temperature variation of pitch.

c. 4CN-3F-OPIMB and C_{12}G_1

4CN-3F-OPIMB has a SmA phase which is followed by the polar SmAP phase at lower temperatures\textsuperscript{10}. In order to avoid overheating the C_{12}G_1, a solvent was introduced in preparing mixtures rather than heating the two components to the isotropic state. Both components were dissolved in small amounts of chloroform (0.5ml). The solvent was then evaporated in open air at room temperature. The residue mixture was heated to 190°C on a heat bench for several minutes. Uniform mixtures with concentration of 91.2%, 80.4%, 70.3%, 60%, 50%, 7.5% were obtained by this method and filled into empty liquid crystal cell. Conductivity and polarization tests were implemented to characterize the phase behavior of the mixtures.

- Phase behavior of binary mixtures of 4CN-3F-OPIMB and C_{12}G_1

The conductivity measurement was carried out by applying 0.5V 2kHz sinuous electric field. The phase diagram of the binary mixtures and typical phase textures are given in Figure 6.13.
C\textsubscript{12}G\textsubscript{1} added into the mixtures has a great influence on the transition temperatures of the mixtures. For the mixture with 91.2\% of 4CN-3F-OPIMB, the isotropic to smectic A transition temperature was 157\degree C, 15\degree C lower than of the pure 4CN-3F-OPIMB. SmA -SmAP transition of 91\% mixture decreased to 106.3\degree C, 30\degree C below the transition of pure 4CN-3F-OPIMB. However SmAP to crystal transition temperature was almost unchanged, therefore the SmAP phase range shrank and the SmA phase range extended when C\textsubscript{12}G\textsubscript{1} added. As the concentration of the mixture decreased to 80.4\%, the SmA phase range increased to 63\degree C (almost twice as large as that of pure one), and SmAP phase range

![Binary phase diagram of 4CN-3F-OPIMB and C\textsubscript{12}G\textsubscript{1} and corresponding phase textures under cross polarizer. The blue bars represent 20\mu m length.](image)

Figure 6.13: Binary phase diagram of 4CN-3F-OPIMB and C\textsubscript{12}G\textsubscript{1} and corresponding phase textures under cross polarizer. The blue bars represent 20\mu m length.
shrink to 20 °C (one third of the pure 4CN-3F-OPIMB SmAP phase range). The size of batonnet domains in the SmA phase became smaller as the concentration of the mixture decreased. For the 70.3% mixture, the I-SmA transition is the same as the 80% mixture and SmA -SmAP transition temperature increased, not as we expected from previous trend. The isotropic transition temperature of the 60% mixture is as high as 204 °C, higher than that of other mixtures, and circular reddish domains formed in SmA phase, different from batonnet domains in higher concentration mixtures. At first we thought it maybe due to some contamination of in process of mixing. Another mixture with concentration close to 60% was carefully made and it was found isotropic transition was 190°C. This indicates the unusual phase behavior of 60% mixture is not due to contamination. Phase separation happened as concentrations below 50%.

Optical intensity test can reveal relative optical birefringence changes for different phases of mixtures. Temperature dependence of the transmitted optical intensity through cross polarizers was plotted in Figure 6.24: It showed that similar optical intensity behavior in 100%, 91.2%, and 80.4%: Birefringence first quickly increases then saturates in the SmA phase as temperature decreases. After the SmA to SmAP transition the birefringence has slight decrease in the SmAP phase range. For 70.3%, 60%, 50% mixtures there was sharp increase of optical intensity at the transition of SmA to SmAP, which is different from that of higher concentration mixtures.

By comparing the textures of different concentrations mixtures with the same film thickness at same temperature we can obtain information about birefringence changes with concentration. We choose the textures at the temperatures close to the isotropic
transition (shown in Figure 6.13, which could reveal the birefringence of SmA domains changes with concentrations) as the test samples. According to interference color chart we can estimate the birefringence of mixture, the result is shown in Table 6.1

Table 6.1: Birefringence of 4F-3CN-OPIMB and C_{12}G_{1} mixtures around 110°C

<table>
<thead>
<tr>
<th>Concentration</th>
<th>100%</th>
<th>91.2%</th>
<th>80.4%</th>
<th>70.3%</th>
<th>60%</th>
<th>50%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Birefringence ± 0.01</td>
<td>0.15</td>
<td>0.165</td>
<td>0.106</td>
<td>0.125</td>
<td>0.09</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Figure 6.14: Temperature dependence of optical intensity of 4CN-3F-OPIMB and C_{12}G_{1} mixtures in cooling process (different transmittance was due to test on different sample film thickness: 100% was 7µm, 80%, 70% were in 8µm cell and 90%, 60%, 50% sample were with 4µm cell).

For mixtures with high concentrations of C_{12}G_{1}, 7.5% 4CN-3F-OPIMB added into mixtures showed dilution effect, i.e. lowers down I-SmA and SmA-Cr transition temperature. We notice that golden yellow stripes appeared inside SmA domains and
elongated parallel to Smectic A layer formed by lipid molecules in the 7.5% mixture

Figure 6.15: Microscopic textures in 4CN-3F-OPIMB and C$_{12}$G$_{1}$ mixtures under cross polarizer: a) 100% at 108.9°C; b) 90.2% at 107.6°C; c) 80.4% at 108.8°C; d) 70.3% at 110.0°C; e) 60% at 110.0°C; f) 50% at 110.0°C; pictures represent 400μm x 300μm area.
(shown in Figure 6.16). This indicates some phase separation. Obvious phase separations happen as the concentration of the mixture is between 7.5% and 50%.

Figure 6.16: SmA domains of 7.5% mixture of 4CN-3F-OPIMB and C_{12}G_{1} at 129^\circ C (left) and 78.7^\circ C (right), pictures represent 160*120\,\mu m^2 area.

- **Switching properties of mixtures**

  Pure 4CN-3F-OPIMB has a SmAP phase\(^{10}\) and it can be polar switched. Antiferroelectric type switching is evident from the time dependence of the polarization current under triangular electric fields as shown in Figure 6.17. Temperature dependence of polarizations of mixtures at different concentrations are plot in Figure 6.18. Influences of C_{12}G_{1} to the polarization of the SmAP phase are more than a dilution effect. From 100% to 80% mixture, the maximum polarization decreases dramatically as concentration decreases. The maximum polarization for the 91.2% sample (molecular number concentration is 80%) drops to 550nC/cm\(^2\), about a one-third decrease, compared with that of pure 4CN-3F-OPIMB, 900nC/cm\(^2\). And the maximum of polarization of 80.4% (molecular number concentration is 60%) decreased to 312nC/cm\(^2\). However, as concentration reached 70.3%, the maximum polarization of mixture increased to
522nC/cm$^2$, about the same value as 91.2%. 60% and 50% mixtures can still be switched with antiferroelectric type polarization current under the triangular electric field. But threshold voltages of these two mixtures were very high. Only as an electric field larger than 30V/μm was applied, polarization peaks could be calculated with proper baseline shown in Figure 6.19.

![Figure 6.17: Time dependence of the polarization current under triangular wave voltage at T=120°C, f=29Hz of pure 4CN-3F-OPIMB.](image)

For 50% mixture, a triangular electric field as high as 32V/μm was applied, no obvious polarization could be calculated (shown in Figure 6.20).

For pure 4CN-3F-OPIMB racemic type of switching (optic axis does not rotate to polarity of electric field) in SmAP was observed as a rectangular electric field was applied$^{10}$. Switching of the 80% and 90% mixtures in the SmAP phase is similar to pure 4CN-3F-OPIMB except a small range of optical axis rotation was observed. However stripes appeared in the switching of 70.3% mixtures (Figure 6.21):
Figure 6.18: Temperature dependence of polarization of 4CN-3F-OPIMB and C$_{12}$G$_{1}$ mixtures with different concentration was plot as relative temperature to Smectic A to smectic AP transition temperature: 100%, 81%, 70% (E= 14V/µm), 91.2% (25V/µm), 60% (E= 39V/µm), 50% (E=35.5V/µm, polarization in glassy state).

Figure 6.19: Time dependence of the polarization current of 60% 4CN-3F-OPIMB and C$_{12}$G$_{1}$ mixture at T=86.6°C, f=31Hz E=39V/µm under rectangular electric field (left) and switching texture (right). The black bar represents 10µm.
Figure 6.20: Time dependence of the polarization current of 50% 4CN-3F-OPIMB and C_{12}G_{1} mixture at E=32V/μm f=29Hz triangular field at 98.5°C.

In the 7.5% mixture no polar switching was found. However as an electric field was applied phase separation occurred and 4CN-3F-OPIMB formed optically isotropic domains (seen in Figure 6.22).

From the temperature dependence of the switching time we can get the activation energy. Far from the phase transitions switching time follows Arrhenius type behavior, i.e. \( \tau = e^{-E_a/kT} \) \( (E_a \text{ is activation energy}) \) shown in Figure 6.23.

Changes of switching time of mixtures at same temperature do not exactly follow the trend of change of concentrations. However from the activation energy obtained from the switching time as a function of inverse temperature, it shows the following trend: activation energies first increase as concentrations of mixtures decrease (8.7kcal/mol in 100% and 18 kcal/mol in 80% mixtures). Continuing decreasing concentration to 70.3%, the activation energy of mixture increases to almost the same value as that in the 91.2% mixture, which matches other sudden changes in the properties of the 70.3% mixtures.
Figure 6.21: Switching texture of 4CN-3F-OPIMB and C\textsubscript{12}G\textsubscript{1} mixtures under rectangular field 14V/\mu m (a,b,c 100% (-, 0 ,+) at 110°C and after electric field ( 100% (d) at 110°C and 70.3% at 95°C (e)). Pictures represent 160\mu m *120\mu m area.

Figure 6.22: SmA domains (white yellow) in 7.5% 4CN-3F-OPIMB and C\textsubscript{12}G\textsubscript{1} mixture textures of and isolated 4CN-3F-OPIMB domain (black ) after 0.5 Hz 22.2V/\mu m triangular electric field applied, picture representing 160\mu m*120\mu m areas.
Figure 6.23: Switching time with function of inverse temperature of mixtures of $C_{12}G_1$ and 4CN-3F-OPIMB at different concentration at 14V/μm.

Figure 6.24: Threshold electric field at the function temperature for 4CN-3F-OPIMB and $C_{12}G_1$ mixtures with different concentrations.
such as phase transition temperatures, the maximum polarization and the threshold voltage (see Figure 6.24).

6.1.3 Discussion

- Physical properties of mixtures

  a) Miscibility of Glycolipid C\textsubscript{12}G\textsubscript{1} and Bent-core liquid crystal

  Three kinds of bent-core liquid crystals have been tested for their physical properties in mixtures with C\textsubscript{12}G\textsubscript{1}. They are respectively regarded to as B7 (SmCG, double tilted layer structure) smectic bent-core liquid crystal (BS10), nematic bent-core liquid crystal (9-CPOB), Smectic A and Smectic AP bent-core liquid crystal (4CN-3F-OPIMB). C\textsubscript{12}G\textsubscript{1} has wide temperature range of SmA phase. As expected from miscibility rule\textsuperscript{11} C\textsubscript{12}G\textsubscript{1} has best solubility in 4CN-3F-OPIMB with Smectic A and Smectic AP phase (up to 50% of C\textsubscript{12}G\textsubscript{1}), followed by the BS10 with the SmC\textsubscript{G} phase (up to 23% of C\textsubscript{12}G\textsubscript{1}). While for nematic bent-core liquid crystals, less than 5% of C\textsubscript{12}G\textsubscript{1} can be dissolved. It is understandable because there is less heterogeneity between the SmA of C\textsubscript{12}G\textsubscript{1} and the SmAP of 4CN-3F-OPIMB, both of which have molecule directors perpendicular to layer plane. In SmC\textsubscript{G} molecule directors tilt both in and out of the layer plane. In mixture of nematic bent-core liquid crystals with lipids, it is hard for the lipid molecules to follow the translational disorder of bent-core molecules in the nematic phase. But in some cases\textsuperscript{1}, uniform mixtures can form between nematic and smectic mesophases with a filling smectic phase appears to compromise difference between the nematic and the smectic phases. Also it is needed to point out that 9-CPOB has a short temperature
range smectic phase. In our case, the interaction energies (hydrogen bonding) between lipids molecules make lipid molecules aggregate into a layer structure rather than coupling with bent-core molecules with long range orientation order.

In mixtures with high concentration of lipids, small amounts of BS10 and 4CN-3F-OPIMB seem to form separated layers between the C_{12}G_{1} layers. The antiferroelectric type of switching in 8% BS10 and C_{12}G_{1} mixture may be due to the small amount of separated BS10 in the lipids. And it is reasonable that at temperatures lower than B7 (AFE) to B3 transition switching ceased. In both cases as an electric field applied, phase separation is obvious (in Figure 6.22).

b) Phase behavior

As a small amount of lipid molecules were added into the ‘ocean’ formed by the bent-core molecules, lipids molecules would firstly locate themselves between the bent-core molecules in favor of keeping the layer structures of bent-core molecules, rather than between smectic layers causing layer fluctuation around lipid molecules. As more lipid molecules was added, lipids molecules may have formed layer structures between bent-core molecules layers. Based on above images we can explain a lot of the observed phase behaviors of the mixtures comparing with that of pure bent-core liquid crystals: As concentrations of lipid molecules increase, isotropic transition temperatures, decreasing the birefringence of the domain, (C_{12}G_{1} has a very low birefringence (<0.05), detail in Chapter Four) especially in mixtures of BS10 and C_{12}G_{1} shown in Figure 6.1). However in mixtures formed by 4CN-3F-OPIMB and C_{12}G_{1} as shown in Figure 6.25 and Figure 6.26, lipids molecules can keep the SmA configuration as lipid molecules in the SmA and
SmAP domains of bent-core molecules. For the 60% mixture of 4CN-3F-OPIMB and C$_{12}$G$_1$, the isotropic transition is surprisingly higher than that of the any pure one. Textures of the SmA phase in the 60% mixture below the isotropic phase is totally different from that of the pure bent-core compounds. This behavior can happen only as new types of molecular structures are formed by two molecules (shown in Figure 6.26). High transition temperature, high threshold electric field for switching indicate higher order smectic phase formed by this new molecule structure.

C$_{12}$G$_1$ was known as a chiral dopant in lyotropic liquid crystals$^{12}$. So It is not surprising that 9-CPOB forms chiral nematic liquid crystal as C$_{12}$G$_1$ as chiral dopant in the mixture.

Small amounts of the bent-core molecules could easily sit in between lipid molecules or layers because of the C$_{12}$G$_1$ surfactant properties. However week interactions between lipids and bent-core molecules were easily broken by strong electric fields and therefore phase separations happen.

c) Switching properties

Switching properties of two polar mesophases (SmCG and SmAP) are largely affected by adding lipids: switching time, macroscopic polarization, and threshold electric field.

In the BS10 and C$_{12}$G$_1$ mixtures, lipids molecules separated the bent-core molecules apart. Polar interactions of bent-core liquid crystals were partial screened by lipid molecules. The dipole moment per unit volume decreased thus the macroscopic polarization decreased but not according to molecular number concentration. Also we can
explain the decreasing of rotation viscosity and the threshold voltage of the BS10 mixtures in the same way: dipole interactions between the bent-core molecules and the lipid molecules were weaker than that between bent-core molecules (except in case of 4CN-3F-OPIMB and C\textsubscript{12}G\textsubscript{1} mixtures). As electric fields were applied, molecules rotate to make the dipole moments of bent-core molecules follow the polarity of electric field. Now hindrance to this rotation is partially due to lipids, rather than totally from bent-core molecules. Therefore smaller fields were needed to switch the mixtures. The role of lipids molecules is similar to the lubrication oil between gears to make gears rotate more smoothly, which results in the decrease of rotational viscosity.

In 4CN-3F-OPIMB and C\textsubscript{12}G\textsubscript{1} mixtures, lipid molecules did not separate the bent-core molecules in the same way as the lipid mixing with BS10 (in fact two kinds of molecules forming close packing at 1:1 and 1:2 molecule number concentration) for lipids molecules also preferred the SmA type packing. At same time, strong interactions form between lipid molecules and bent-core molecules due to strong dipole moments of F atoms on benzene rings. Therefore it is more difficult for bent-core molecules to rotate responding to external electric field, which results in the increasing of the threshold field and the activation energy. When the numbers of lipid molecules and bent-core molecules are equal (1:1), new molecular structures form (Figure 6.26) which are polymer like structures linked by strong dipole interactions between bent-core molecules and lipid molecules. In this way lipids molecules could be electrically polarized and contribute to macroscopic polarization\textsuperscript{6}, which explains high activation energy of 70% mixture however larger polarization compared with 80%. As the number of the lipid molecules
continue increasing (60%wt concentration and 1:2 molecular number ratio), a stronger network structures formed due to alternated bonding formation between the lipid and the bent-core molecules (shown in Figure 6.26). This network structure is the reason of high threshold field and high isotropic transition temperature observed in experiments. As much as 50% lipids (molecular ratio of bent-core to lipid is 1:2.42) in the mixtures, some lipid molecules form separate layer structures.

- **Model of lipid molecules packing in mixtures**

  There are two ways that C<sub>12</sub>G<sub>1</sub> molecules can pack with bent-core molecules in mixtures: i) lipid molecules forms separated layers between bent-core molecules layers (not necessary as double layer); ii) lipid molecules sitting between bent-core molecules in the layers. Based on physical properties of mixtures we studied we believe both situations existing in our mixtures. But lipids molecules are more likely sit between bent-core molecules at low concentrations of lipids in mixture. This is different from situation reported<sup>6</sup> that lipids nano-separated layer structure formation in lipid and bent-core mixtures. It is obvious that bent-core molecular structures result in totally different packing positions of C<sub>12</sub>G<sub>1</sub> molecules in mixtures. Though the three bent-core molecules have same molecular backbone, including BO14Cl<sup>6</sup>, they have different mesophases with different substituted functional group: B7 in BS10 (S substituted tail), SmAP in 4CN-3F-OPIMB (F substituted tail and CN group at centered benzene group), and SmCP in BO14Cl (Cl atom at centered benzene group). Space hindrance induced by center group (Cl, CN) makes lipids molecules try to stay far from bent-core molecular center (close to tail or between layers). For 4CN-3F-OPIMB, strong electro negative group-F atom (small
molecular volume) induces large dipole thus attracting the lipids close to the tail of bent-core molecules. For BO14Cl it is reasonable to understand that lipid molecules try to stay far from the center of the bent-core molecules. Finally the lipid molecules would form separate layers between layers of bent-core molecules. In mixtures of BS10 and C_{12}G_{1}, however, the hydrophilic head of the lipid molecules would prefer to approach the O atom (stronger electro negative compared with N and S atoms and no space hindrance in center). The proposed packing models for mixtures of BS10 and C_{12}G_{1}, 4CN-3F-OPIMB and C_{12}G_{1} are shown respectively in Figure 6.25:

![Figure 6.25: Packing model of BS10 and C_{12}G_{1} into layer structure (left): BS10 is bow shape structure (yellow ball is sulfur atom). Rod like structure is lipid molecule. Right is packing model of 4CN-3F-OPIMB molecules with C_{12}G_{1} molecules. In left picture lipid molecules are close to center of bent-core molecules, while lipid molecule is close to tail of bent-core molecules in the right picture.](image)

Based on physical properties of mixtures of 4CN-3F-OPIMB and C_{12}G_{1}, we propose there is a super molecular structure formed when concentrations of mixture is around 60%. Details of this structure are shown in Figure 6.26. In this kind of packing style there is still space available in the center of bent-core molecules for adjacent bent-
core molecules to close pack. At same time opportunities of lipid molecules interactions between two neighbor bent-core molecules increase. In packing with BS10, lipid molecules sit close to the center of bent-core molecules, which prevents other bent-core molecules to come closer.

Figure 6.26: Molecular packing model of 4CN-3F-OPIMB and C12G1 mixtures at various concentrations. Red dots refers to sugar head of lipid and dotted blue line means strong bonding between sugar heads and bent-core molecules. As concentration increased to 55% (molecular numbers is 1:2), strong bonding makes whole structure like polymer network.
6.2 Mixtures of chiral and achiral bent-core materials

6.2.1 Introduction

In liquids, macroscopic chirality requires chirality at molecular level, whereas solid materials can be chiral without chiral molecules. Liquid crystals of rod-shape molecules show mesoscopic chirality in form of helical director structures, for example in the N* and SmC* phases, or in form of optical activity, for example in the blue phases, when they contain chiral molecules. In addition it was shown for tilted smectic materials SmC*, that the simultaneous molecular chirality and director tilt may lead to the appearance of the macroscopic polarization. The research during the last decade revealed that tilted smectic phases of bent-core molecules posses’ macroscopic chirality even when the molecules do not contain chiral centers. In fact, these materials may have two types of chirality: the layer chirality ($C_L$) due to simultaneous polar order and tilted director arrangements, and conformation chirality ($C_T$) due to spontaneous twisted molecular structure.

Depending on the relative orientations of the two-fold symmetry axis and the tilt direction, the layers can be either right-, or left-handed. In the adjacent layers, the sign of the chirality can alternate or can remain unchanged over micrometer ranges. Accordingly, two types of domains are possible: “racemic” (or antichiral) if the layer - chirality in the adjacent layers alternates, and “chiral” (or “homochiral”) if the next layers have the same handedness. Experimental observations of the SmCP phase verified that the ground states are mainly antiferroelectric (AFE), although ferroelectric (FE)ground
states have been observed, too.\textsuperscript{19,20,21} The \textit{AFE racemic SmCP} phase is synclinic, i.e. the molecules in the neighbour layers tilt in the same direction. In the \textit{chiral domains} the \textit{AFE} state is anticlinic and the optical axis is parallel to the layer normal regardless of the handedness of the domains. The \textit{AFE} arrangement can be easily switched to a ferroelectric (\textit{FE}) state by applying a sufficiently large external electric field. The racemic \textit{FE} state is anticlinic and the chiral \textit{FE} state is synclinic. Although in first approximation the individual layers keep their chirality during switching between \textit{AFE} and \textit{FE} states\textsuperscript{15}, extended application of electric fields can alter racemic domains to chiral or vice versa\textsuperscript{22,23}, or the sign of the layer chirality can even be flipped.\textsuperscript{24} Racemic domains can be rendered chiral by surface interactions, too.\textsuperscript{25} It is important to note that tilt chirality does not seem to cause either optical activity or helical textures, although they have been assumed theoretically.\textsuperscript{26}

Observing planar textures between slightly uncrossed polarizers, it is often found\textsuperscript{27,28,29,30,31,32} that the texture splits to darker and brighter domains. For polarizers uncrossed in the opposite sense, the darker and brighter domains exchange and for crossed polarizers, they have the same brightness. This behavior is attributed to optical activity and is argued to be due to a helical twisted configuration characteristic of the particular type of bent-shape molecules (twist, or conformational chirality, $C_T$). The simplest realization of twisted conformation is a propeller – type structure due to ester linkages connecting benzene rings at an angle with respect to each other.\textsuperscript{33} Optically active domains with clear boundaries were observed both in antiferroelectric and ferroelectric states in an all-ester banana-shaped substance.\textsuperscript{28} Importantly, the domain
boundaries do not correlate to those of different twist-chirality, indicating that the optical activity has a distinct origin from the layer chirality. The helical structure is thought to be formed with helical axis parallel to the layers$^{28,34}$, just like in twisted grain boundary (TGB) phase.

Of course, just like in case of rod-shape molecules, one can incorporate chirality on the molecular level ($C_m$), too. *Molecular chirality* can be introduced when one or more chiral carbons are incorporated in the molecules, for example in the hydrocarbon terminal chains, or by addition of chiral dopants. Although studies indirectly revealed the simultaneous existence of two kinds of polarizations $P_b$ and $P_c$ ($P_b$ is due to the closed packing of the bent-shape molecules, and $P_c$ is due to the chiral and tilted molecular structure), the value of $P_c$ could not be measured$^{35}$. 

In thesis we describe dielectric, electro-optical and polarization current measurements on binary mixtures of a chiral and achiral bent-core substances. The measurements not only directly prove the existence of $P_c$, but also give us new insights on the so-called $B_7$ structures.

### 6.2.2 Experiments

The two bent-core compounds were mixed by heating two compounds at isotropic temperature for several minutes. Molecular structure and rough properties of these two compounds could be found in Chapter 2 Table 2.2 (Sc242, here we refer as B-Ch for chiral cholesterol unit attached to one end of the bent core) and Table 2.3 (U496, here we assign as B-2F for it differs from the bent-core of the B-Ch by the two fluor atoms
attached to one of the benzene ring of the bent-core). Note that it has the same hydrocarbon units as the one attached to the one end of B-Ch. The synthesis and physical properties of these materials will be described elsewhere. Here we only summarize their main physical properties without the detailed measurement data.

The phase sequence of B-Ch in cooling is the following:

I \(174.5^\circ C\) BPIII \(153^\circ C\) N*\(138.3^\circ C\) SmC* \(52^\circ C\) Glass (Cr)

In heating from the crystal state, that eventually replaces the glassy state, directly melts to the cholesteric phase, which then turns to BPIII state only at \(7^\circ C\) below the clearing point of \(175^\circ C\).

Note the SmC* phase of the bent core B-Ch means that the bulky cholesterol side chain prohibits the polar closed packing of the bent-cores, i.e., the bent-cores can basically freely rotate around the long axis (along the line connecting the average two ends of the molecules). The spontaneous polarization therefore is arising only from the chirality – director tilt duality (Meyer’s mechanism\(^{13}\)), and not due to the closed packing of the bent – cores. This picture is consistent with the measured value \(P_s \sim 30 \text{nC/cm}^2\), which is an order of magnitude smaller than typical for “banana smectics”. The tilt angle in the whole SmC* phase is very near to \(45^\circ\), which is typical for SmC* with direct transition from the isotropic phase. As the consequence of the molecular chirality the director has a helical structure with pitch decreasing from about 4-5\(\mu m\) from the high end of the phase to about 1\(\mu m\) at the low temperature range of the SmC* phase.

B-2F has two antiferroelectric polar SmC phases with as large as \(900 \text{nC/cm}^2\) polarizations. The higher temperature phase is synclinic (SmC\(_s\)P\(_A\)) in between \(143.3^\circ C\)
and 114.5 °C. Due to the synclinic structure it shows racemic switching, which however eventually transfers to a chiral state when strong rectangular electric field is applied for a few minutes. After field removal an anticlinic chiral state forms and the original racemic synclinic state reforms only eventually. The lower temperature phase is anticlinic (SmC\textsubscript{apA}) even at zero field and shows linear electro-optical switching almost down to room temperature. Similar to the B-Ch material in the SmC* phase, B-2F also has a large (~45°) tilt angle in the SmCP phases.

Due to the similarities between the temperature ranges of the tilted smectic phases, one expects complete miscibility between the two substances. This offers an excellent opportunity to study how the molecular chirality and the chirality - tilt induced polarization in the SmC* phase of the B-Ch material can interfere with the bent-core packing driven polarization and the polarity - tilt induced layer polarization.

We have studied both contact preparations and uniform mixtures of B-Ch and B-2F by dielectric spectroscopy, polarizing optical microscopy, electric current and electro-optical measurements.

### 6.2.3 Results

As expected a complete mixing between the two materials was achieved without any phase separation over the entire 0 -100% range. Based on their characteristic optical (Figure 6.27), dielectric (Figure 6.28), polarization and electro-optical (Figure 6.29) properties, three concentration regimes can be distinguished.

Regime I: Mixtures containing less or equal than 40wt% of B-2F behave similarly to the pure B-Ch. The dielectric constants of these mixtures are low, although slightly
increasing from maximum of 4 to about 6 (Figure 6.28). In this range the blue phase and the cholesteric range continuously shrink and disappear at about 20wt% and 40wt% of B-2F concentrations, respectively. The smectic range however only slightly changes. The smectic textures forming under cooling without electric fields are similar to that of the pure B-Ch, i.e., they have low birefringence with chiral patterns indicating tilted layer structure (see Figure 6.30/b). Under relatively low bipolar electric fields the optical axis rotates back and forth, as can be seen in Figure 6.30/a and c. In this initial state no polarization peak can be resolved in the polarization current under triangular electric field (see Figure 6.31). However, just as for the pure B-Ch, after high field treatment the
Figure 6.28: Relative dielectric constant at the function of relative temperature of B-Ch and B-2F mixtures with different concentrations (in wt% of the B-Ch compound).

Figure 6.29: Concentration dependence of the polarizations $P_c$ and $P_b$ in B-Ch and B-2F mixture, furthermore the threshold electric fields $E_c$ and $E_b$ needed to switch them, respectively.
texture gradually transfer to a focal conic texture and ferroelectric polarization peak appears (see Figure 6.31), although the magnitude of the polarization decreases at increasing B-2F concentrations. Under low frequency electric fields in this range the texture does not show optical change upon field reversals between crossed polarizers (Figure 6.30/d). The optical axis however rotates by ±45°, which can be seen when a birefringent waveplate is inserted at 45 degrees between the crossed polarizers (Figure 6.30/e). When the field is removed a striped texture forms, which indicates helical structure of a few microns periodicity (Figure 6.30/f). Qualitative analysis of the patterns at different concentrations shows that the periodicity is slightly increases at increasing B-2F concentrations.

Regime II: (40wt%< \(c_{B-2F}<70wt\%\)) In this range the smectic phase appears directly below the isotropic phase. The virgin texture has even lower birefringence than of the pure B-Ch, but increases with B-2F concentration within this range (Figure 6.27). The static dielectric constant is still low and its maximum reaches only 7 (Figure 6.28). The textures show linear electro-optic response at fields less than 20V/µm (see Figure 6.32/a, b and c). However in this regime at higher fields the texture breaks into small domains, with each rotating with the frequency of the fields (see Figure 6.32/d), similar to that observed previously in some B7 materials. Simultaneously with this texture formation a single polarization peak appears in each half period of the triangular electric waveform with integrated area corresponding to \(P_s\sim70nC/cm^2\). Under cooling the peak area shifts to higher fields, and the texture contains both small moving and steady fan-shaped domains between crossed polarizers with apparent optical axis at 45 degrees with
the smectic layers. Just as for regime I, inserting birefringent plates reveal rotation of the optical axis by ±45°. Simultaneously with the appearance of these domains a polarization peak appears at low fields. At the transition temperature of about 120°C the low field peak is centered at around zero voltage, then it increases toward lower temperatures, as it can be seen in Figure 6.33: Below 115°C only fan shape focal conic domains can be seen.

Figure 6.30: Textures of 6wt% B-Ch and B-2F mixtures @130°C (area: 320µm x240µm).

Upper row: textures that have not been treated by high fields before. (a) +6.7V/µm; (b) E=0; (c) E=-6.7V/µm. Lower row: textures that have been treated by 15V/µm for a few minutes before taking the pictures. (d) E=±8.8V/µm; (e) textures seen with birefringent plates inserted between the crossed polarizers under +8.8V/µm (upper part) and -8.8V/µm (lower part); (f) at E=0.
Figure 6.31: Time dependence of the polarization current of pure B-Ch before and after high field treatment.

Figure 6.32: Textures of 4.5μm thick samples (0.4mm x 0.3mm) of 63wt% B-Ch & B-2F mixture at rectangular field (a) 125°C @ 0V/μm; (b) 120°C @ 16V/μm f=33Hz rectangular fields; (c) 80°C @ 16V/μm f=33Hz; (d) 125°C @ 22.2V/μm; (e) 120°C @ 22.2V/μm; (f) 80°C @ 22.2V/μm f=33Hz.
Figure 6.33: Time dependence of the polarization current in 63wt% B-Ch and B-2F mixture.

(Figure 6.32/f) and the magnitude of the low-field polarization is about 30nC/cm², slightly decreasing toward lower temperatures.

Regime III: At more than 70% of B-2F the mixtures resemble to the pure B-2F substance. The optical transmittance shows a transition from a high birefringent texture (indicating synclinic configuration) to a low one (indicating anticlinic structure) at about 20°C below the clearing point. This transition also shows up in the dielectric susceptibility, which decreases from a high value (25 for pure B-2F and 10 for the 75wt%) to about 3 at the transition to the anticlinic state (Figure 6.28). At low fields the time dependence of the polarization current shows a ferroelectric – type single peak at relatively low fields, very similar to regime I (Figure 6.34). Such a peak is absent during the switching of the pure B-2F, and amount to a polarization of less than 100nC/cm², indicating that it has the same origin as of the SmC* polarization of the B-Ch material. In contrast however to the pure B-Ch and the regime I mixtures, above a temperature and
concentration dependent threshold the polarization current shows antiferroelectric switching, similar to the pure B-2F material (Figure 6.34). Important to note that once the antiferroelectric peaks appear, the low field ferroelectric peak disappears and the texture becomes dark between crossed polarizers (see Figure 6.35/b) indicating the formation of anticlinic structure. Similar to the pure B-2F, the low birefringent state (with optical axis parallel to the smectic layers) remains metastable after field removal (Figure 6.35/c). It is also noteworthy to mention that the texture during high field switching breaks into stripes and small domains that mechanically rotate upon field reversals (see Figure 6.35/b and e). This observation is congruent with the increasing threshold toward increasing B-Ch concentrations as shown in Figure 6.29.

Another similarity with the pure B-2F is the observation that the low birefringent texture appears during high fields is optically active, i.e. the texture splits to darker and brighter domains under slightly uncrossed polarizers. For polarizers uncrossed in the

![Figure 6.34: Polarization peaks versus applied voltage for different ranges of applied voltages in region III of B-Ch and B-2F mixtures.](image)
opposite sense, the darker and brighter domains exchange and for crossed polarizers, they have the same brightness (see Figure 6.35/d, e, f).

### 6.2.4 Discussion

Based on the above observations we sketch the phase diagram of the mixtures as shown in Figure 6.36. The phase diagram, and the main observations can be understood by the molecular model illustrated in Figure 6.37.

*B-Ch* is characterized by a bent-core that is freely rotating around the “long axis” connecting the terminal groups, and as such forms ferroelectric structure dictated by the molecular chirality (left column of Figure 6.37). On the other hand, B-2F is characterized

Figure 6.35: Textures of 4.5μm films with 75wt% of B-2F. Textures represent 320μm x 240μm areas. (a) 125°C @ zero fields; (b) 125°C 22V/μm fields applied (c) at zero fields after the field of 22.2V/μm applied; (d) textures at 120°C under 22V/μm fields applied with analyzer uncrossed by +20°(d) -20° (f) or crossed (e).
by a bent-core that forms antiferroelectric order in the direction perpendicular to the tilt plane. Mixing these properties at the same temperatures where the individual structures form, they naturally form structures where the rotation around the long molecular axis becomes more and more restricted and biased along molecular planes pointing normal to the tilt plane. Similarly we can state that at increasing B-Ch concentrations the position of the molecular plane compared to the tilt plane becomes liberalized. The situations when the molecular plane is perpendicular to the tilt plane ($\phi$=90°, or 270°) correspond to

![Phase diagram of the binary mixtures between B-Ch and B-2F. Boundaries with sharp transitions are shown by solid lines, whereas those where the phase transitions are not sharp illustrated by dotted lines.](image)

Figure 6.36: Phase diagram of the binary mixtures between B-Ch and B-2F. Boundaries with sharp transitions are shown by solid lines, whereas those where the phase transitions are not sharp illustrated by dotted lines.

the B$_2$ or (SmCP) phases characterized by $C_2$ symmetry (see right hand side of Figure 6.37). In this case the local layer polarization is parallel to the smectic layers, so when the layers are parallel to the electric field, they do not have to be deformed during fully
switching of the spontaneous polarization. When the disorder is introduced by the addition of the B-Ch molecules $\phi \neq 90^\circ, 270^\circ$ states will also appear, although $\langle \phi \rangle = 90^\circ$ may still hold. The $\phi \neq 90^\circ$ states have $C_1$ symmetry, where the layer polarization has out of plane components, too. Without molecular chirality those out-of plane polarizations would average out in every layer on mesoscopic scale, and they would behave as “normal” SmCP materials. However the molecular chirality may introduce helical structures. In contrast to the SmC* phases of rod shape molecules (as seen on the left hand-side of Figure 6.37), however now the helix can form not only by a variation of the azimuth angle of the c-director, $\Phi$, but also by rotating the angle between the molecular plane and molecular tilt, $\phi$ as one crosses the layers. The rotation of $\phi$ therefore means the introduction of the out-plane polarizations in entire layers (see middle columns of Figure 6.37). We believe that all mixtures (except the pure substances) have some out-of-plane polarizations.
polarization components, with the largest importance in the regime II, where the switching threshold is the largest. This also can explain the observations that switching above this threshold involves breaking of the continuous texture and lead to mechanical deformations associated with the electro-optical switching in mixtures between 50-75% B-2F concentrations. Interestingly, under cooling this phase appears in form of helical filament and other exotic chiral superstructures, resembling to the so-called $B_7$ textures. This supports earlier models suggesting that some of the $B_7$ textures have $SmC_G$ structures. The ferroelectric switching is also typical for the $B_7$ structures and is consistent with the relatively small polarization ($P_o<100nC/cm^2$) in this range. We note that the $\phi \neq 90^\circ$ structure is equivalent with a tilt of the long axis with respect to the layer normal, which imposes steric stress resulting in deformation of the layer planes, furthermore a splay deformation of the out-of layer polarization component. This can explain the observations that the $B_7$ materials usually have modulated layer structures.

At the low (<40wt%) B-2F concentrations the polar packing of the bent-cores appear only in short (submicron size) range, and the phase macroscopically behaves as $SmC^*$. Interestingly the presence of the short-range bent-core packing appears in form of decreased polarization value from 30nC/cm$^2$ @ 0% to basically zero at high temperature range of the 50% concentration. At lower temperatures however the chirality – related polarization $P_c$ remains basically constant, maybe because the packing of the B-2F molecules tend to be anticlinic locally. This explains the $SmC^*$ type polarization switching below 115$^\circ$C of the 50-65% mixtures.

B-Ch in less than 20-30wt% concentrations mainly acts as chiral dopant, and
introduces chirality related ferroelectric polarization. In the antiferroelectric racemic domains at low fields, $P_b$ of the synclinic - racemic domains averages out but, due to the synclinic order and of the chiral molecules, a $P_c$ normal to the tilt plane similar to the SmC* phase is possible (see Figure 6.38). In this case, a relatively low electric field is able to unwind the helical structure, but would not able to switch the antiferroelectric $P_b$ which requires a higher threshold. Upon this antiferroelectric to ferroelectric transition, the synclinic structure becomes anticlinic and $P_c$ vanishes, leaving only a $P_b$ (Figure 6.38). Since it is ferroelectric, it cancels out for anticlinic structures, such as it was observed when the transition to the anticlinic structure was established. Comparing to previous results, it is very important that now the chirality – induced polarization $P_c$ could be separated from the bent-core packing related polarization $P_b$. $P_c$ is found to be an order

![Figure 6.38](image)

Figure 6.38: Illustration of the interplay of $P_b$ and $P_c$ for structures where $C_1=0$.

of magnitude smaller than $P_b$, but larger than of the pure B-Ch. This is because the molecular dipoles of $B-2F$ are much larger than of $B-Ch$ due to the presence of the highly
polar fluorine atoms. At lower temperatures when the anticlinic antiferroelectric
($C_L \neq 0$) phase forms, both $P_c$ and $P_b$ average out below the transition to the ferroelectric
state where the effective polarization becomes either $P_b+P_c$, or $P_b+P_c$. Since $P_c<<P_b$,
the measurements of $P_c$ is much more difficult in that case.

The optical activity observed in regime III seems to have the same origin as for
the pure B-2F substance, and should be related to the conformational chirality described
briefly in the Introduction.
References:


Chapter 7

Colloidal Crystal - Liquid Crystal Systems

7.1 Deposition of colloidal particles on patterned surface

7.1.1 Introduction

Micrometer size colloidal particles can self-assemble into periodical crystal structure which has various applications, such as photonic band gap (PBG) materials.\textsuperscript{1,2,3} PBG materials can even be tuned, for example if infiltrated by liquid crystals.\textsuperscript{4,5} This motivated recent studies of liquid crystals in regular (mainly 0.2-0.5 μm diameter) colloidal interstitial spaces\textsuperscript{6,7}, where the band-gap was tuned by temperature variation\textsuperscript{6}, or by electric fields\textsuperscript{7}. Full stop-band requires large difference of refractive index between the liquid crystal and the PBG material, for example such as envisioned by Busch and John\textsuperscript{4} with silicon backbone (n\textsubscript{Si}=3.45 and n\textsubscript{LC}~1.5). However such a large difference also amplifies the scattering effect of any defect, which can ruin the band gap. The effect of defects are much less important for colloid – templated liquid crystal systems, where the refractive index variation is small (<0.1-0.3), such as in silica (SiO\textsubscript{2}) particles system, where n\textsubscript{s}=1.45. Although such small refractive index modulation does
not produce band gap, even these colloid-templated structures can be useful, for example as switchable Bragg diffraction devices.\textsuperscript{8} If the difference of refractive indices between the LC and template is small, the maximum achievable change of the refractive index (tuning) is $\Delta n_{\text{max}} \approx c \cdot \Delta n_{\text{LC}}$, where $c$ is the concentration of the liquid crystal in the colloid crystal medium, and $\Delta n$ is the birefringence of the liquid crystal. For example, in case of face - centered cubic packing $c \sim 1 - \pi / \sqrt{18} \approx 0.26$, and for a typical liquid crystal material with $\Delta n \sim 0.15$, the tuning of the peak of the reflection spectra is expected to be less than 4%. In fact the experimentally observed\textsuperscript{7} value was only 2% in case of planar anchoring between the LC and silica particles, and it was zero for the homeotropic alignment. A third problem is that the tuning requires a very high field, which for strong anchoring between the liquid crystal and particles surfaces can be given as

$$E = \frac{\pi}{l} \sqrt{\frac{K}{\varepsilon_o \varepsilon_a}} \quad (7.1)$$

Here $K \sim 10^{-11} N$ is the effective elastic constant associated to director deformations (Frank elastic constant), $\varepsilon_o \varepsilon_a \sim 10^{-11}$ (SI) is the dielectric anisotropy, and $l$ is the average void size between the particles. Since, for close packed colloid particles the average void size is smaller than the diameter of the particles ($l < D$), for $D \sim 0.3 \mu m$ $E > 30V/\mu m$. In fact the experiment observations on an infiltrated opal system (silica backbone) with the same particle size the tuning required $E_{th} \sim 80V/\mu m$ fields.

In spite of these difficulties the subject is of high interest and any progress overwhelming any of the above problems should be considered as important step. This
may justify our present work, where we are focusing on the first problem, i.e. of the formation of the defects of both the colloid crystal and the infiltrated liquid crystal. Although there are number of methods to form single and multilayer colloidal packing, such as sedimentation from dilute solution, electric deposition, spin coating, vacuum filling, etc. They all are common in that the deposition starts at some substrates. For this reason the properties of the surfaces, e.g., surface roughness, are important factors in determining the structure of the photonic material. In addition, the interaction of the substrate surfaces with the infiltrated liquid crystals, and in between the colloid and liquid crystal, are also essential in determining the structure and optical properties of the colloid templated liquid crystal system.

The aim of this part in thesis is to investigate how different surfaces influence the structure of the colloid particles, and of the infiltrated liquid crystals. We also investigated how the interaction between the colloid particles and liquid crystals compare with the previous two surface interactions.

### 7.1.2 Experimental technique

Seven different types of substrates (clean, ITO coated and 5 different polyimide coated fused silica glasses) were prepared for the studies. The bare glasses were cleaned in ultrasonic bath filled with surfactant solution, rinse with distilled water, then with acetone, methanol, and isopropanol; the Indium Tin Oxide (ITO) was deposited in vacuum chamber. The polyimide (PI) coating was achieved by spin-coating with PI 2555 solution at 700rpm for 5s, in 10s ramping to 3000 rpm and then at 3000 rpm for 30s. The substrates then were pre-baked at 90°C for 5 minutes and further cured at 250°C for 90
minutes. The PI coatings were either non-rubbed, or rubbed by nylon wrapped roller unidirectionally, in two orthogonal directions, or in three directions making 120 degree to each other. We note that rubbed polymer surfaces are commonly used to align liquid crystals, although the physical mechanism of the alignment is still under discussion. The Berreman’s model\textsuperscript{11} based on the steric interaction between nanometer size grooves along the rubbing direction and liquid crystal molecules is generally accepted, however other theories, for example surface tension model\textsuperscript{12}, van der Waals’s force model\textsuperscript{13}, excluded volume effect\textsuperscript{14}, the “frictional rubbing and hot spot model”\textsuperscript{15}, have also been published to explain the surface alignment by rubbing. As a reference we have also studied the effect of photobuffing\textsuperscript{16,17} on non-rubbed PI substrate achieved by linearly polarized UV light.

To study the effect of rubbing on the deposition particles first we have recorded the surface profiles of the different surfaces by atomic force microscope (Digital Instruments MMAFM-2). As it is seen in Figure 7.1, grooves are about 100nm wide, and 10 nm deep, which are much smaller than the diameter of the colloidal particles used in the experiments.

Hydrophobic colloidal particles with negative surface charge due to ionized sulfate groups with diameters of 0.3µm and 2.6µm were purchased from Interfacial Dynamic Co. The originally 2wt% particles solution in distilled de-ionized water was diluted to 0.05wt% in the experiments.
For the deposition technique, the simple evaporation method was used, which has two competing effects on the deposition of the particles. Firstly in the presence of water the mobility for the particles allows them to find their positions most compatible with the surface properties; for example polystyrene particles are hydrophobic, and they prefer to be in contact with more hydrophobic ITO covered area compared with areas of non-ITO covered. Secondly, as the water evaporates, the air - water interface moves, dragging the particles to the interfaces. The air water interface tends to follow the hydrophilic areas, therefore constraining the particles to go to hydrophilic areas. Due to these competing effects, in spite of the simplicity of the method, by varying the evaporation speed one can deposit the same hydrophobic particles either on the hydrophobic or hydrophilic areas of patterned substrates as we demonstrate it in Figure 7.2.

Figure 7.1: AFM image of different rubbed surfaces: a) Rubbed in one direction (5µm x5µm); b) Rubbed in two orthogonal directions (10µm x10µm); c) Rubbed in three direction making 120° to each other (2µm x2µm).
Figure 7.2: Deposited monolayers of 0.3μm and 2.6 μm size polystyrene particles on silica glass surface with patterned indium tin oxide (ITO) stripes. a.) 0.3μm particles deposited on the ITO covered (hydrophobic) areas after dipping the glass fully in solution and letting the water evaporate. The black bar represents 100μm length. b.) 2.6μm particles deposited on the ITO covered (hydrophobic) areas after dipping the glass fully in solution and letting the water evaporate. The black bar represents 20μm length; c.) 2.6μm particles deposited on the non-ITO (hydrophilic) areas when a drop of solution placed on the glass and the water shrank to the hydrophobic area dragging the particles with it. The black bar represents 20μm length.

The deposition process and the colloid crystal structure were observed under optical and scanning electron (SEM) microscopes.

The colloidal crystals were infiltrated at room temperature by simply placing a drop of liquid crystal pentyl-cyanobyphenyl (5CB), which has a nematic phase at room temperature up to 35.5°C, where it goes to an isotropic liquid phase. Due to the capillary effect formed by the particles 5CB spread out and infiltrated the voids. After the process
finished the extra liquid crystal material has been wiped away and the film was covered by one of the surfaces used to study the formation of the colloid particles.

7.1.3 Result and Discussion:

1.) Particle deposition

The effect of rubbing on the deposition of 2.6µm diameter particles during a free evaporation process is shown in Figure 7.3. The particles far from the edge of the droplet tend to form 10~100µm long strings (depending on length of grooves) along the rubbing directions. In case of rubbing in multiple directions strings tend to form in all the rubbing directions.

Figure 7.3: Sedimentation of 2.6µm colloidal particles in freely evaporating water solution. a) Surface rubbed in one direction and far from the droplet boundary the particles tend to form lines along rubbing direction. The black bar represents 20µm length; b.) water boundary moving more or less following grooves; The black bar represents 20µm length.
As the solution dries the water boundary moves inward and drags the particles at the water- air interface. During this process the majority of the previously formed strings breaks apart, and rearrange to patterns corresponding to the shape of the boundary surface. This however does not always completely ruin the previously formed structures, because the water boundary itself tends to move along the rubbing grooves. Although, similar to rubbing, photobuffing is also effective for aligning nematic liquid crystals\textsuperscript{16,17} we have found no effect of photobuffing on the deposition of the particles. This indicates that the steric effect of the grooves is necessary for the alignment of the colloid structures, whereas it is not necessary for the liquid crystal alignment.

During the evaporation of the water from 0.3\,\mu m diameter particle suspensions the water boundary moves inward in increasing speeds, resulting in spectacular radial defect structures, for example such as shown in Figure 7.4.

Figure 7.4: Texture of a colloid crystal film of 0.3\,\mu m polystyrene balls. The lines are cracks in the crystal formed during evaporation of the water. The direction of the cracks is normal to the moving water-air front during the evaporation process (left, the black bar represents 100\,\mu m length). With SEM we could see that in 0.3\,\mu m colloidal particles formed hexagonally packing on the substrates (right, view angle was 45\degree to substrates).
The local packing of the particles is easily seen by optical microscope for the 2.6µm particles, which reveal point defects and grain boundaries (see Figure 7.5). It is also seen that the structure is considerably influenced by the structure of the underlying substrates. Typical close-packed structures of 2.6µm diameter polystyrene particles are shown in Figure 7.5. The majority of the particles form close packed hexagonal structure (each particles have 6 neighbors (coordination number: Z =6), however perpendicularly rubbed surfaces often provides rectangular local structures (see Figure 7.5/d), or on non-rubbed surfaces disordered clusters with fluidlike order.

We have measured the areas and linear sizes in two orthogonal directions of monodomains (those that do not contain grain boundaries) for several hundreds of domains. We determined the size distribution of the linear dimensions and the average areas of the monodomains formed on the different substrates. The surface anisotropy was characterized by the ratio of monolayer domain size parallel and perpendicular to the rubbing direction. For substrates that had been rubbed in three directions, anisotropy was defined as ratio of the largest value to the smallest value in three rubbing directions. We found that the distribution of the domain sizes can be best fitted by a Lognormal distribution \( f(x) = \frac{e^{-\ln(x/c)^2/2\sigma^2}}{\sqrt{2\pi} \sigma x/c} \) which is useful for random variables constrained to be greater than zero (it also describes the size distribution of rock fragments crashed by repeated hammering action).
Although within the measuring error we cannot see convincing effect of the surface anisotropy on the anisotropy of the monodomain size, we do see significant effect of the surface on the average size of the monodomains (see Table 7.1).

Figure 7.5: Optical microscope texture of typical domains of \( D=2.6\mu m \) colloidal particles on different substrates: (a) on ITO plate; (b) on unidirectionally rubbed PI substrate; (c) monodomain hexagonal structure on 3x rubbed PI substrate; (d) monodomain with rectangular structure on 2x rubbed PI substrate [Diffraction pattern were observed by inserting Bertrand lens of microscope to focus the interference light.]
Figure 7.6: Size distribution of monodomains measured parallel and perpendicular to the rubbing direction of PI substrates and the fits assuming Lognormal distribution.

Table 7.1: Average sizes and anisotropies of the domains on different surfaces. The average anisotropy is defined by the ratio of average domain size measured in horizontal and vertical directions.

<table>
<thead>
<tr>
<th>Type</th>
<th>Size(μm)</th>
<th>Anisotropy</th>
</tr>
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<tbody>
<tr>
<td>ITO coated substrates</td>
<td>53±2</td>
<td>0.97±0.1</td>
</tr>
<tr>
<td>Clean glass (no coating)</td>
<td>33±2</td>
<td>1.02±0.1</td>
</tr>
<tr>
<td>PI coating, no rubbing</td>
<td>28±2</td>
<td>1.02±0.1</td>
</tr>
<tr>
<td>PI rubbed in one direction</td>
<td>43±2</td>
<td>1.1±0.08</td>
</tr>
<tr>
<td>PI rubbed in two directions</td>
<td>44±2</td>
<td>1.01±0.1</td>
</tr>
<tr>
<td>PI rubbed in three directions</td>
<td>46±2</td>
<td>1.06±0.1</td>
</tr>
</tbody>
</table>
The average sizes of the monodomains vary between 30µm and over 50 µm, which is larger than that typically found in silica colloids. In our case the largest monodomains found on ITO substrates, whereas the non-rubbed PI substrates produce the smallest monodomains. Rubbed PI substrates result intermediate size domains basically independent of the number of rubbing directions. These observations can be related to the wetting properties of the water on the substrates. Water best wets clean glass and worst the ITO coated one. This can be seen when the solution is dipped in glasses with patterned ITO layers, where the solution completely covers the non-ITO area and avoids the ITO areas. The wetting on the polyimide is moderate. For good wetting the droplets extend to large areas forming thin films that evaporate quickly, leading to a number of simultaneous aggregation sites and small domains. On the other hand, when the solution does not wet the surface, lenses form that evaporate slower due to the decreased surface per volume ratio. This slower evaporation allows more time the particles to find their lowest energy positions corresponding to the closest packing thus resulting in larger monodomains. The effect of the polymer coating is probably related to the roughness of the surface, which hinders free sliding of particles on the surface, thus make them more difficult to find their best positions. Although the grooves resulted by the rubbing are only about 10nm deep (see Figure 7.1) which is much smaller than of the diameter of the balls, they provide smoother channels, thus able to guide the deposition of the particles along rubbing direction.

2.) Alignment of infiltrated liquid crystal
To study the alignment of liquid crystals on the substrates in the presence of the colloid particles we have infiltrated pentyl-cyanobyphenyl (5CB) in colloid crystal formed by 0.3 μm and 2.6μm diameter polystyrene balls. In case of 0.3μm particles we have found optically isotropic texture, which means isotropic distribution of the liquid crystal director in the visible optical range (high transmittance under non cross polarized microscope indicates optically isotropic texture is not due to light scattering).

Figure 7.7: Polarizing microscopic textures of 6μm thick film of 0.3μm diameter polystyrene particle crystal infiltrated by 5CB (pictures represent 0.4mm x 0.3 mm areas) at zero electric field (a) and under 20V/μm field (f=1 kHz).

This is in agreement with the observations of Kang et al.\textsuperscript{7}, and shows that the surface extrapolation length $b=K/W$ ($K$ is the curvature elastic constant and $W$ gives the surface interaction strength) is small compared to the void size. This means that the surface is strong enough to establish the surface-preferred pattern of the director in the voids. Visible transmission measurements by OceanOptics 2000 spectrophotometer placed in the eyepiece of the polarizing microscope is shown in Figure 7.8. From the
downward shift of the peak positions we conclude that the average refractive index decreased by 0.5% and 1.6% for the 60V and 120V, respectively. Based on the considerations of Kang et al., this indicates planar anchoring between the liquid crystal and the polystyrene particles. Considering the birefringence and fill factor of the liquid crystal this indicates switching of the director structure from the isotropic to the almost fully homeotropic configuration at about 4 times smaller fields than that found in the silica opal system.

Figure 7.8: Transmission spectra of 6μm thick film of 0.3μm diameter polystyrene particle crystal infiltrated by 5CB at room temperature under 0, 60 and 120V applied.
Because the surface properties of the 0.3 μm and 2.6 μm PS balls are supposed to be identical, we expect therefore deformed liquid crystal alignment consisting of defects in the voids formed by 2.6 μm particles. However after infiltrating liquid crystal 5CB in colloid crystal formed by 2.6 μm diameter polystyrene particles we observed formation of uniform liquid crystal domains over 20-40μm sizes. Interestingly in each domain the director is always along one of the crystallographic axis of the colloid crystal. Although the typical size of the liquid crystal monodomains are comparable to that of the colloid crystal mono domains, the domain boundaries do not coincide with each other. During infiltration we found jerky motion of the front of the liquid crystal moving along one of the crystallographic axis, then stopping, and then moving again along another axis. This may indicate that the flow alignment breaks the anchoring at the colloid particles, thus resulting in the uniform domains. However, in liquid crystals one usually sees that the broken anchoring eventually relaxes back to the equilibrium value, which we have not observed here. To exclude the role of the flow alignment we have tested cells that were infiltrated in the isotropic phase of the liquid crystal, but we have still obtained uniform areas with director along one of the crystallographic axes. Interestingly this situation is very similar to the alignment typically observed on single crystals of atomic size lattice dimensions when the easy directions are parallel to one of the crystallographic axes.\textsuperscript{18}

An example of the \textit{LC} alignment in a 20μm thick film is shown in Figure 7.9, where we illustrate the fluorescent confocal polarizing microscopy (FCPM) image inside the film by about 5μm away from the boundary plate (the measurements were carried out by Dr. Ivan Smalyukh and the results were discussed with Dr. Oleg Larventovich). In the
brightest domains the fluorescent dye molecules align parallel to the polarizer (indicated by arrow on the figures), whereas in the darkest areas they are perpendicular to it. The excitation under non-polarized light is nearly uniform (Figure 7.9/c), indicating that the distribution of the dye is fairly uniform.

![Figure 7.9: Confocal microscopic images of a liquid crystal 5CB in D=2.6μm diameter polystyrene template. (a) Polarizer in vertical direction; (b) polarizer is horizontal direction, and (c) no polarizer; (d)V=100V f=1 kHz.](image)

In thin films with non-covered upper surfaces deposited on uni-directionally rubbed polymer surfaces the alignment of the liquid crystal appears uniform with director along the rubbing direction. This indicates that the easy axis of the substrate is able to
distinguish the crystallographic axis that is parallel to the rubbing direction. This is a very important and promising observation for practical applications, because defects would deteriorate the performance of the Bragg diffraction.

The homogeneous planar texture of the infiltrated liquid crystal could be switched to homeotropic by $E>5V/\mu m$ AC electric field, a value, at the given dimension of the particles, agrees with Eq (7.1) After field removal the planar texture with the original easy axis reforms (see Figure 7.9) without hysteresis, thus demonstrating the possibility to use the polystyrene - liquid crystal system as reversibly switchable Bragg diffraction device.

**Conclusions**

(i) We have shown that the surface properties (hydrophobicity, roughness, rubbing) of the substrates are important in determining the size and symmetry of colloid monocrystals. We found that with proper surfaces even the simpliest deposition technique can provide over 50$\mu m$ size monodomains, which is better than previously observed on similar systems.

(ii) In case of submicron size colloid particles the liquid crystal has an isotropic distribution, which can be switched to homeotropic by less than 20V/\mu m fields, which is again an improvement to previous electronic tuning observations.

(iii) The alignment of the liquid crystal in over micron size particle system is along one of the crystallographic axis of the colloid template in domains over 20$\mu m$ sizes. Using unidirectionally rubbed polymer substrates we have demonstrated macroscopically
uniform alignment of the liquid crystal. Although this alignment is not understood at this moment it offers fabrication of high quality Bragg diffraction devices.

7.2 Electro-rotation and -translation of colloidal particles in liquid crystal

Electrophoresis, i.e. electrically-induced rotational and translational motion of small particles in fluids, is an ancient, but still active science. Most electrophoretic motions are allowed by symmetry (e.g. along the field), however some motions require symmetry breaking transitions, and appear only above a threshold electric field. An example of the latter is a DC electric-field-induced steady rotation of solid spherical objects that, in isotropic liquids, was observed first in 1893 by Weiler (Quincke rotation), but was explained only in 1984 by Jones. Another interesting example is an induced translational motion normal to the electric field. This has been observed only for long, slender particles whose charges vary along their contour and was explained in terms of coupling between surface charge and shape modulation. Electrophoretic studies in liquid crystals are scarce and are limited to motions of nanoparticles in lyotropic liquid crystals that do not require symmetry breaking transitions. It is clear, however, that the techniques based on one-bead microrheology developed recently to monitor the mechanical properties of viscoelastic soft materials, might be extremely helpful in analyzing rheological properties of smectic liquid crystal materials, which can be considered as stacks of two-dimensional fluid layers. The experimental verification of the two-dimensional fluid nature of the smectic phases by traditional macro-rheology however is very difficult due to generation of defects by the macroscopic flow. In this letter we report the first observations of electro-rotation and electro-
translation of microscopic cylindrical and spherical inclusions dispersed in smectic materials. We show that quantitative analysis of the electro-rotation can be used to determine the in-plane viscosity of the smectic liquid crystals.

We have studied two commercially available liquid crystalline (LC) materials: octyl cyano biphenyl (8CB) from Aldrich, and a mixture CS 2003 from Chisso, Inc. 8CB has a smectic A (SmA) phase in temperature range 23 - 33°C characterized by a large positive dielectric anisotropy ($\Delta \varepsilon = 8$ at 32°C). CS2003 is a room temperature ferroelectric SmC* mixture with ferroelectric polarization $P_o \sim 40\text{nC/cm}^2$ and negative dielectric anisotropy ($\Delta \varepsilon = -0.6$ at 50°C). It also has a SmA* phase between 56°C and 64°C, and a chiral nematic (N*) phase between 64°C and 90°C. For Fluorescence Confocal Polarizing Microscopy (FCPM) observations the LCs were doped with ~ 0.01 % of fluorescent dye BTBP (N,N'-Bis(2,5-di-tert-butylphenyl)-3,4,9,10-perylenedicarboximide) $^{31}$. Glass spheres (beads) of 4.5µm diameter and cylinders of 4.5µm and 10µm diameters with length/diameter ratios varying between 1 and 10, were dispersed at low concentrations in LC films of thicknesses in the range of 6-30µm. We investigated films with uniform thickness (uniformity is ±0.5µm over 1 cm$^2$) and wedge shape cells (wedge angles ~ 20µm/1cm). The observations were carried out by polarizing microscopy (Olympus BX60), and by a fast version of FCPM based on a scanning CARV® system with a spinning Nipkow disk integrated with a Nikon microscope (Eclipse E-600) that enabled taking motion pictures of the textures (the measurements were carried out by Dr. Ivan Smalyukh and results were discussed with Dr. Oleg D. Lavrentovich). The electric field was applied normal to the film surfaces via a potential difference between transparent
indium tin oxide (ITO) layers deposited on the glass plates of the cells. The ITO layers were coated with a polyimide (PI2555 from HD Micro Systems) film rubbed uni-directionally to promote director alignment parallel to the rubbing direction.

Far from the dispersed particles such a surface treatment produced uniform bookshelf layer structure (layers are normal to the substrates). In case of CS2003 ($\Delta \varepsilon < 0$) this alignment remained stable in electric fields applied across the substrates. In case of 8CB ($\Delta \varepsilon > 0$), a sufficiently strong field realigns the layers from their original bookshelf vertical orientation. In the transition range ($2.5V/\mu m < E < 4V/\mu m$) the layers are tilted with numerous defects. At $E > 4V/\mu m$ a fairly uniform homeotropic configuration forms, i.e. the smectic layers are parallel to the substrates. If the field is switched off, the resulting texture depends on the pre-applied field: if it is smaller than $7V/\mu m$, the bookshelf structure gradually restores itself; however, if the field is larger than $7V/\mu m$, the surface anchoring is broken, the homeotropic texture is preserved at zero electric field as a metastable state.

In the bookshelf textures at zero electric fields, most of the glass cylinders are aligned parallel to the rubbing direction, i.e., along the director. FCPM textures of the vertical cross-sections of the 8CB samples, Figure 7.10 (a), show that the director is parallel to the cylinder surface everywhere; two toric focal conic domains cup the ends of the cylinder.

When the DC field exceeds the threshold $E_r$, the cylinders start to rotate about their symmetry axes. The rotation of the cylinders is easily observable under the microscope, as the edges of the cylinders are often slanted. Both the threshold field, $E_r$,
and the angular frequency of rotation, \( \omega(E) \), could be measured by recording the rotation and tracking the frames. The electric field dependence of the angular velocity for CS2003 at 59°C (SmA phase) and at 50°C (SmC* phase) are plotted in Figure 7.11/a. The threshold \( E_r \) was observed rapidly increasing at decreasing temperatures (0.34V/\( \mu \)m at 59°C and 2.1V/\( \mu \)m at 50°C), however the slope of the curves at field much higher than

![Figure 7.10](image)

Figure 7.10: (a): In plane FCPM texture of a 4.5\( \mu \)m cylinder in 8CB; (b): The FCPM color coded intensity scale; (c): The reconstructed director and layer structure that has rotational symmetry with respect to the cylinder axis.

the threshold only slightly depend on the temperature. The determination of the threshold is not precise (~10% error), because the onset varies slightly from particle to particle, and some of the particles oscillates back and forth near the threshold. Within the measurement error cylinders with different radii rotate with the same angular velocity.
The rotation velocity is basically independent of the length of the cylinders if the length/diameter ratio is larger than about 5. Shallow cylinders rotate significantly slower.

Figure 7.11: (a) The measured electric field dependence of the angular frequency of 4.5μm and 10μm diameter cylinders embedded in 12μm thick CS2003 at 50°C and 59°C. Dashed lines are fits using Eq (7.2) with viscosities $\eta=5.5$Pas and $\eta=0.9$Pas, respectively. (b) Illustration of the proposed physical mechanism leading to the electro-rotation, because the defects near the edges become more important. Similar angular velocity values could be measured at around 3 times smaller fields in 8CB at 32°C (for example at 2.5V/μm $\omega$~30s$^{-1}$), although there, the data scatter much more due to the field-induced layer realignment.

Electro-rotations with lower thresholds were also observed in the nematic, and in the isotropic phases of both materials, indicating that the effect does not require anisotropy, similar to the classical Quincke rotation, which only require that the charge relaxation time of the inclusion ($\tau_s = \varepsilon_s / \sigma_s$) be larger than the charge relaxation time of
the liquid matrix \((\tau_i = \varepsilon_i / \sigma_i)\). This is easily satisfied for liquid crystals \((\tau_i > \tau_{lc})\), because the conductivity of the glass particles \((\sigma_s < 10^{-12}\text{Sm}^{-1})\) is much smaller than that of the liquid crystals \((\sigma_{lc} = 0.9 \times 10^{-9}\text{S/m for CS2003, and } \sigma_{lc} \approx 0.7 \times 10^{-9}\text{S/m for } 8\text{CB})\), whereas the relative dielectric constants are comparable \((\varepsilon_s = 3.9, \varepsilon_{||}(8\text{CB}) = 14, \varepsilon_{\perp}(8\text{CB}) = 6, \varepsilon_{||}(\text{CS2003}) = 3, \varepsilon_{\perp}(\text{CS2003}) = 3.6\). In such a case, the distribution of free charges on the inclusion's surface is such that they are repelled from the electrodes (i.e., the negative charge on the cylindrical surface is close to the negative electrode, Figure 7.11/b). This situation is unstable against small rotational perturbations, and the solid inclusion will rotate around the axis perpendicular to the applied field, as observed in the experiment. Although the theoretical description of the Quincke rotation for the case of spheres in isotropic fluids cannot be directly adopted for describing cylinders rotating in the liquid crystals, the underlying physics is similar. Neglecting edge effects, the rotation of slender cylinders involves a two dimensional flow; consequently we need a 2-D model. Such a model was worked out by Feng\(^{33}\) and provides formula for the threshold electric field \(E_r\), given as:

\[
E_r^2 = \alpha \cdot \eta \left[ \frac{(1 + S)(1 + R)}{(1 - \varepsilon_i / \tau_i - \tau_{lc})} \right] \frac{\varepsilon_{||} \varepsilon_{\perp} (1 - \tau_i / \tau_s) \tau_{MW}}{1 + \tau_{MW}}
\]

(7.2)

This expression is valid both for spheres and slender cylinders, only the parameters are different. For spheres\(^{34}\) \(\alpha = 4 / 3, \ S = \frac{2 \varepsilon_i}{\varepsilon_s}, \ R = \frac{\sigma_s}{2 \sigma_i}, \text{ and } \ \tau_{MW} = (\varepsilon_s + 2 \varepsilon_i) / (\sigma_s + 2 \sigma_i)\), whereas for slender cylinders\(^{33}\) \(\alpha = 1, \ S = \frac{\varepsilon_i}{\varepsilon_s}, \ R = \frac{\sigma_s}{\sigma_i}, \text{ and } \ \tau_{MW} = (\varepsilon_s + \varepsilon_i) / (\sigma_s + \sigma_i)\). In these expressions \(\varepsilon_i, \sigma_i (\varepsilon_s, \sigma_s)\) are the dielectric constant and electrical conductivity of
the liquid (solid), respectively, $\tau_{MW}$ is the Maxwell-Wagner interfacial polarization relaxation time, and $\eta$ is the viscosity.

For both spheres and cylinders the angular velocity as a function of the applied field can be given as

$$\omega = \frac{1}{\tau_{MW}} \sqrt{\frac{E^2}{E_r^2} - 1}$$  \hspace{1cm} (7.3)

In case of our slender cylinder – liquid crystal system, where $\sigma_{lc} \gg \sigma_s$ and $\varepsilon_{lc} \sim \varepsilon_s$, the expression for the threshold electric field simplifies to

$$E_r^2 = \eta \frac{\sigma_{lc}}{\varepsilon_0 \varepsilon_{lc} \varepsilon_s}$$  \hspace{1cm} (7.4)

where the relevant viscosity corresponds to the Miesovitz component $\eta_a$, because the shear plane is perpendicular to the director.\footnote{From the measured threshold field, additional electrical conductivity and the dielectric constants data one can get the viscosity from Eq.(7.4). With the parameters of CS2003 at 50°C listed above, we get $\eta=6$ Pas, whereas in case of 8CB at 32°C we obtain only $\eta \sim 1$ Pas.}

Actually, we can determine the viscosity even without the need of measuring the conductivity and the dielectric constant of the LC, by measuring both $E_r$ and $\omega$, and combining Eq.(7.3) and (7.4), giving

$$\omega(E) = \frac{E_r^2 \varepsilon_s \varepsilon_0}{\eta (1 + \varepsilon_s / \varepsilon_{lc}) \sqrt{\frac{E^2}{E_r^2} - 1}}$$  \hspace{1cm} (7.5)
For $E >> E_r$, this further simplifies to $\omega(E) = \frac{E_r \varepsilon_s \varepsilon_\omega E}{\eta (1 + \varepsilon_s / \varepsilon_\omega)}$. In spite of the ambiguity in determining the angular velocity near the threshold, the electric field dependence of the measured angular frequency can be satisfactorily fitted by Eq. (7.5) (see Figure 7.12(e) for CS2003 at 50°C and 59°C), giving $\eta_a = 5.5 \text{Pas}$ and $\eta_a = 0.9 \text{Pas}$, at 50°C and 59°C, respectively. Electro-rotation measurements for 8CB at 32°C gave $E_r = 0.6 V / \mu m$ and $\omega(E \gg E_r) / E \sim 12 \cdot 10^{-6} m V^{-1} s^{-1}$ which provide $\eta_a = 1.6 \text{Pas}$. These values are in fairly good agreement with the results obtained using conductivity and dielectric data, and only the threshold field measurement. We note that $\eta_a$ was already measured for 8CB and it was found to be $\sim 1.5 \text{Pas}$ at shear rates corresponding to the highest rates ($50 s^{-1}$) in our experiments. This agreement clearly indicates that electro-rotation of cylindrical inclusions can be used to study the rheology of liquid crystals.

At further increasing fields ($E > E_m$), the rotating cylinders are set into translational motion, too. In the isotropic and nematic phases the direction of the motion occurs in three dimensions; however, in the smectic phases the axes of the cylinders move strictly along the smectic layers, i.e., the motion is two-dimensional. Due to the irregular shape of the edges of the cylinders the speed of the motion is somewhat irregular. To obtain more reliable results from the field-induced translational motion we studied spherical beads instead of cylinders.

At zero electric fields in the bookshelf smectic layer alignment, the spherical beads are surrounded by two defect “wings” spanning along the layer normal (Figure 7.12), similar to defect lines around isotropic droplets in SmA liquid crystals of planar
anchoring reported by Blanc and Kleman.\textsuperscript{36} The length of the wings is about 30-100μm in the SmA phases of both 8CB and CS2003, whereas in the SmC* structure the wings are much shorter (~5-10μm), and sometimes are not even observable.

Although their electro-rotation cannot be easily seen (they are too symmetric), careful observations revealed that they also spin around their axes normal to the field, with a threshold in reasonably good agreement with Eq.(7.5). Similar to the cylinders, the translational motions occur at threshold electric fields $E_{th}$, which is higher than $E_r$ ($E_{th} \sim 3.5V/\mu m$ for CS2003 at $T=50^\circ C$ and $E_{th} \sim 2.5V/\mu m$ for 8CB at $T=32^\circ C$), suggesting that the translation might be a consequence of the rotation.

The translational motion takes place along the smectic layers and its direction do not seem to depend on the direction of the gradient of the film thickness up to the wedge angle of $2 \cdot 10^{-3} \text{ rad}$. FCPM studies show that at zero fields the beads are evenly distributed between the substrates, but when the translational motion is induced, they eventually all end up at either the top or bottom of the film (Figure 7.12/d-g), where they move along the substrates. When the fields are turned off the beads stick to the substrates and do not move back toward inside of the film.
Figure 7.12: In-plane FCPM texture of the director distortions of 8CB at room temperature around a 4.5μm spherical particle. (a-d:) Far from the beads the liquid crystal is in bookshelf geometry (layers normal to substrates). A linear polarizer is orthogonal (a) and at about ±45º(b,c) to the rubbing direction; (d): Vertical FCPM cross-section with the particle at rest close to the center of a 30μm thick cell at zero field. Note that the director distortions at the particle are similar to those in the in-plane section, indicating rotational symmetry around the defect line; (e-g): Vertical FCPM cross-sections indicating changes of particle positions and distortions in director field around the spheres at different electric fields. The layers are distorted in (e,f) and practically parallel to the substrates in (g); (h): The FCPM color-coded intensity scale; (i):Reconstructed layers and director pattern around the particle embedded in the system of parallel smectic layers.
In the SmA phase of the studied materials there is a narrow range above $E_{th}$ where the particles travel by less than their diameter and bounce back after the field is turned off. This indicates elastic behavior, which is due to the layer distortions around the particles (see Figure 7.12(i)). At higher fields the particles travel much further than their diameter and only partially recoil after the field removal, indicating viscoelastic behavior. In this range the defect wings shrink and gradually vanish (Figure 7.12(e-g)). At fields higher than $E_v$ (≈7V/μm for 8CB at T=32°C and ≈6V/μm for CS2003 at 50°C) the particles simply stop after field removal indicating a purely viscous response. In this range the speed of the translation is about 100μm/s for the Cs2003 and about 20μm/s for 8CB.

In the films where the homeotropic texture remains stable after field removal, similar to the bookshelf alignment, defect lines form at zero field, but now they span vertically normal to the cell substrates (see Figure 7.13(a-c)). In addition, some of the particles, that were originally close to a substrate (Figure 7.13(a)), gradually (in about 10 minutes) move toward the center of the cell (Figure 7.13(b)) probably because the spheres at the surfaces lead to inclined smectic layers which cost surface anchoring energy. When we apply electric fields in the horizontal layer alignment, the vertical defect lines gradually disappear just as in the bookshelf alignment (see Figure 7.13(d-g)).

In summary, we have presented the first observations of DC electric-field-induced rotational and translational motion of finite particles in liquid crystals. We showed that the electric field – induced rotation is analogous to the Quincke rotation, and its proper analysis can be used to measure the viscosity coefficient $\eta_a$ of smectic liquid crystals.
Figure 7.13: Vertical FCPM textures of 8CB at room temperature in horizontal layer alignment. (a,b): Textures around 4.5\(\mu\)m glass bead right after the field has been turned off (a) and 10 minutes later (b); (c): The corresponding layer pattern around a sphere. The director structure has rotational symmetry around the vertical defect lines. (d-g). Textures around a bead under different electric fields: 3V/\(\mu\)m (d), 4V/\(\mu\)m (e), 6V/\(\mu\)m (f) and 8V/\(\mu\)m (g).

This is especially important, because this method does not require uniform alignment over centimeter ranges, and allows one to probe local viscous properties. We have also demonstrated the onset of a translational motion along the smectic layers. The details of
the physical mechanism of the field – induced translational motion, and the defect disappearance mechanism will be subject of future studies.

7.3 *Orbiting three-dimensional colloidal particles in two-dimensional fluid under DC electric fields*

Electric field induced motion of spherical and cylindrical glass particles were studied in a smectic A liquid crystal octyl cyanobiphenyl (8CB) medium. The 4.5μm particles were dispersed in the smectic A (8CB) medium, sandwiched between glass plates of different cell gap with conductive inner surfaces. Under DC fields the smectic layers become parallel to the glass substrates. Such configuration corresponds to a two dimensional isotropic fluid structure along the film surface: the motion of solid particles results viscous forces along the substrates, whereas the motion across the layers is opposed by elastic permeation forces. As described in previous Chapter 7.2 Under DC fields above a threshold instability occurs and the particles move with constant speed in arbitrary directions normal to the electric field. The moving spheres and the cylinders rotate about their symmetry axis along the layers. When air bubbles are present in the film the, spheres tend to stick to the bubbles, and rotate collectively with a field-dependent speed that is independent of the radius of the bubbles (the angular velocity is inversely proportional to the radius).

- **Experiment Results**

As DC electric field was applied, 4.5μm spherical particles in 8CB were found rotating around air bubbles existing in 8CB (Figure 7.14). Diameter of air bubbles are in
the range from 20 to 100 μm. Rotation speed is strongly dependent on the amplitude of DC field applied (Figure 7.15) and basically independent of diameter of air bubbles (Figure 7.16). Under high enough electric field, liquid crystal molecules are perpendicular to

Figure 7.14: Rotation of 4.5 μm spheres particles around a 90μm air bubble in the SmA phase of 8CB (31°C). Upper row: uniform rotation; lower row: The spheres rotate back and forth due to bouncing back from a particle (indicated by arrow), which are stick to the film surface.
Figure 7.15: Rotation speed of the 4.5μm spheres in a 6μm thick homeotropically aligned SmA film at the function of the DC electric field.

Figure 7.16: Rotation speed of the 4.5μm spheres around air bubbles as the function of diameter of the air bubbles.
substrates. Three temperature ranges were tested for spherical particles rotation around air-bubbles: SmA phase (31°C); b: nematic phase (34°C); isotropic phase (41°C). We found in SmA phase particles tightly attached to outskirt of air bubbles and therefore rotation could be realized. During rotation more particles will join in until all positions are occupied. In nematic phase particles rotation was often interrupted by particles passing by. In isotropic phase under DC field particles were found difficult to get close to air-bubbles (Figure 7.17). During our study we also found air bubbles and bare particles themselves sticking and rotating around each other (Figure 7.18).

Figure 7.17: Arrangement of 4.5μm spheres particles around the air bubble at different phases. a: SmA phase (31°C); b: nematic phase (34°C); isotropic phase (41°C).

Figure 7.18: Illustration of the rotation of three air bubbles stuck together. Pictures represent 200*200μm² area.
We are still exploring the details of the motion and the underlying physical mechanism and here we just present experiment discover on this subject. The studies may have relevance to understanding particle motions in cell membranes under electric actuations and will contribute to our understanding of the hydrodynamic properties of two-dimensional fluid systems.
References:

Chapter 8

Summary

Four types of unconventional liquid crystal systems - amphotropic glycolipids; novel bent-core liquid crystals, bent-core liquid crystal and glycolipid mixtures, and colloidal crystal - liquid crystal systems - were studied in this thesis and characterized by polarizing microscopy, electrical current, digital scanning calorimetry, and dielectric spectroscopy. During our study, we have made the following achievement.

- Glycolipids are amphotropic liquid crystals forming lyotropic liquid crystals in aqueous solutions and thermotropic liquid crystals in their dry form as well. We reported studies on thermotropic properties of seven different neat glycolipids: four maltosides, two glucosides and one pyranoside lipids. Optical birefringence, electrical conductivity, differential scanning calorimetry (DSC), and dielectric spectroscopy measurements were employed to characterize the phase structures of the materials. In general they exhibit a wide (>100°C) mesophase (smectic, columnar) range with low (0.01-0.04) birefringence. They have large (60-120) dielectric susceptibility basically proportional to the number of polar sugar heads. Depending on the temperature the relaxation frequency of the susceptibility varies between <100Hz and >1MHz, mainly determined by the hydrogen
bonding between the polar sugar heads. The results of these studies have been submitted to the Journal of Liquid Crystals. (G. Liao, K. Zewe, J. Hagerty, R. Hashim, S. Abeygunaratne, V. Vill, A. Jákli, “Thermotropic liquid crystalline properties of amphiphilic branched chain glycolipids”, Submitted to Liq. Cryst, 2005)

- We have found that the optically isotropic phase observed recently below the nematic phase of the bent core liquid crystal, 4-chlororesorcinol bis[4-(4-n-dodecyloxybenzoyloxy)benzoate], shows ferroelectric-type switching and polarizing microscopic, electric current, dielectric, and dynamic light scattering studies reveal that the structure in the ferroelectric phase consists of interconnected orthoconic racemic smectic (SmC\textsubscript{a}P\textsubscript{F}) granules with random layer directions. This model is directly analogous to that of the magnetic spin glass structure with the important difference that in our case the polarization of each grain can be switched in the plane of the smectic layers without rotating or flipping the grains themselves. Near the nematic phase the granular structure can be poled by electric fields. The relaxation back to the non-poled structure follows an inverse logarithmic rule. Details of these studies of this material have been published in Physical Review E. (G. Liao, S. Stojadinovic, G. Pelzl, W. Weissflog, S. Sprunt, A. Jákli, “Optically isotropic liquid crystal phase of bent-core molecules with polar nanostructure”, Physical Review E, 72, 021710 (2005))

- We have studied the phase sequence and physical properties of an asymmetric bent-core material with chiral rigid cholesteryl in one, and a flexible achiral alkyl side chain at the other end. The combination of the achiral bent-core unit with the chiral cholesteryl results in properties different from both usual calamitic and bent-core
materials. We found that the presence of the bent-core units induces a wide range of blue phase (BPIII) between the isotropic and cholesteric phase. Below the cholesteric phase a ferroelectric SmC* structure occurs, where the bent-core units do not seem to form a polar closed packing. Two papers are submitted along with the chemist who synthesized this compounds. We prepared one paper about the principle properties of this material (G. Liao, C. V. Yelamaggad, D.S. Shankar-Rao, K. Prasad, A. Jákli, “Ferroelectricity of a bent-core material with cholesteryl terminal chain”) and it will be submitted soon to Physics Review Letter.

- We have studied the phase sequence and physical properties of an asymmetrically fluorinated achiral bent-core material. We found that there were mesophases in this material: high temperature M₁ phase with SmC₃Pₐ layer structure and SmC₄Pₐ layer structure in low temperature M₂ phase. The M₁ has antiferroelectric polarization with racemic type of switching, which has large birefringence in the racemic state. It can be switched to ferroelectric state anticlinic SmCaPF under rule of chirality conservation, which is of low birefringence. Long time of electric field applied would induce chiral transformation. Conformational chirality is observed during switching of SmC₃Pₐ, which is assumed to be due to a propeller – type helical twisted configuration characteristic of the particular type of bent-shape molecules. The SmC₄Pₐ of M₂ phase has low birefringence anticlinic structures at zero fields. It can be switched to synclinic ferroelectric SmC₅Pₚ, which is chiral. As a summary we see a transition between racemic to chiral antiferroelectric SₘCP phases. This transition could be induced either by temperature variation or by electric fields.
• Mixtures of several bent-core substances with nematic, polar SmA and SmC phases, and a simple amphiphilic sugar lipid with SmA mesophase found to obey the well-known miscibility rules, i.e. the sugar lipid mixes best with the polar SmA bent-core material. In addition, the chiral sugar lipid was found to induce tilt to the non-tilted polar SmA phase, which represents a new direction among the chirality – polarity – tilt relations. Electro-optical properties of bent-core and lipid mixtures indicated that lipid molecules are most likely sitting between bent-core molecules, reducing dipole-dipole moment interaction between bent-core molecules. Particular bent-core molecular structure of 4-CN-3F-OPIMB enables formation of strong bonding polymer network like structure as mixing with C_{12}G_{1}. The paper about these studies is currently under preparation.

• We have studied binary mixtures of bent-core liquid crystal molecules: one with a chiral cholesterol unit attached to one end of the bent core (B-Ch), the other one is an achiral molecule with two fluor atoms in the bent-core (B-2F). B-Ch has a helical SmC* phase with tilt and chirality – induced polarizations $P_c=30\text{nC/cm}^2$, whereas B-2F possesses synclinic and anticlinic antiferroelectric SmCP phases with as high as $900\text{nC/cm}^2$ polarization. Mixtures with low B-Ch content show ferroelectric $P_c$ at low and antiferroelectric $P_b$ at high fields. Mixtures of intermediate concentrations are found to be ferroelectric SmC$_G$ phases at high temperature ranges and SmC*+SmC$_p$F at lower temperatures. The B-Ch dominated mixtures have lower $P_c$ than of the pure B-Ch, whereas in the B-2F range $P_c$ is larger than of the pure B-Ch. The paper about these studies has been prepared (G. Liao, U.S. Hiremath, C. V. Yelamaggad, A. Jákli,
“Chirality and polarity transfers between bent-core smectic liquid crystal substances” and soon it will be summated to *Advanced Material*.

- We have studied the effect of substrate properties on the structures of colloid crystals and colloid-templated liquid crystals. It is found that the surface characteristic (hydrophobicity, roughness, rubbing) of the substrates are important in determining the size and assembling direction of colloid particles. Even the simplest deposition technique can provide over $50\mu\text{m}$ size monodomains, which offers high quality tunable band gap materials. As liquid crystal 5CB in submicron size ($0.3\mu\text{m}$) colloid particles the liquid crystal has an isotropic distribution, which can be switched to homeotropic by less than $20\text{V}/\mu\text{m}$ fields. The alignment of the liquid crystal in monodomains formed by over micron size particle is along one of the crystallographic axis of domains. Although this alignment is not understood at this moment, it offers fabrication of high quality Bragg diffraction devices. The manuscript (G. Liao, A. Olivares, J.R. Kelly, I. Smalyukh, O.D. Lavrentovich, A. Jakli, “Surface effects on colloid crystals and colloid – templated Liquid Crystals”) is under preparation and planned to submit to *Journal of Applied Physics*.

- We presented the first observations of DC electric-field-induced rotational and translational motion of finite particles in liquid crystals. We showed that the electro-rotation is essentially identical to the well-known Quincke rotation, which in liquid crystals triggers an additional translational motion at higher fields. In the smectic phase the translational motion is confined to the two-dimensional geometry of smectic layers, in contrast to the isotropic and nematic phases, where the particles can move in all three dimensions. We demonstrated that by proper analysis of the electro-rotation one can
determine the in plane viscosity of smectic liquid crystals. This method needs only a small amount of material, does not require uniform alignment over large areas, and allows one to probe rheological properties locally. This part of work has been published in *Physical Review E* (G. Liao, I. I. Smalyukh, J. R. Kelly, O.D. Lavrentovich, A. Jákli, “*Electro-rotation of colloidal particles in liquid crystals*”, Physical Review E., 72, 031704 (2005)).

- Electric field induced motion of spherical and cylindrical glass particles were found in a smectic A liquid crystal octyl cyanobiphenyl (8CB) medium. Under DC fields above a threshold and air bubbles are present in the film the, spheres tend to stick to the bubbles, and rotate collectively with a field-dependent speed that is independent of the radius of the bubbles (the angular velocity is inversely proportional to the radius). The details of spherical particles rotating around air-bubbles under DC electric field and the underlying physical mechanism are still in discussion. Clear image of physical mechanism can direct us into future design of microsized motor which has a lot of applications in now ‘nano’ age.

In addition to the above detailed studies, there are a number of interesting phenomena that we have noticed and which deserving future attentions and studies:

1. A number of asymmetric bent-core liquid crystals with/without chiral cholesterol unit attached have been characterized regarding their phase sequences, typical phase textures and conductivity. It will be very important to carry out more detailed studies of their electro-optic switching properties in polar phase.

2. Glycolipids are one of three lipids in cell membrane. Information obtained
from branched lipids offered great help to further study of interaction of lipids and protein in dry form. This may help in future design of liquid crystal based bio-sensors. Also study of their corresponding lyotropic free standing films will be directly related to study of cell-membrane properties which will provide important information to understand cell membrane functions.

3. Electric induced rotation of cylinder and spherical particles have been studied in calamitic nematic, SmA and SmC* medium. It will be very interesting to study behavior of these particles in bent-core nematic and smectic liquid crystal phases under electric field. This study can help us to understand viscosity properties of bent-core liquid crystals.