

Chapter I

Introduction

Brief introduction of bent shaped liquid crystals and its associated mesophases.

Introduction

In 1888 an Austrian botanist 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, unconventional liquid crystals systems are studied: thermotropic mesophases formed by the bent-core molecules.

1.1 Liquid Crystals [2,3]

All matter exists in one of several states, for example, solid, liquid or gas having different degree and type of positional and orientational order. In the isotropic liquid or gas phases, molecules move randomly and have no long-range positional or orientational order.

The solid state can be divided to several categories, such as glass or crystal. In a typical crystalline phase, molecules or atoms have three-dimensional long-range positional order and in molecular crystals there is also long-range orientational order. The mesomorphic phases between the isotropic liquid and the crystalline phases, liquid crystals, are fluids with some degrees of positional and/or orientational ordering of the molecules. Several examples of typical structure of LC phases are shown in **Figure. 1.1.1**. On a broad level, liquid crystals are classified into two categories, thermotropic and lyotropic liquid crystals. Thermotropic liquid crystals consist of one or several kinds of molecules mixed homogeneously and exhibit liquid crystal phases depending on temperature, where as lyotropic liquid crystals generally consist of mesogens and one or more fluids that do not mix homogeneously, microscopically segregate, and exhibit different structure depending of mixing ratio of components.

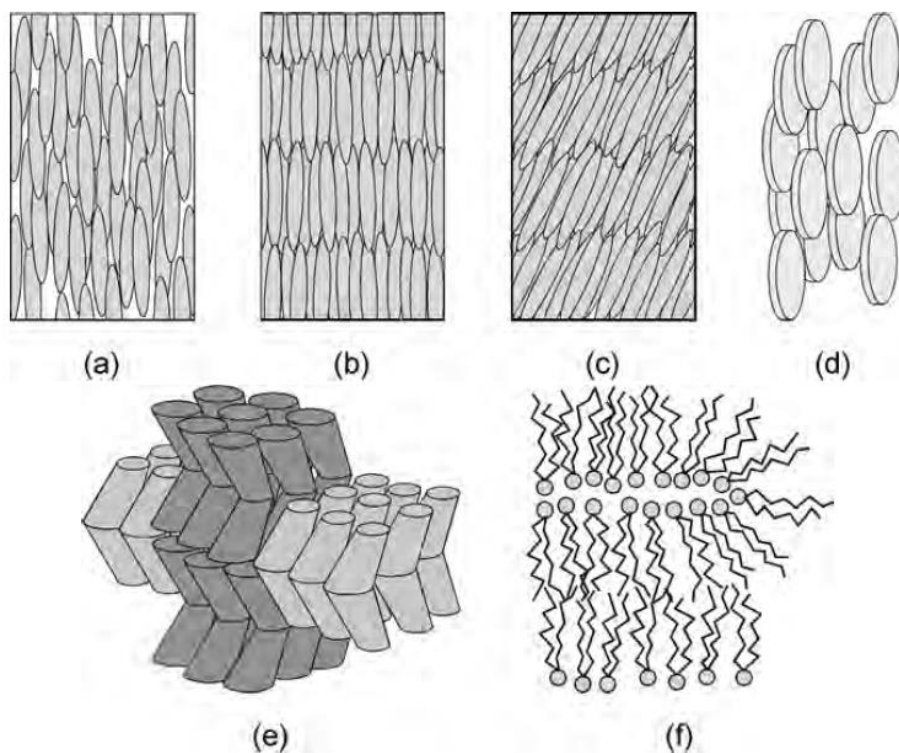


Figure 1.1.1. Examples of liquid crystal phases. (a) Nematic, (b) Sm-A, (c) Sm-C, (d) discotic nematic, (e) the columnar phase of bent-shaped molecules and (f) the lamella phase organized with lipid and water.

Thermotropic liquid crystals are classified by molecular shape or structure of the phases. The “rod-like” molecules which exhibit “rod-like” or “calamitic” LC phases have been extensively studied and widely used for technical applications. The “discotic” mesogens (molecules exhibiting discotic liquid crystal phases) and “bent-shaped” mesogens (molecules exhibiting bent-shaped liquid crystal phases) are used for few technical applications, but have been widely studied because these molecules produce unique structures due to the molecular shape.

On further classification, both thermotropic and lyotropic liquid crystals are broken into groups depending their order or their macroscopic structure. For example, the rod-like mesogens have the nematic (N) phase and smectic phases while discotic mesogens have the N (discotic nematic), smectic (discotic lamellar) and columnar phases. In the nematic liquid crystal phases, nematic (N), chiral nematic (N* or Ch), and blue phases (BPs), molecules have long-range orientational order, but no positional order. Molecules have both the orientational

order and the one-dimensional positional order in the smectic liquid crystal phases in which molecules form a layer structure. More than 10 smectic liquid crystal phases have been known and were named using alphabets like “smectic-A” (Sm-A). Examples of these smectic liquid crystal phases were shown in figure 1.1.2. Gray et al. reported detailed classification of these smectic phases of rod-like mesogens and their properties [4]. Discotic mesogens and bent-shaped mesogens exhibit liquid crystal phases and some of these phases have a quite different structure from liquid crystal phases of rod-like mesogens. Discotic mesogens exhibit the nematic, smectic and columnar phases. Nguyen et al. reported a classification of these LC phases of discotic mesogens [5]. Bent-shaped mesogens also exhibit the nematic, smectic and columnar phases. Details about liquid crystal phases of bent-shaped mesogens were introduced and discussed in following section.

In the lyotropic system, segregation of molecules in micro-scale results to form ordered fluid phases. Even in a material with single component of molecule, like thermotropic LCs, each functional group with different electron density or different chemical potential segregates and enhances to form ordered structure as like smectic phases. Especially, an aromatic group which often have been designed as a central core in liquid crystal molecules and alkyl chains on the tail part of molecules often segregate each other and produce various ordered phases. Recently, Tschierske reported series of molecules which exhibit lamella, micelle, and columnar phases based on the segregation of functional groups on each molecule [6], and such segregation is now regarded as an important factor for forming LC phases.

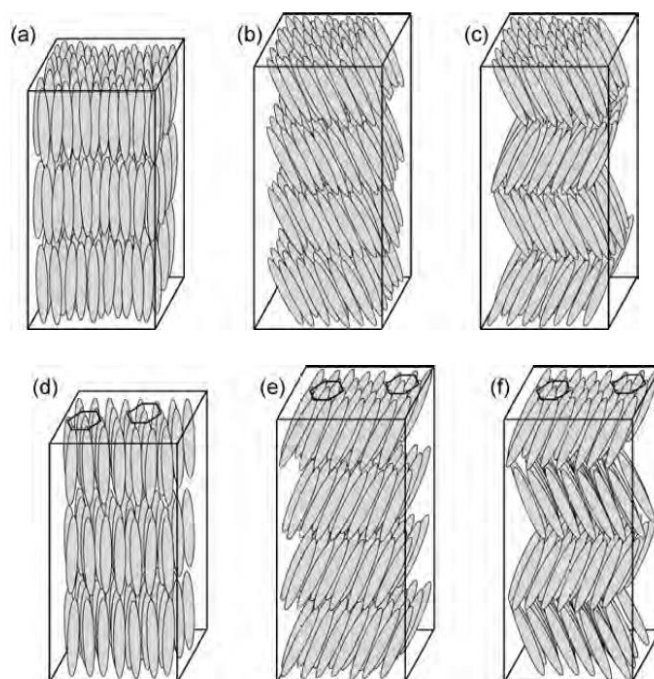


Figure 1.1.2. Examples of layer structure of smectic phases. (a) Sm-A, (b) Sm-C, (c) Sm-CA, (d) Sm-B, (e) Sm-I and (f) Sm-IA. In the phases, (a)-(c), molecules have no in-plane positional order in a smectic layer, while in the hexatic phases on (d)-(f) molecules have the short range positional order even in a plane of smectic layer.

1.2. Symmetry in Liquid Crystal Phases [7]

Materials that exhibit liquid crystal phases usually consist of organic molecules with complex chemical structure heavier than at least 150-molecular weight (g/mol). Each molecule forms one conformation in sufficiently short time and many of these conformations do not have symmetry operations more than C1 (lowest symmetry). However, in liquid crystal phases, we have to consider only time averaged conformations of molecules and then molecules can be regarded to form simple “rod”, “bent” or “discotic” shapes. The point group of a cylindrical rod is $D_{\infty h}$, bent-shape and disc-shape are in C_{2v} and $D_{\infty h}$ respectively. The symmetry class of liquid crystalline phases is not always the same as that of molecules in the system. Let us consider the symmetry of LC phases using point groups (in principle, we have to use the space group to describe the symmetry of LC phases as well as we do for crystal structures) based on the local symmetry of

these phases. The point group of the nematic and smectic-A phase of rod-like molecules is $D_{\infty h}$ which is the same as that of molecules, while the smectic-C phase belongs to the C_{2h} point group which is the lower symmetry comparing to molecules. Because molecules do not have positional order in the N phase and in one smectic layer of Sm-A and Sm-C phase, the symmetry class of these phases is simply presented with its point group. In highly ordered smectic phases, however, molecules have the positional ordering even in one smectic layer and then the symmetry class of these phases should be presented by space groups as we do for crystal structures. Almost all of the liquid crystal phases are anisotropic and hence these phases exhibit anisotropy in physical properties. Even the N phase whose point group has inversion-symmetry ($D_{\infty h}$), exhibits anisotropy in mechanical properties and optical properties, for example, anisotropy in elasticity and refractive indexes (birefringence). But in N ($D_{\infty h}$), Sm-A ($D_{\infty h}$), Sm-C (C_{2h}) [see figure 1.2.1] and hexatic phases of D_{6h} and C_{6h} , the symmetry is still high enough not to allow the system to become piezo-electric.

1.3 Ferroelectricity and Antiferroelectricity in Liquid Crystals [8-10]

1.3.1 Ferroelectric Liquid Crystals and Surface Stabilization

As Meyer pointed out, introduction of chirality to the Sm-C phase lowers its symmetry from C_{2h} to C_2 and allows the spontaneous polarization normal to the tilt plane. However, in bulk, chirality of molecules forces the tilt direction rotating from layer to layer; the tilt direction of molecules forms a helical structure as shown in figure 1.3.1 and spontaneous polarization is usually cancelled out macroscopically. To observe the spontaneous polarization, the helix in the Sm-C* phase should be unwound. In bulk, the helix usually does not unwind (in some particular material the helix unwinds only at one temperature) and hence the bulk spontaneous polarization is not easy to be observed.

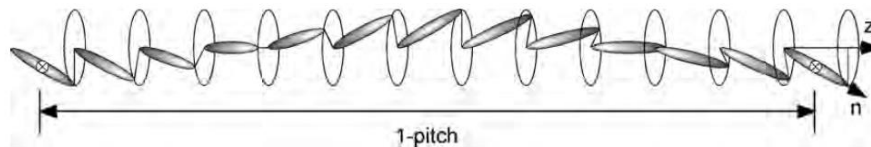


Figure 1.3.1 Helical super structure in the Sm-C* phase.

Clark and Lagerwall solved this problem by using surfaces[14]. In a thin cell in which smectic layers align perpendicular to the substrates (smectic layer normal is parallel to the substrates), the helix in the Sm-C* phase is unwound when the cell thickness is smaller than the helical pitch. Domains in which spontaneous polarization is not cancelled out are observed in such cells and the polarization switches by application of an external electric field [see figure 1.3.2]. The state in such thin cells is called as *surface stabilized state* because the helix unwound by the surfaces. Not only substrates of cells but also any surfaces force the helix unwound. Spontaneous polarization is easily observed in systems with a large surface area, for example, freely suspended films.

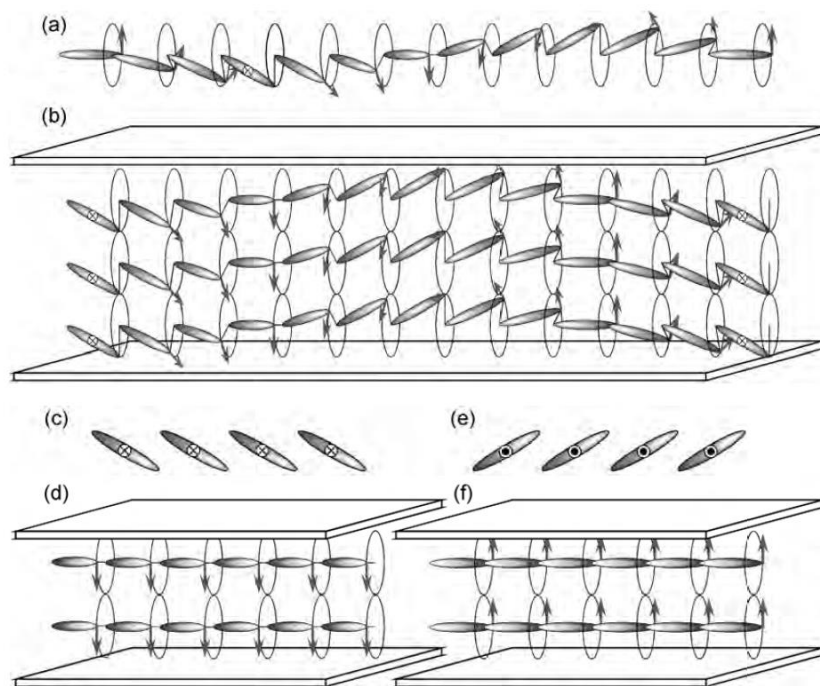


Figure 1.3.2. The helical structure and the surface stabilized state of ferroelectric Sm-C* phase. In a thick planar cell, molecules wind helix with its axis parallel to the surface. (a) top-view and (b) side view of the deformed-helical ferroelectric liquid crystal cell (DHFLC). However the cell thickness is thin around the helical pitch, the helix is unwound by surface interactions and molecules uniformly align as shown in (c) and (d) or (e) and (f); (c) and (e) are top view and (d) and (f) are side view of the surface stabilized ferroelectric liquid crystal cell (SSFLC). (model from Nakata thesis).

Molecules changes the orientation between (d) and (f) by application of an electric field, because spontaneous polarization in these states switches to be parallel to the applied electric field.

1.3.2 Antiferroelectric Liquid Crystal Phase and Smectic- C^* Sub-phases

In the Sm- C^* phase, molecules tilt in the same direction from layer to layer except small rotation from the chiral twisting power and hence direction of spontaneous polarization aligns almost uniformly as expected to be so in the ferroelectric phase. If molecules alternate in tilt direction from layer to layer, the direction of the spontaneous polarization also alternates from layer to layer canceling out the bulk polarization. That is the phase called antiferroelectric chiral smectic- CA phase (Sm- CA^* phase) found by Chandani *et al.* [15,16] and Galerne *et al.*[17], in which spontaneous polarization in two adjacent layers alters the direction without external fields and aligns uniformly as in the Sm- C^* phase when a strong external electric field are applied [15,16] [see figure 1.3.3]. Because the field induced transition from Sm- CA^* to field-induced Sm- C^* state is usually first order, switching between these two states occurs at the certain field strength (threshold field, E_{th}) and exhibits hysteresis, i.e., the threshold field is different whether the process is the switching from Sm- CA^* to Sm- C^* or that of switching back from the field induced Sm- C^* to Sm- CA^* . In addition, there are several similar structures known as the Sm- C^* sub phases. In these phases, molecular tilt direction changes repeatedly in a short period around 3 to 4 layers [19-25]. Two models had been proposed in terms of the molecular orientation in these phases, Ising model and Clock model[22,26-30]. Although the detailed molecular orientation in these sub-phases has been investigated by means of conoscopy, resonant x-ray scattering and optical polarized ellipsometry, the origin of these various Sm- C^* sub-phases including the Sm- CA^* phase is still under discussion.

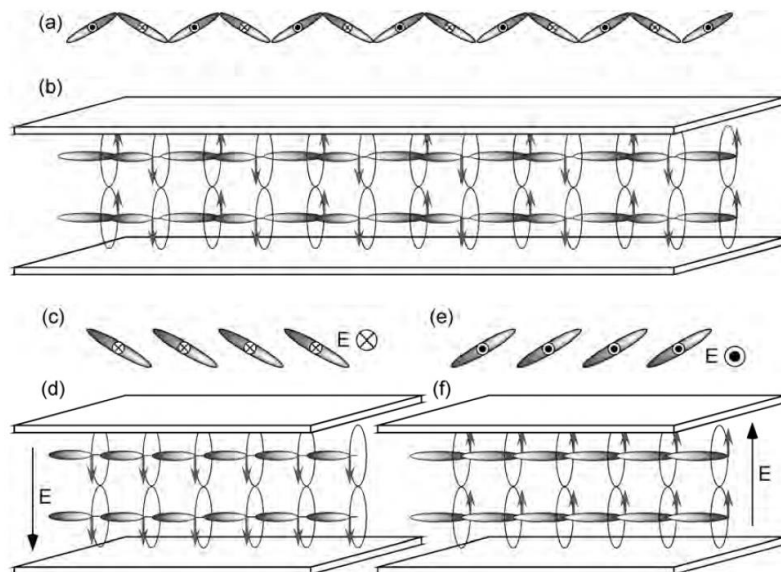


Figure 1.3.3. Molecular orientation in the antiferroelectric Sm-CA* phase. (a) top-view and (b) side view of the antiferroelectric Sm-CA* phase in a planar cell. Spontaneous polarization in each smectic layers is canceled out because of anticlinic orientation of molecules. However the spontaneous polarization re-orientes and uniformly aligns along an external electric field direction when the electric field is applied ((c) and (d) or (e) and (f)). These two states (d) and (f) are having the same molecular orientation which observed in the Sm-C* phase and only stable under application of an external field, so that these states are called as field-induced Sm-C* state.

1.4. Liquid Crystal Phases of Bent-core Molecules

Bent-core molecules exhibit several meso-phases, some of which are significantly different from the liquid crystal phases of rod-like molecules. Because of the molecular shape with no C_∞ symmetry along the molecular long axis, bent-core mesogens produce unique smectic phases that rod-like molecules never form. After the Berlin workshop on 1997[32], liquid crystal phases of bent-core molecules have been named as the ‘Bi’ (i is an integer number) phase in the chronological order of their discovery. After the B1 to B7 phases were defined [33], however, people realized that there were several different structures or states in one phase. Also, as the detailed structure of new phases was gradually

investigated, people found that there were a lot of phases having very similar but slightly different structure. In the Boulder workshop on 2002, the nomenclature of these liquid crystal phases were discussed and people agreed to make another rule of naming. The most absolute definition of the phase would be using the space group of the phase but it was not convenient for all the people. For both convenience and precise, people almost agree to name the phases of bent-core mesogens using the same name used for the rod-like mesogens, for example Sm-A or Sm-C, and additional characters and suffixes. Also the space group of the phase will be added for a detailed definition. In this thesis, both ‘Bi’ and ‘Sm-’ names will be used. Structures and properties of smectic phases of bent-core molecules are summarized on Table 1.4.1.

	Structure	Polar	Tilting in a layer
B1	Frustration(columnar)	Usually not	Tilted, non-tilted
B2	SmCP	Polar	Tilted
B3	Sm(crystal-like)	Non-polar	Non-tilted
B4	TGB (chiral domain)	Non-polar	Non-tilted
B5	SmCP(hexatic order)	Polar	Tilted
B6	Interdigitation	Non-polar	Tilted, non-tilted
B7	SmCP(modulation)	Polar	Tilted
B8	SmCP	Polar	Tilted

Table 1.4.1. Liquid crystal phases of bent-core molecules. “Polar” indicates that the phase shows responses to an applied electric field or not. “Tilting in a layer” indicates that the average molecular long axis in a smectic layer is tilted with respect to the smectic layer normal direction or not tilted.

The B1 phase [**Figure 1.4.2 (d) and (e)**] exhibits two periodicities like a columnar phase, i.e. smectic layer ordering and another periodicity in a plane of smectic layers. Three different structures have been reported [34,35] as shown in **Figure 1.4.2 (a)-(c)**. All of these phases do not exhibit macroscopic spontaneous polarization[36] and no response is usually observed under an applied electric

field (there are several reports about the field induced transition from B1 phase to the Sm-CP state[37,38]. But these were not conformed yet by means of x-ray).

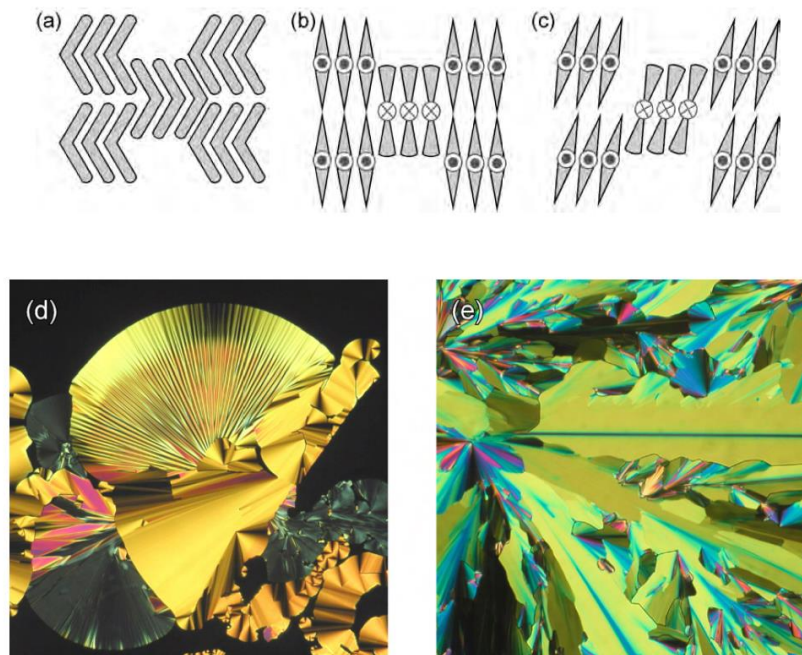


Figure 1.4.2. (a-c) Three proposed structures of the B1 phase[34,35]. (d) Photomicrograph of the B1 phase, P6OPIMB in a 4-micron thick cell. (e) Photomicrograph of the B1 phase, W503 in a 4-micron thick cell (M.Nakata thesis).

The B2 phase is also known as the Sm-CP phase, in which molecules forming a smectic layer are tilted with respect to the layer normal (Sm-C) and the smectic layer exhibits macroscopic spontaneous polarization perpendicular to the molecular tilt plane.

In the B3 phase [Figure 1.4.3], molecules in a smectic layer are not tilted from the layer normal and having positional order in layer plane as indicated by x-ray diffraction measurements. The B3 phase might be a crystalline phase since several sharp diffraction peaks are observed in wide angle x-ray scattering[39-41].

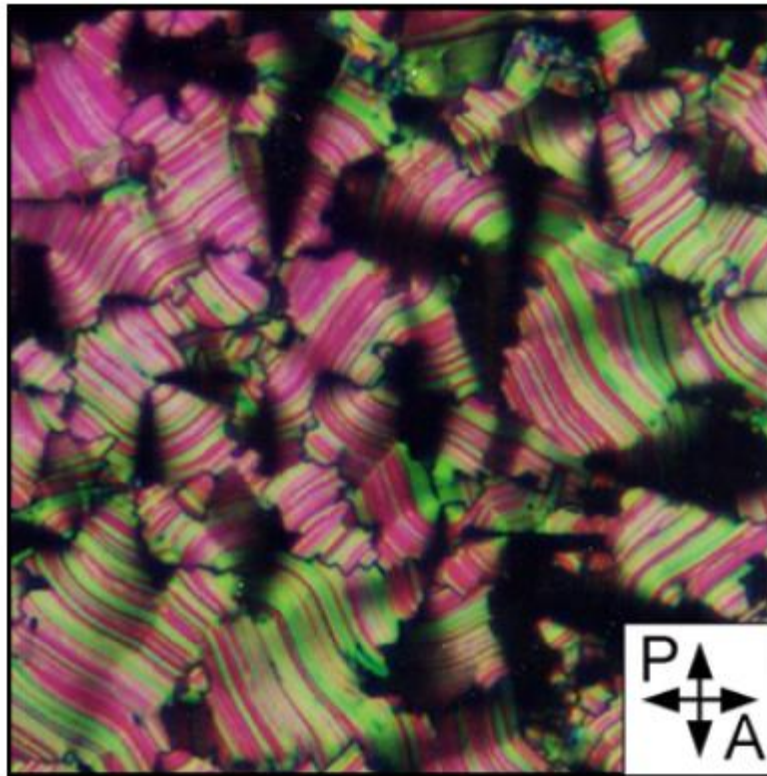


Figure 1.4.3. Photomicrograph of the B3 phase, P8OPIMB in a 6-micron thick cell (M.Nakata thesis).

The B4 phase is one of the phases of “under investigation”. From x-ray experiments, there is the smectic layer ordering and molecules are thought to be not tilted from the layer normal because the layer spacing is comparable to the molecular length. Characteristic points of this phase are blue scattered color and chiral domains[42]. Photomicrographs of the B4 phase are shown in **Figure 1.4.4 (a-c)**. From AFM (atomic force microscope) observations[32,43]and TEM (transmitted electron microscope) observations of freeze fractures, the phase is now thought to have the TGB[12,13] structure as shown in figure 1.4.4 (d). The phase also might be a crystalline phase and no electrooptic response is observed.

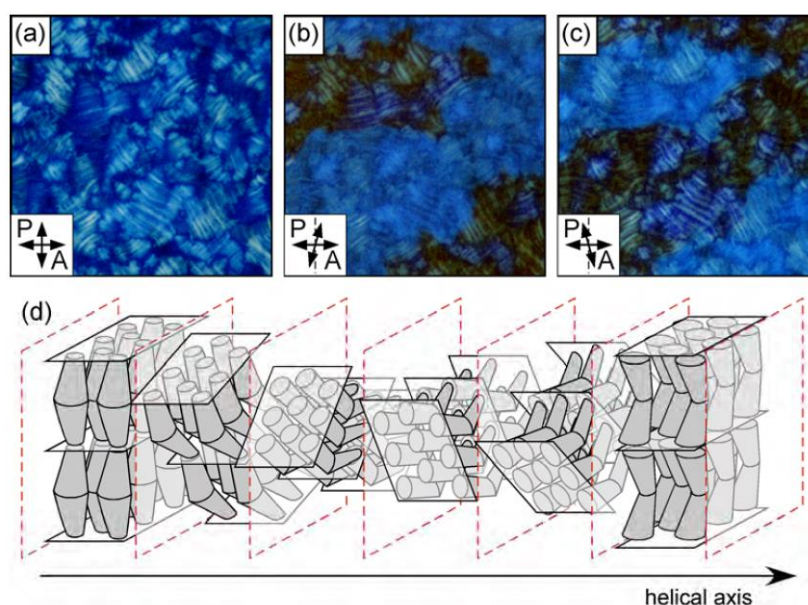


Figure 1.4.4. Photomicrographs of the B4 phase, P8OPIMB in a 6-micron thick cell (M. Nakata thesis). (a) Under crossed polarizers the texture looks dark because of low birefringence. Blue color is often observed in this texture. Two domains of opposite optical rotation exist and these domains are clearly observed in (b) and (c) by uncrossing polarizer and analyzer, where polarizer rotated clockwise 5-degree in (b) and counter-clockwise 5-degree in (c).

The B5 phase is the Sm-CP phase with the in-plane positional ordering. Electrooptic response in this phase is similar to that in the B2 phase [44]. From x-ray scattering measurements, the phase is known to have a positional ordering in the smectic layer. W. Weissflog *et al.* reported three distinct B5 phases in which electrooptic response and x-ray scattering profile were the same but distinguishable only in DSC measurements [45]. The B6 phase [Figure 1.4.5] is similar to the B1 phase in terms of interdigitation of molecules each other for the half molecular length [Figure 1.4.5 (b)], but this phase does not exhibit 2-dimensional ordering which easily determined by x-ray scattering experiments. Also the phase exhibits a reflection corresponding to the half molecular length (002) while the reflection corresponding to the molecular length (001) is cancelled out and not observed.

The B6 phase is sometimes observed in an upper temperature range of the B1 phase[46]. Because dipole moments of molecules are cancelled out each other, no electrooptic response is observed except a dielectric response.

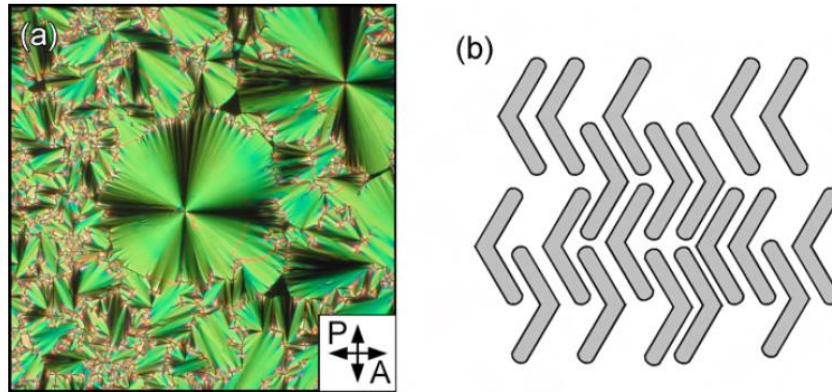
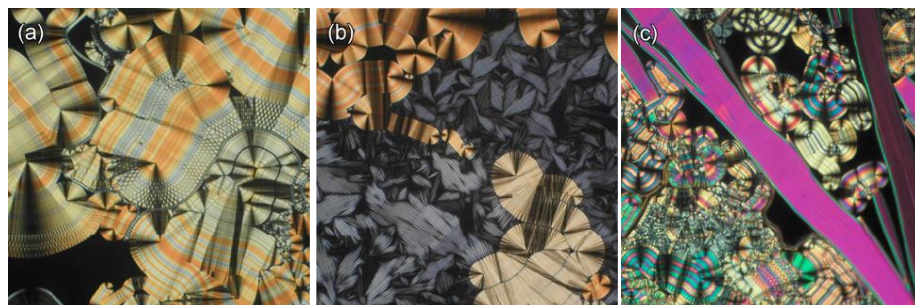


Figure 1.4.5. (a) Photomicrograph of the B6 phase, 6OAm5AmO6 in a 6-micron thick cell (M.Nakata thesis) and (b) molecular orientation in the phase.

The B7 phase is also one of Sm-CP phases[47]. The detailed structure of B7 phase is recently investigated by means of x-ray scattering and observations of freeze fractures[48]. The B7 phase was first defined by texture observed using optical microscope, which exhibits huge variation of spiral domains, helical ribbon like domains, focal conics and leaf-like domains [49]. From high-resolution x-ray measurements, several different structures that show the same texture under an optical microscope are known to exist. Hence the name “B7” is often used as the name of texture not of phase and the phase is called as the *polarization modulated* phase.



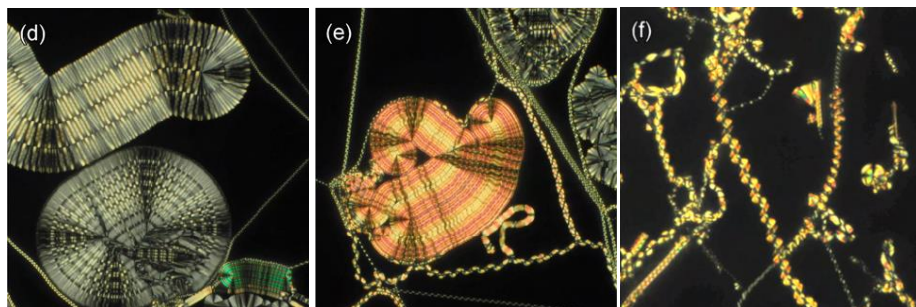


Figure 1.4.6: Typical textures observed in B7 phase, (a), (b) In a 4-micron thick cell, (c) Racemic MHO-Bow in a 6-micron thick cell and (d)-(f) Chiral MHO-Bow in a 8-micron thick cell.

B8 phase:

This phase was discovered recently in a symmetric bent compound as shown in **Figure 1.4.7** [74]. The homologues of this compound with shorter end chains did not exhibit the B8 phase. The microphotographs of the B8 phase are displayed in **Figure 1.4.7 a, b and c**. Upon gradual cooling from the isotropic phase, spiral domains grow as in the B7 phase. By further cooling, a fan-shaped texture is also observed, in which the extinction direction is parallel to the layer normal, and antiferroelectric-type switching is observed. The X-ray diffraction suggests that the B8 phase has a bilayer structure. This is the first and only report on the B8 phase thus far, and further investigations are expected.

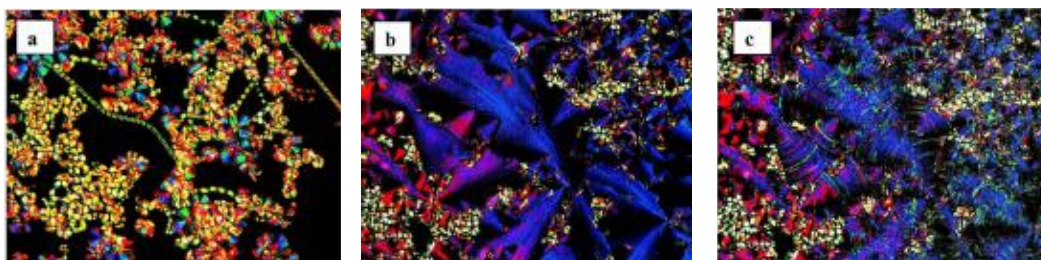


Figure 1.4.7: Microphotographs of texture observed in B8 phase at (a) 181⁰C, (b) 175⁰C and (c) 166⁰C.

1.5 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 1.5.1**). The angle between two linking arms ranges from 100° to 170° . The first bent-core liquid crystal was synthesized in the research group of Vorländer by Schröter in 1923[50], 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 [51].

Bent-core molecules did not get too much attention until Matsunaga[52] synthesized new mesogenic compounds with “banana-shaped” molecular structures, but no polarization was reported. In 1996 at 6th International Liquid Crystal Conference in Kent, Ohio Niori[53] 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 (rodlike) 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[54], smectic A[55] and the new ones actually classified with names ranging from B1 to B7 defined at the 1997 Berlin workshop[56] and after. The B1 to B7 series represent phases in the sequence of their discovery and do not correspond to their real layer structures in the mesophases.

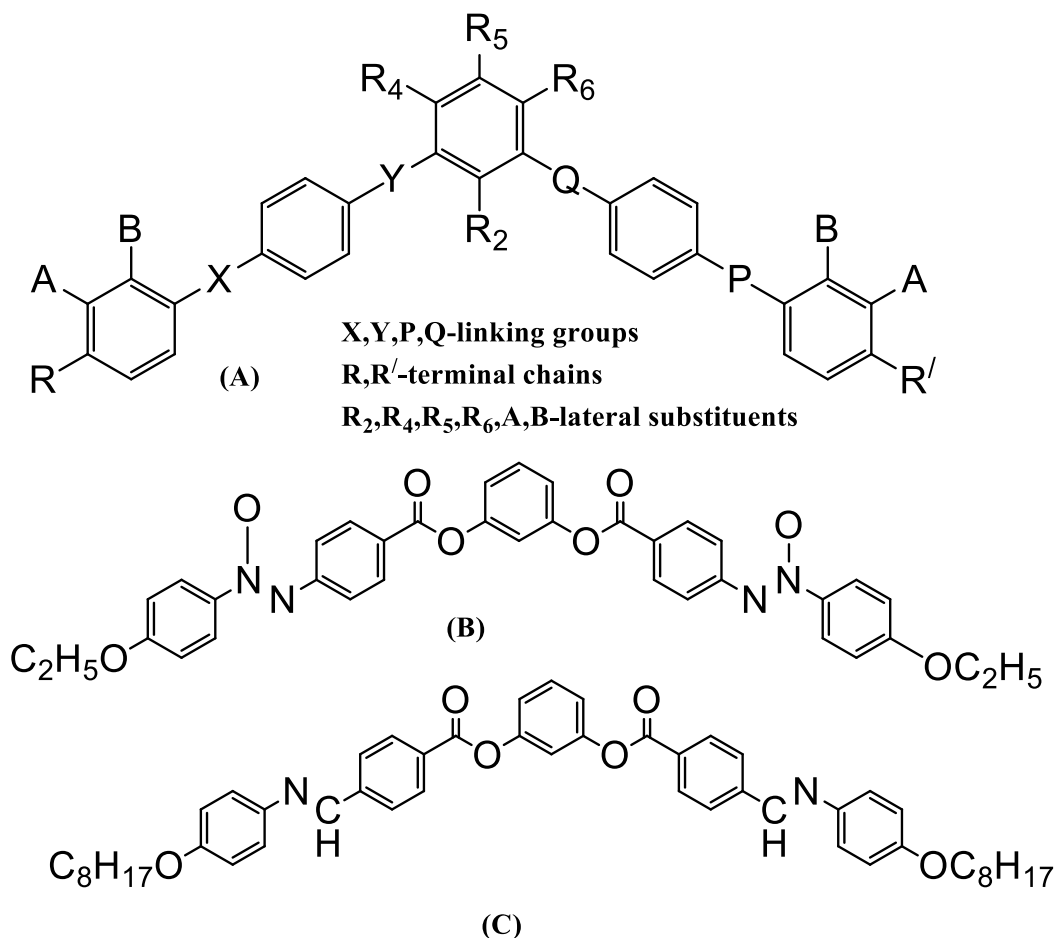


Figure 1.5.1: Molecular structure of typical bent-core liquid crystals: (a) typical molecular structure of a bent-core liquid crystal; (b) first bent-core liquid crystal synthesized by Vorländer[51]; (c) first recognized bent-core liquid crystal in 1994[57].

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[58]. The B2 phase corresponds to the phase first discussed by Niori[53] and is of a special interest because it is the first liquid crystal showing antiferroelectric behaviour. Another phase which shows similar electro-optical switching properties was named as B5[59]. B3 and B4 are crystalline-like modifications, the B4 phase is also designated as the “blue phase” of bent-core mesophases[60,61]. The B6 phase can be compared with an interdigitated smectic C phase generated by bent-core molecules[56]. The growing of helical filaments along with myelinic, ribbons, spirals has been the hallmark of B7 phase [62,63] . In my 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 $s=\pm 1/2$ form on homeotropic alignment substrates. The first theoretical model of the SmAP phase was proposed by Niori *et al.* [53]. 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 antiferroelectric (shown in **Figure 1.5.2**).

The first bent-core compound with SmAP phase was experimentally confirmed recently [55]. It is worthwhile to mention that this material also forms Smectic A at high temperature range (**Figure 1.5.3**). Small energy needed in the transition between SmAP and SmA (1.2kJ/mol) indicates the transition is of weakly first order[55]. Also the layer spacing and the tilt angle do not change obviously from SmA to SmAP[55]. 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 cannot 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 [55],

	<i>Antiferroelectric</i>		<i>Ferroelectric</i>	
<i>SmAP</i> Sm: smectic A: orthogonal P: polar <i>C_{2v}</i> symmetry				
<i>SmCP</i> C: tilted SC: synclinic AC: anticlinic <i>C₂</i> symmetry	SC 	AC 	SC 	AC
<i>SmCP^L</i> L: leaning SL: syn-leaning AL: anti-leaning <i>C_s</i> symmetry	SL 	AL 	SL 	AL
<i>SmC_G</i> G: general (double-tilted) <i>C₁</i> symmetry	SC&SL 	AC&SL 	SC&SL 	AC&SL
	SC&AL 	AC&AL 	SC&AL 	AC&AL

Figure 1.5.2: 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. ⊥ and ⊤ : upper (lower) part of the director tilt toward the observer. ↑ and ↓ indicates that out-of-plane polarization component P_n points down (up) [64]

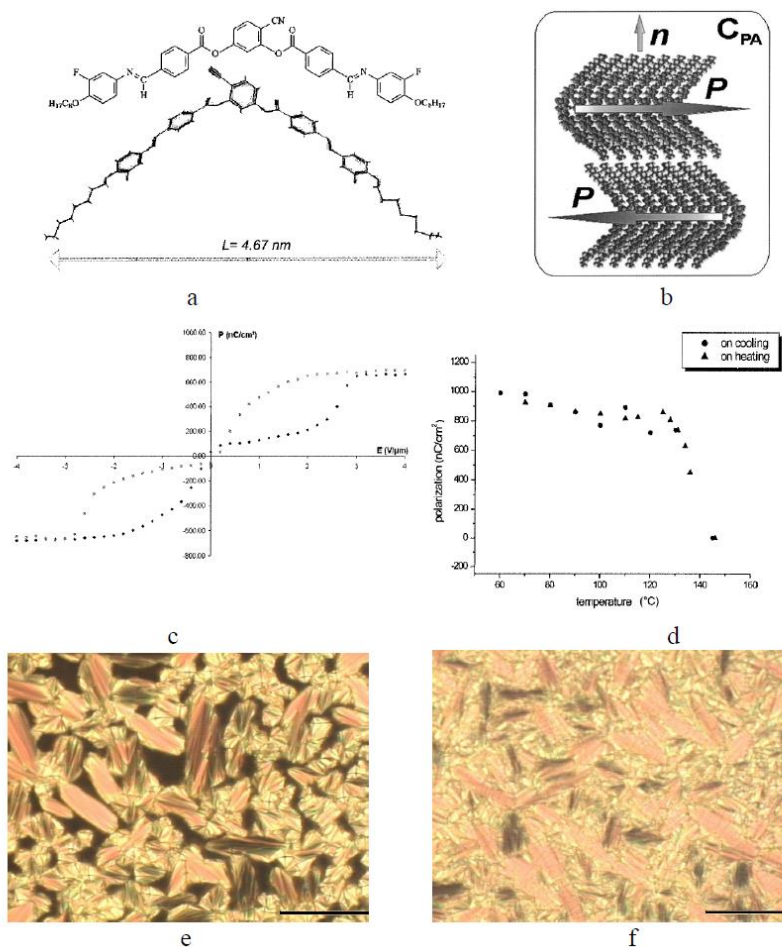


Figure 1.5.3: First experimentally proved SmAP bent-core mesophase[55] (a). Molecular structure of 4CN-3F-OPIMB, which shows SmAP mesophase[55]; (b) SmAP type of arrangement of bent-core molecules in smectic layer[55]; (c) polarization of 4CN-3FOPIMB at the function of electric field[55]. (d) polarization of 4CN-3F-OPIMB at the function of temperature[55]; (e) corresponding textures under cross-polarized microscope at 170°C-SmA (f) 130°C-SmAP. The black bar represents 100μm length (M.Nakata thesis).

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^L : single tilted Bent-core smectic liquid crystals

When bent-core molecules tilt in layers, they could form SmCP or SmCP^L which are polar smectic phases. In SmCP & SmCP^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 1.5.2**). Phases of bent-core molecules with a monoclinic tilted layer structures is called B2 [58] or SmCP [65] (‘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[65]. So SmCP smectic layers are monoclinic chiral symmetry C₂. 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 1.5.4). 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[66] 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[67,68]. It is assumed that the chirality of layer is conserved[65] 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[66,69]. 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. SmCsPA (‘s’ stands for synclinic and ‘a’ stands for antiferroelectric) is synclinic (Figure 1.5.4): the molecules tilt the same way in adjacent layer. The textures of the SmCsPA always contain fan domains with a few micrometers wide stripes

(**Figure 1.5.5**). In every stripe the molecular planes tilt at the same direction but polarization directions are opposite in the adjacent layers. SmCsPA can be switched to FE state (SmCaPF) as sufficient high electric field is applied. SmCaPF is an anticlinic tilted layer structure with the optic axis parallel to the layer normal. In SmCaPF, 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 1.5.4**). Chiral AFE SmCP i.e. SmCaPA is an anticlinic layer structure and its optic axis is parallel to the layer normal. SmCaPA can be switched to FE state and it changes to the synclinic structure (SmCsPF). During the switching of AFE of the SmCaPA to FE of the SmCsPF, 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^L. In SmCP^L, molecular directors tilt with respect to the layer normal but the molecular planes are not tilted. The SmCP^L has a non-chiral mono leaning symmetry Cs. Therefore in the SmCP^L

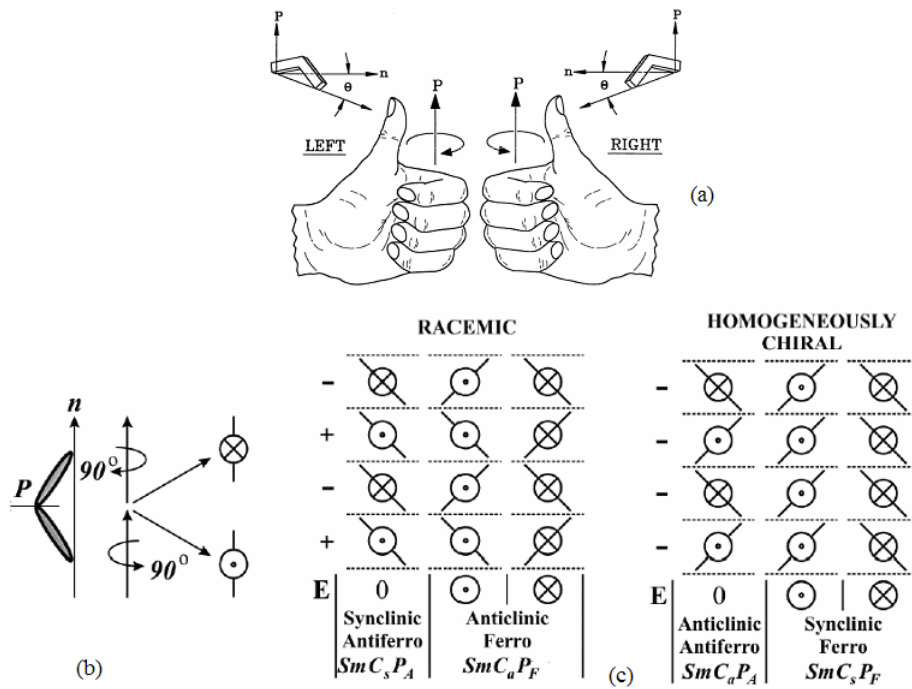


Figure 1.5.4: handedness and chirality of SmCP: P is polarization of layer, n is the layer normal. (c) is the side view of bent-core molecules in a layer structure.

⊗ and ⊙ 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). SmCsPA 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. SmCaPA is chiral smectic phase. As the electric field is applied, the optic axis rotates with an angle of twice the tilt angle.

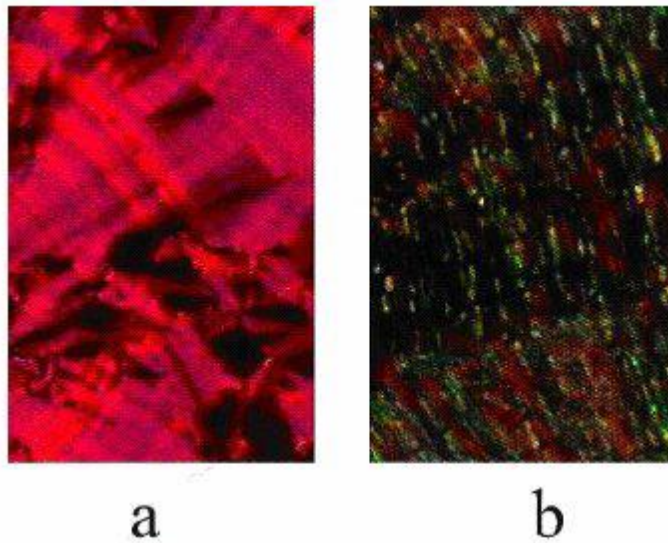


Figure 1.5.5: Typical textures between crossed polarizers of SmCsPA (b) at ground state and switched to SmCaPF (a) [66]. Pictures represent $100\mu\text{m} \times 150\mu\text{m}$ areas. (M.Nakata thesis).

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 SmCPL, 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.

1.6 Spontaneous Polarization, Layer Chirality, and Molecular Chirality

The sign of spontaneous polarization is defined using the direction of the tilt and polarization, i.e., the sign is plus when \mathbf{P} points to the same direction of $\mathbf{z} \times \mathbf{n}$ (where \mathbf{z} points along the layer normal and \mathbf{n} is parallel to the molecular long axis). In the case of ferroelectric Sm- C^* phase or antiferroelectric Sm- CA^* phase of rod-like molecules, spontaneous polarization is originated from breaking of mirror symmetry by introduction of chirality. Hence, at any given temperature, all of the layers in these chiral smectic phases have a uniform sign of spontaneous polarization that is completely determined by the handedness of molecules.

On the other hand, in the tilted polar smectic phases (Sm- CP phases) of *achiral* bent-core molecules, two types of layers exist, and one of which is the mirror image of the other [Figure 1.8.1 (a)]. Then as in the case of the Sm- C^* phase of rod-like molecules, the spontaneous polarization of each layers is uniquely defined. However, the situation is little complicated because molecules in each layer have a bent-direction \mathbf{b} . \mathbf{P} and \mathbf{b} are assumed to be parallel but their directions are not always the same. For this case, the layer chirality, instead of the sign of spontaneous polarization, is defined by D. R.Link et.al [70] using the molecular tilt direction and \mathbf{b} . The handedness of a layer (layer chirality) is plus when \mathbf{b} points along the same direction as $\mathbf{z} \times \mathbf{n}$ as shown in Figure 1.8.1 (b). It is difficult to determine the direction of \mathbf{P} and \mathbf{b} experimentally. The director \mathbf{b} points in the same direction (or opposite direction) to the electric field when \mathbf{P} and \mathbf{b} are parallel (or anti-parallel). Recently, it was reported that these two vectors were anti-parallel, which was indicated by the molecular orbital calculations for the molecules of PnOPIMB [Figure 1.4.1] homologues.

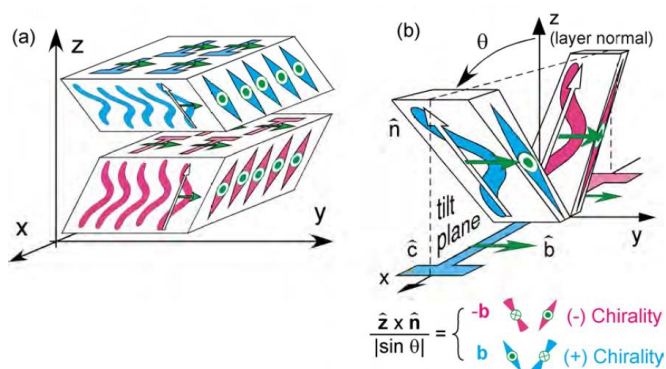


Figure 1.8.1. (a) Geometry for smectic layers and layer stacking in tilted smectic phase of bent-core molecules. (b) In one smectic layer with layer normal along the z -axis composed of bent-core molecules with polar order along \mathbf{b} parallel to the y -axis, two possible layer structures one of which is mirror image of the other, are defined by the director \mathbf{n} tilting by θ either along the positive or negative to x -axis. The two dimensional \mathbf{c} -director (nail) is defined by the projection of \mathbf{n} onto a layer surface with the head of the nail indicating which end of the molecule is closest the top surface.

In all figures illustrating molecular orientations, only the \mathbf{b} -director will be used instead of \mathbf{P} . The direction of \mathbf{P} should be thought of as being the same (or opposite) direction as \mathbf{b} when \mathbf{P} and \mathbf{b} are parallel (or anti-parallel). In the ferroelectric Sm-C^* or antiferroelectric Sm-CA^* phase of rod-like molecules, layer chirality (handedness of a layer) is defined using \mathbf{P} instead of \mathbf{b} and then the layer chirality and sign of spontaneous polarization is the same. Of course all layers have the same chirality at a given temperature. The layer chirality (also the sign of spontaneous polarization) is completely defined by chirality of molecules. However, both handednesses of layers exist in the Sm-CP phase of achiral bent-core molecules since molecules are achiral. If it is not the chirality of the molecules, what difference is possible to exist between the molecules in the (+) and (-) layer of the achiral Sm-CP phase? Several reports point out that the conformation of the molecules is chiral and the molecules in the (+) and (-) layer are forming a chiral conformation which is the mirror image of that of molecules in layers of opposite handedness[71-73]. It is easy to imagine that the layer chirality in the Sm-CP phase becomes uniform if chirality is introduced to the system.

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