

CHAPTER 1

Introduction

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1.1 INTRODUCTION TO THE LIQUID CRYSTAL

Liquid Crystal is a delicate phase of matter intermediate between the crystalline solid and the amorphous liquid. In 1888 Friedrich Reinitzer, an Austrian botanist, was performing investigations about cholesterol at Charles University in Prague [1]. He synthesized the benzoates and found that cholesteryl benzoate does not melt in the same manner as other compounds, but has two melting points. At 145.5 °C it melts into a cloudy liquid, and at 178.5 °C it melts again and the cloudy liquid becomes clear [2]. Reinitzer send his sample to German physicist Otto Lehmann, who was an expert in optics, for better examination. Lehmann examined the intermediate cloudy fluid and reported it as crystalline state and he named the new state as “Liquid Crystal”. Reinitzer presented his results, with due credits to Lehmann at a meeting of the Vienna Chemical Society on May 3, 1888 [3]. Thus Reinitzer discovered the novel state of matter by chance. The notion ‘Liquid Crystal’ suggests that it is an intermediate state of a matter, in between the liquid and the crystal. It possesses some typical properties of a liquid (e. g. fluidity, inability to support shear, formation and coalescence of droplets) as well as some crystalline properties (anisotropy in optical, electrical, and magnetic properties, periodic arrangement of molecules in one spatial direction, etc.). The important characteristics of liquid crystals (LC) are that it is affected by electric and magnetic fields and can rotate plane of polarization of light. For their electro-optic properties, they find applications in display industries. The Liquid crystal display (LCD) is more energy-efficient and can be disposed of more safely than a CRT. Its low electrical power consumption enables it to be used in battery-powered electronic equipments. LCDs are used in a wide range of applications including computer monitors, televisions, cameras, instrument panels, aircraft cockpit displays, medical appliances, clocks, watches, calculators, etc.

1.2 CLASSIFICATION OF LIQUID CRYSTAL

Liquid crystal is divided into two categories – lyotropic and thermotropic. Lyotropic liquid crystalline phases show mesomorphic behaviour by the change in the concentration of the solute in a solution. On the other hand, the term “thermotropic” arises because transitions involving these mesophases are effected by changing temperature. These liquid crystals are divided into main two categories – calamatic

and discotic. Calamatic liquid crystals are composed of rod-like molecules and discotic liquid crystals are composed of disc-like molecules [3]. George Friedel, a French scientist, proposed in 1922 a classification scheme based on the molecular arrangement of thermotropic liquid crystals. These are named as nematic, cholesteric and smectic [4].

1.2.1 NEMATIC LIQUID CRYSTAL

The nematic phase is a one dimensional ordered elastic fluid. In this type of liquid crystals, there is only long-range orientational orders, i.e., molecules tend to align parallel to each other, shown schematically in **Figure 1.1(a)** but there is no positional order. The orientational order is defined by an average direction of molecules called the director and is denoted by the vector **n**. In practice, the orientations of individual molecules are not exactly parallel to the director, therefore the nematic phase can be characterized by an orientation order parameter S. This order parameter S, based on the average of the second order Legendre polynomial is defined as:

$$S = \langle P_2(\cos\theta_i) \rangle = \frac{1}{2}(3 \langle \cos^2\theta_i \rangle - 1) \quad (1.1)$$

Where θ_i is the angle between the long axis of the i^{th} molecule and the director **n**, the statistical average is taken over all θ_i . In a perfectly ordered state (crystalline state) θ_i s are zero giving $S=1$, whereas in perfectly random state (isotropic liquid) average of $\cos^2\theta_i$ is 1/3 so that $S=0$. So, higher is the order parameter, the more ordered is the nematic liquid crystal. The typical value of the order parameter in the nematic phase lies between 0.3 and 0.9. Strictly speaking the order parameter is real, symmetric and zero trace tensor. The nematic phase is sensitive to external electric and magnetic field and mechanical stresses, and it modifies the optical path of visible rays, for which they find wide application in display devices [5], most of the commercial LC displays are based on nematics.

1.2.2 CHOLESTERIC LIQUID CRYSTAL

When a nematic liquid crystal mixed with chiral molecules, the structure undergoes a helical distortion about an axis normal to the preferred molecular

direction \mathbf{n} . Thus the structure of a cholesteric liquid crystal is periodic and the director varies its direction. The period of this is known as the pitch p (**Figure 1.1(b)**).

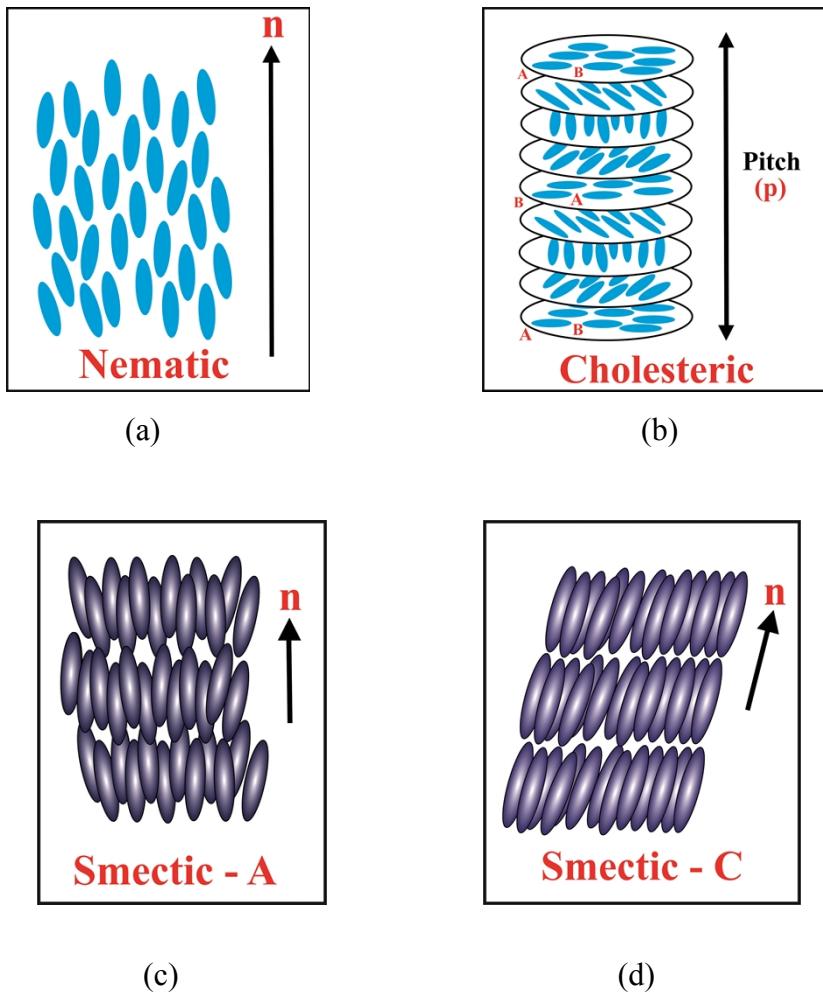


Figure 1.1. (a) Nematic, (b) Cholesteric (c) Smectic–A and (d) Smectic–C liquid crystals.

1.2.3 SMECTIC LIQUID CRYSTAL

Upon cooling from the nematic phase (in some cases directly from the isotropic phase), LC molecules often self-assemble into layers (**Figure 1.1(c) and (d)**). These layered phases are called smectic liquid crystals. In the smectic phase, the molecules maintain the general orientational order of nematics, but also tend to align themselves in layers; with a well-defined interlayer spacing, which can be measured by X-ray diffraction [6]. Thus molecules in this phase show additional degrees of translational order not present in the nematic phase. The interlayer attractions are weak compared to the lateral forces between the molecules, and the layers can slide over one another

relatively easily. This gives rise to fluidity to the system but with higher viscosity than nematics.

Smectic liquid crystals have stratified structure but a variety of molecular arrangements are possible within stratification with a difference in the way of layer formation and exhibiting difference in order inside the layers [7-9]. The simplest is the smectic A (SmA) phase where the director (**n**) is perpendicular to the smectic layers and thus parallel to the layer normal. In this phase, within the layers, molecules are randomly distributed. Thus, the structure may be defined as an orientationally ordered fluid on which a 1-D density wave is superimposed. On decreasing temperature, the SmA phase may transform into a phase possessing lower symmetry. The breaking of symmetry may lead to tilting of the molecules relative to the smectic layers normal. The phase thus formed is called the smectic C (SmC) phase. In this phase also no positional correlation is observed within the layer plane. There are many other types of smectic phases which, if exist, appear with increasing temperature according to a sequence rule, which may be in generalized form written as **Solid crystal - SmH - SmK - SmE -SmG - SmJ – SmF – SmB (cryst.) -SmI-SmB (hex.)- SmC - SmA – N – blue – isotropic** [10]. In general, most of the compounds show only a small part of the numerous phases, so that the generalized sequence rule is a combination of many compounds and is a hypothetical one. Ferroelectric and antiferroelectric liquid crystals are important smectic C type liquid crystal and their structures are discussed in sections 1.2.5 to 1.2.7.

1.2.4 CHIRALITY

Before the discussion of ferroelectric and antiferroelectric liquid crystals, we introduce the term ‘chirality’ which is essential characteristics of these liquid crystals. An object or a molecule that is not superimposable on its mirror image is termed as chiral. Chirality is generated by four different structural moieties attached to a tetrahedral, sp^3 carbon atom (often described as a chiral center). Molecular chirality leads to a wonderful variety of equilibrium structures. All of the chiral smectic mesophases takes the form of a helical structure.

1.2.5. FERROELECTRIC LIQUID CRYSTAL

Idea of the ferroelectric mesophase was first presented by R.B. Meyer at the 5th International Liquid Crystal Conference in 1974. From symmetry considerations, he deduced that all tilted smectic phases composed of rod-like chiral molecules have to exhibit a (local) spontaneous polarization if the molecules contain a permanent transverse dipole moment. In this phase molecules are arranged in fluid layers. On average the molecules are tilted from the layer normal by an angle. The angle made between the layer normal (**k**) and the director (**n**) is termed the tilt angle (θ). The tilt defines a plane containing **n** and **z**, called the tilt plane. The phase is optically biaxial [11].

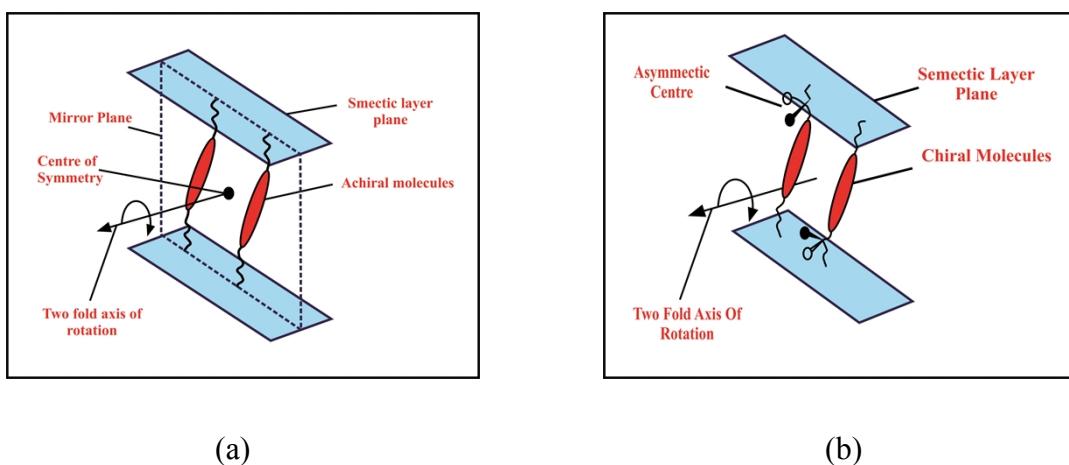
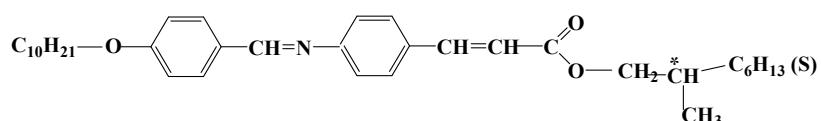


Figure 1.2. Symmetry elements of (a) SmC and (b) SmC* phase after reference [12]



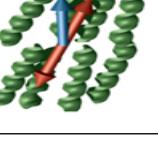
Cr 76 SmC* 95 SmA* 117 Iso

Figure 1.3. Structure of DOBAMBC, first FLC compound

The maximum symmetry that an achiral SmC phase can possess is (i) C_2 axis normal to the tilt plane, and (ii) σ plane congruent with the tilt plane. Meyer first realized the simple fact that a chiral phase can possess no reflection symmetry, and therefore the maximum possible symmetry for a chiral C phase is C_2 (**Figure 1.2**). Any medium with C_2 symmetry must possess polar order, and therefore Meyer

predicted that the chiral SmC phase (SmC*) would be ferroelectric, i.e. the direction of the polarization in the polar LC phase would be switchable [13]. The molecular organization and symmetry elements of different phases Nematic, SmA, SmC and SmC* are mentioned in **Table 1.1**.

Table 1.1. The symmetry elements of the N, SmA, SmC, and SmC* phases [14, 15]

Phase	Molecular Organization	Symmetry
Nematic (N)		$D_{\infty h}$
Smectic A (SmA)		D_{∞}
Smectic C (SmC)		C_{2h}
Chiral Smectic C (SmC*)		C_2

The first synthesized compound fulfilling Meyer's specification is known by an acronym DOBAMBC, standing for (S)-(-)-p'-decyloxybenzylidene p'-amino 2-methylbutyl cinnamate [16] (**Figure 1.3**). The molecule of DOBAMBC contains an asymmetric carbon atom C rendering molecular chirality, while a lateral C=O group provides a transverse permanent dipole moment. The aliphatic chain attached to the other end of the molecule by an oxygen atom is relatively long, favouring the SmC mesophase. The other aspect of chirality is the rotation of the director and hence the rotation of the direction of dipole moment about the smectic layer normal (**Figure 1.4**). Due to the formation of the helical superstructure, the spontaneous polarization is compensated to zero within one pitch of the helix, p , and the material appears to be non-polarized. With the synthesis and evaluation of DOBAMBC, the experimental study of the phenomenon of ferroelectricity in liquid crystals began. Since then, an

explosion of research and invention aimed at using and improving these novel materials has occurred.

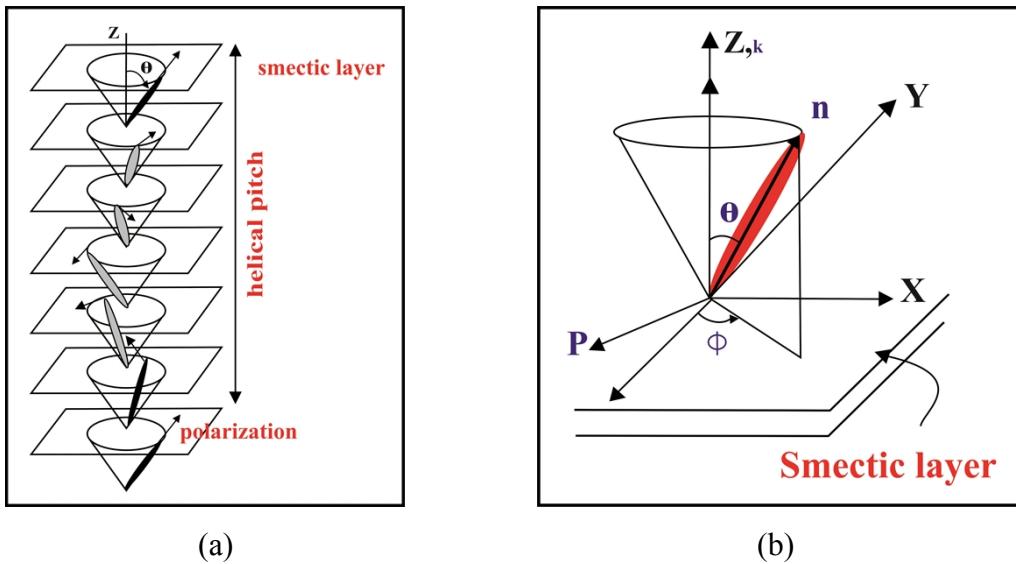


Figure 1.4. (a) The helicoidal structure of chiral smectic C (SmC^*) liquid crystal, polarization is tangential to the circle of intersection of the cone with the boundary plane of the layer. (b) The molecular polarization P is always perpendicular to the director n , the angle between n and k is the tilt angle (θ), and the azimuthal angle (ϕ) differs from layer to layer and is a function of the coordinate Z parallel to the layer normal. [17]

1.2.6 SURFACE STABILIZED FERROELECTRIC LIQUID CRYSTAL

Although the individual molecules in SmC^* phase possess spontaneous polarization, the whole ferroelectric sample in a bulk do not have any macroscopic polarization because the molecules in layers form a helix and the net polarization is zero via helix. The stable structure of the SmC^* phase is characterized by the helicoidal structure in which the polarization is hidden and externally canceled. So it will not be possible to get macroscopic polarization in SmC^* phase in the absence of an electric field unless the helix is unwound. Thus the smectic C^* phase is not ferroelectric per se. The SmC^* phase in bulk more correctly is called helielectric [9]. In his review in 1977, Meyer addressed by pointing out that it is always possible to obtain helix-free materials by mixing (and this can be done in several ways), and thus achieving a permanent non-zero polarization that may be homogeneous in space [18].

This was demonstrated in 1980 by Clark and Lagerwall and they showed that the SmC* phase could be rendered helix-free and bistable in a surface-stabilized structure [19].

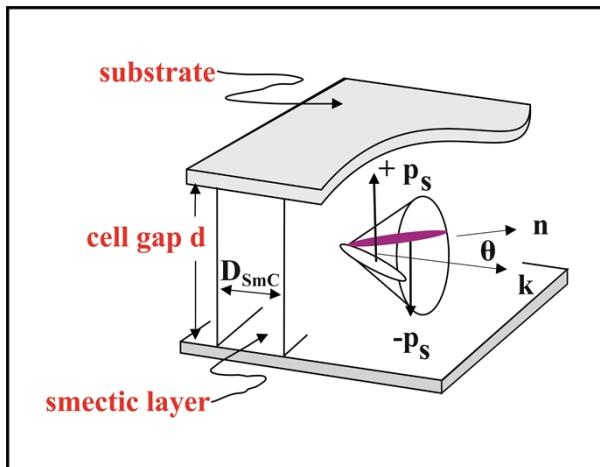


Figure 1.5. Schematic surface stabilized ferroelectric SmC* liquid crystal (SSFLC) geometry with tilt angle θ (T) and spontaneous polarization p_s (T). [20]

In the surface-stabilized structure the helix is inherently unwound by the elastic interaction with the surrounding surfaces. The surface interaction is equivalent to a permanently applied external field, but of different nature and this interaction is non-interacting with the electric field which is to be applied. In the helix-free sample the SmC* structure has a uniform polarization and is of special electro-optic interest. The ideal bookshelf geometry of SSFLC layers sandwiched between the glass plates of a capacitive cell, as suggested by Clark and Lagerwall is shown in the **Figure 1.5**. They illustrated that in a surface-stabilized ferroelectric liquid crystal (SSFLC) structure, the uniform polarization points in either of two ways, and this giving rise some unusual properties. These are:

- (i) A change of sign in the electric field applied across the sample switches the optic axis of the molecule symmetrically between two equivalent ‘off’ and ‘on’ states. After application of a pulse the optic axis stays in its position until a pulse of opposite sign switches it back to the other position. This means that the device is bistable (symmetrically).
- (ii) The SSFLC device extends the switching speed from milliseconds regime in nematics to below microseconds.

- (iii) In contrast to other liquid crystal electro-optic mechanisms, in the SSFLC the optic axis (that switches by 2θ , twice the tilt angle, around the cone) is essentially perpendicular to glass plates and switched around an axis parallel to the transmitted/reflected light. This gives rise to a large optic effect with an excellent viewing angle.

SSFLC is a concept by which the energy degeneracy of SmC* phase can be broken. If we rotate the polarisation P_s around the cone to the opposite position, corresponding to a change of sign in tilt θ , then we see that P_s has reversed its direction. Thus a change of sign in θ corresponds to a sign reversal of P_s , and from this, it follows that, at least for small θ , P_s and θ must be linearly related i.e.,

$$P_s \sim \theta \quad (1.2)$$

The discovery of SSFLC saw great interest from the liquid crystal community due to its submicron response time, bistability and novel electro-optic effects. The bistability is a consequence of the broken symmetry in the phase variable. The potential curves along this variable, whether symmetric or slightly non-symmetric (**Figure 1.6**), illustrate that the bistability is an inherent property of the chosen geometry. It will be there as long as there are energy maxima between the states 1 and 2 that correspond to the two tilt directions.

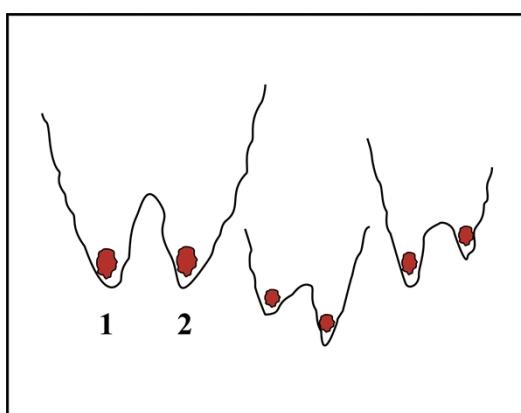


Figure 1.6. The potential curve along a phase variable

1.2.7 ANTIFERROELECTRIC LIQUID CRYSTAL

During the studies of ferroelectric liquid crystals a few groups [21-23] noticed some peculiar behaviors in their ferroelectric materials (still then they thought the materials to be ferroelectric). Hiji *et al.* [24] reported a third stable state exhibiting a dark view between crossed polarizers when one of the polarizers was parallel to the smectic layer. Furukawa *et al.* [25] reported a very small dielectric constant and a threshold behavior in the electro-optic response in the lower-temperature region of SmC*, suggesting a new phase SmY*. Finally, Chandani *et al.* [26] in 1989 discovered the novel antiferroelectric phase (SmC_A*) which exhibits tri-stable switching in a compound named as MHPOBC (**Figure 1.7(a)**). In the antiferroelectric phase, the direction of the molecular tilt, and hence the direction of the spontaneous polarization of the adjacent layers, are in the approximately opposite directions (~180°) [13, 27-29] as shown in **Figure 1.7(b)** and (c).

This type of molecular conformation is known as anticlinic conformation [25, 33-34]. Due to chirality in the SmC_A* phase, the direction of molecular tilt and hence the electric polarization precess from layer to layer along the layer normal and develops helix and leads to the formation of a double helicoidal structure with axis parallel to the layer normal.

“Antiferroelectric liquid crystal” is the common name for smectic liquid crystals that exhibit a number of smectic (Sm) tilted structures with variation of the tilt, azimuthal direction from layer to layer in non-synclinic structures in which the periodicity of crystallographic unit varies. The crystallographic unit periodicity may vary from a few (SmC_a*), four (SmC_{F12}*), three (SmC_{F1}* or SmC_y*), to two (SmC_A*) smectic layers and all of the phases arising in such a variation, possess liquid-like order inside the layer [27]. Nature of SmC_{F1}* and SmC_{F2}* is ferrielectric.

In AFLC materials sandwiched between two glass plates in homogeneous orientation (in surface stabilized structure), the smectic layers are arranged perpendicular to the glass plates giving rise to a bookshelf geometry. If an electric field E is applied parallel to smectic layers of AFLC material (i.e. perpendicular to the glass plates), placed under the cross polarizers, the material switches from the

antiferroelectric state at $E=0$ (dark) to one of two symmetric ferroelectric states (bright) depending on the polarity of the field and show double hysteresis loops (**Figure 1.8**). This phenomenon in AFLC materials is known as tristable switching and is of great interest [35-36].

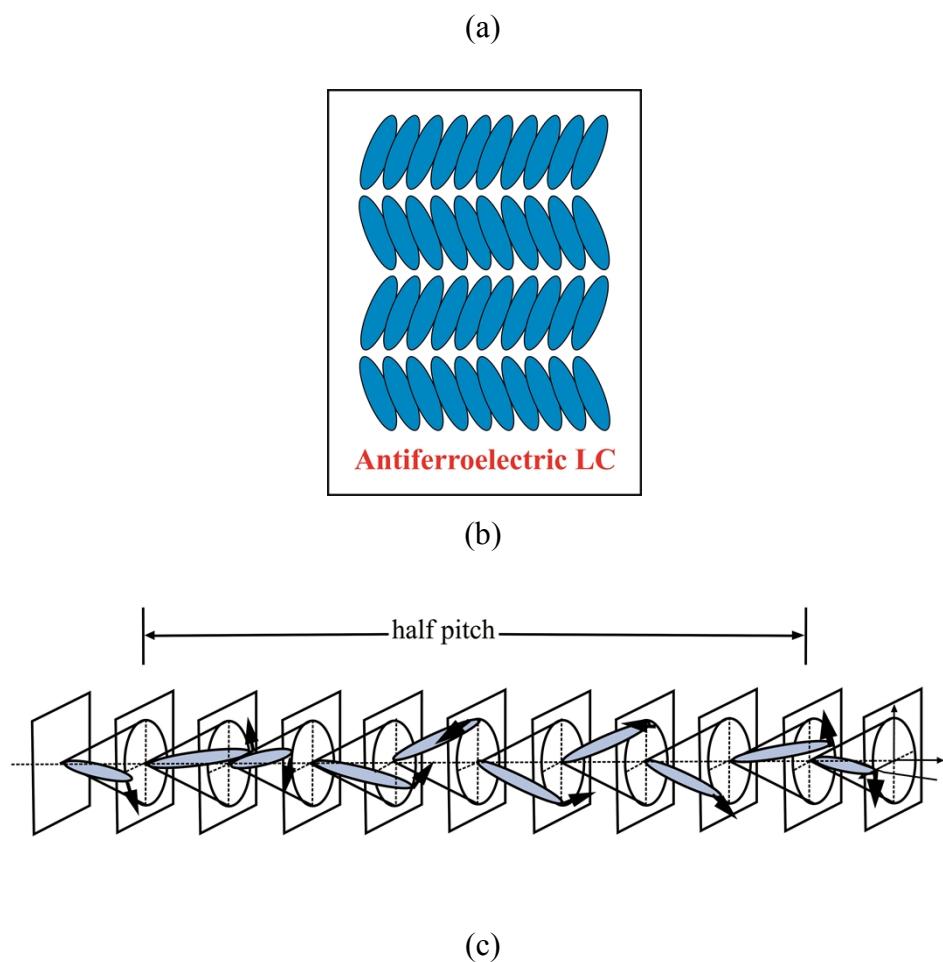
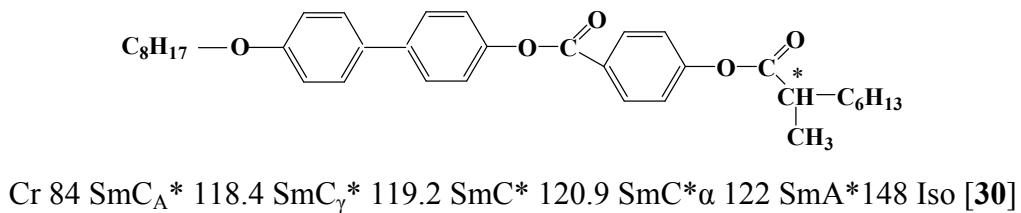


Figure 1.7. (a) Structure and transition temperature of MHPOBC, first AFLC compound [31], (b) Herring-bone pattern in the hypothetical structure of antiferroelectric liquid crystal, (c) Molecules, on average, have alternating tilt in alternating layers, corresponding to dipole moments pointing in opposite direction in alternate layers form double helix [32]

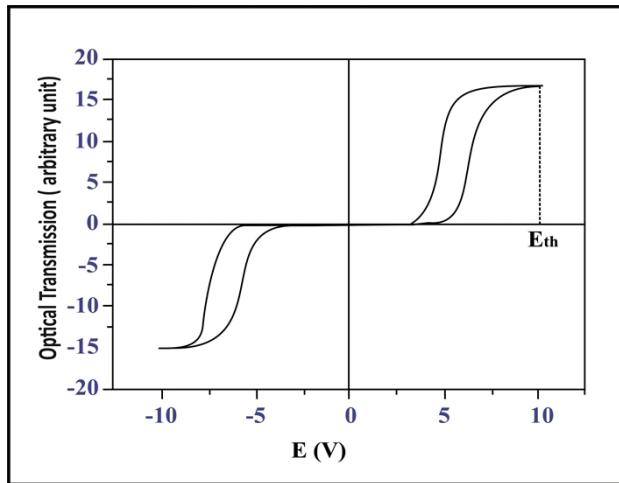


Figure 1.8. Double hysteresis loop of antiferroelectric liquid crystal under applied AC field (E). At $E=0$, the antiferroelectric state is stable. For a field $E > E_{th}$ or $E < -E_{th}$, the ferroelectric states are obtained from antiferroelectric states as shown to right and left and corresponding to the two saturated states at the ends of the double hysteresis loop beyond the threshold fields $\pm E_{th}$ [20]

1.2.8 ORTHOCONIC ANTIFERROELECTRIC LIQUID CRYSTAL

Conventional AFLC materials are usually tilted between 20° and 35° . AFLCs with extremely high molecular tilt (equal or nearly equal to 45°) are the most promising for special display and photonic applications due to their unusual optical properties which resulted from the high tilt angle of the molecular director in smectic layers [37-39]. In this phase, the conic angle between the directors of adjacent layers is nearly 90° . Therefore such antiferroelectrics were termed as orthoconic antiferroelectric liquid crystals (OAFLC). Typical structural defects within the surface stabilized structure of smectic phases of conventional AFLCs, corresponding to local disorientation of the smectic layers normal, deteriorates the optical contrast of such structures. Such materials in surface stabilized structures are usually optically biaxial positive liquid crystal and the effective optic axis is along the smectic layer normal i.e., parallel to cell plates. Whereas orthoconic antiferroelectric liquid crystals are a uniaxial negative liquid crystal with optic axis perpendicular to the glass plates of the cell at normal incidence (**Figure 1.9**).

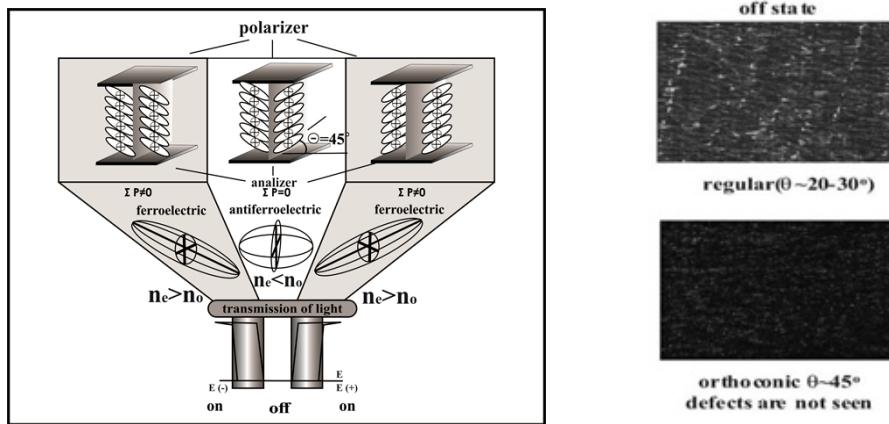


Figure 1.9. Electro-optical properties of orthoconic AFLCs in compared to ferroelectrics. (Adapted from [42])

OAFLCs placed between crossed polarizers behaves as an isotropic medium at zero fields [39-41] for the incident light beam orthogonal to the sample plane and surface defects are not observed, which generates the excellent true dark state even the sample is rotated under crossed polarizers [42]. Abdulhalim *et al.* [43] calculated that orthoconic antiferroelectric LCs with dielectric constants fulfilling the condition:

$$\varepsilon_1 = \frac{\varepsilon_2 + \varepsilon_3}{2} \quad (1.3)$$

behave as an isotropic medium for all incidence angles of light. Such unusual optical properties of orthoconic antiferroelectrics open up new areas of applications. A partially fluorinated terminal chain promotes the high tilt of molecules in smectic layers. The Military University Group, Warsaw synthesized different families of such compounds with partially fluorinated chains having a biphenyl, naphtyl or terphenyl unit in the rigid core of molecules, un-substituted or laterally substituted with one or a few fluorine atoms [42, 44-45]. These compounds are proposed as the basis for liquid crystal displays and photonic devices with attractive advantages over existing nematic and ferroelectric technologies [39, 41].

1.3 EFFECT OF FLUORO-SUBSTITUTION IN FERROELECTRIC AND ANTIFERROELECTRIC LIQUID CRYSTALS

From the earlier discussions, it is clear that for the appearance of ferroelectric SmC* phase the molecule should have chirality i.e. there should exist a terminal chiral center and transverse dipole moment. Considering these factors an FLC (or AFLC) molecule can be divided in several parts as R–A–X–A–Y–A–Z–R*. Central linear rigid core is formed by two or three aromatic or heteroaromatic rings denoted as ‘A’ which are connected by linkage groups X and Y. As a rule, X and Y represent a simple bond e.g. –COO–, –CN=N–, –N=N– etc. R is a non-chiral terminal chain (as a rule an unbrached alkyl– or alkoxy group). R* is a chiral terminal chain with one or more asymmetric carbon, as a rule, it is $-\text{C}^*\text{H}(\text{CH}_3)(\text{CH}_2)_m\text{CH}_3$, m=1-6. Sometimes chiral terminal chain is attached at both ends [46]. The linkage group Z between the core and the terminal chain formed either by a single bond or combination of more groups, some of them bringing the molecule transverse dipole moment (e.g. –CH2–, –CH=CH–, –COO–, –CO–) [47].

In the majority of FLCs, the linkage Z is the source of the transverse dipole moment and frequently it is carbonyl group (–CO–) is employed. The additional increase of spontaneous polarization can be achieved by lateral substitution of electronegative atoms or functional groups that behave as an acceptor of electrons. The location of the substitution is very important for the increase of Ps. Especially by the fluoro-substitution in different positions of ferroelectric and antiferroelectric liquid crystals the properties of parent system can be manipulated and improved predictably by changing melting point, mesophase types, transition temperatures and other physical properties [48].

1.3.1 EFFECT OF LONGITUDINAL FLUORO-SUBSTITUTION

Fluoro-substitution at the hydrocarbon chain of compound favours smectic chiral phases, enhances the dielectric anisotropy and elastic constants by introducing high polarity of the C – F bond. The Compounds having terminal fluoro substitution posses a high resistivity, high photochemical stability and low viscosity which is suitable for active matrix (thin-film transistor, TFT) displays [49]. The possibility of

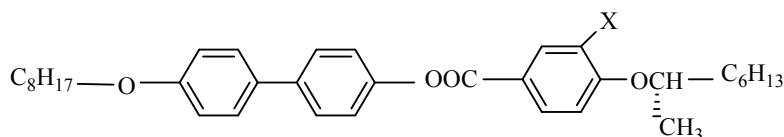
the appearance of a new phase and the modified temperature span of new mesophase are achieved by changing the degree of association between the molecules by introducing some substituent at the terminal chain [50]. R. Dabrowski *et al.* [51] reported that the fluorination at the terminal chain part of a chiral molecule is the key factor for the appearance of SmC_A* phase. A large temperature difference in phase transitions between the hydrogenous and fluorinated structure is observed as a typical feature of fluorinated compounds by Janulis *et al.* [52]. Liquid crystals with fluorinated chains are very promising materials. Their physical and electro-optical properties in many aspects are quite different from their hydrogenous analogues, which creates new possibilities for their applications. As for example, stability of SmC* phase observed to increase in 4‘-(2-fluoro-octyloxy) phenyl4-[{(perfluoroalkyl) alkyloxy} benzoates for the increasing number of fluorinated in achiral chain [49]. The influence of the perfluorinated part in the alkoxy $[-(\text{CF})_n-(\text{CH}_2)_m-\text{O}-]$ terminal chain on the existence of the SmC_A* phase was studied by Nugyen *et al.* [53]. For the fixed length of the methylene spacer $m = 5$ the increase of the fluorinated part eliminates the SmC_A* phase. The same appears for the smaller odd number $m = 5$ of the fluorinated carbon atoms in the chain. In homologous series of perfluoroalkanoyloxy biphenylates, the antiferroelectric SmC_A* phase was observed for members with a short as well as with a long fluorinated part of the tail. For a highly fluorinated compound a big temperature difference in phase transitions between the fluorinated and Hydrogenous structure was observed [53].

1.3.2 EFFECT OF LATERAL FLUORO-SUBSTITUTION

The lateral substitution of electronegative atom or functional groups (electron acceptor) is effective in the vicinity of the asymmetric carbon as well as on distant parts of the central skeleton. It not only brings additional transverse dipole moment but also influences the steric hindrance of both rotations of molecules (i) about the long axis and (ii) intra-molecular rotations. These rotations decrease the bulk spontaneous polarization. The chiral center which is depicted as an uneven tipod with unequally long arms plays an important role to influence steric hindrance to restrict the molecular rotations also. Methyl group ($-\text{CH}_3$), nitril group ($-\text{C}\equiv\text{N}$) and halogens (F, Cl, Br) are mostly used for a lateral substituent. These substituents (at the

vicinity of chiral center) generally influence the temperature stability of any mesophase [Table 1.2]. The increase of lateral dipole moment in FLCs is due to the dipole moment of C-X (X= F, Cl, Br) bond and when –O– group of the linkage Z is nearly parallel with this C-X bond, the dipole moment is thus added up. The increase of dipole moment and hence spontaneous polarization (Ps) occurs in the following sequence of substituents H<F<Cl<Br<CN.

Table 1.2. Values of the ‘spontaneous polarization Ps’ (nC/cm^{-2}) at temperature T_c -10 °C and temperature range of the SmC* mesophase as they influenced by the substitution on the central core near an asymmetric carbon in an ortho position to the linkage group Z (–O–) [55].



X	Ps (nC/cm^{-2})	Range of SmC*
H	45	78-99
F	78	64-97
Cl	123	72-95
Br	131	42-87
CN	160	67-90

Similarly when the lateral substitution is made at the opposite end of asymmetric carbon the value of polarization is also observed to increase [54]. With the increasing volume of the substituent thermal stability of the mesophase decreases and its temperature range becomes narrower. Considering the view that the span of a mesophase should be broad, only F is suitable for lateral substitution.

1.4 LIQUID CRYSTAL MIXTURES

For the application of ferroelectric and antiferroelectric materials in display technology, broad temperature range, low melting point, high switching speed, low viscosity, etc. are the essential properties which need to be optimized. Optimization of these properties can be achieved by (i) engineering of liquid crystalline molecular

structures i.e. by synthesis of new liquid crystalline compounds, (ii) formulation of mixtures. Generally, it is observed that no single FLC/AFLC compound can satisfy the above requirements. Therefore the formulation of a mixture (binary, multi-component, and host-dopant, nanocomposite) is a useful technique [56]. However, the nature and concentration of the host and dopant influence the phase behavior and properties of the resulting mixture enormously.

A binary mixture of one protonated oligomethylene spacer based chiral compound and one achiral biphenyl pyrimidine compound exhibits room temperature ferroelectric mixture with moderate spontaneous polarization and sub-millisecond switching time [57]. A partially fluorinated mesogenic chiral dopant homologue of the pure components when mixed with an achiral host mixture, results in an electroclinic mixture with large field-induced tilt and very small layer contraction at lower concentrations [58], however, at higher concentrations, wide range ferroelectric mixtures with a few hundred micro-second switching time are observed [59]. But a different flourinated chiral dopant, with oligomethylene spacer, produces ferroelectric mixture with much faster (99 μ s) response time [60]. Intermolecular attractive forces, like Van der Waals forces, hydrogen bonds and electron donor-acceptor interaction influence the configurations of molecular arrangements in the mesophases of a mixture. Each of these forces, collectively or separately, may be responsible for increasing or decreasing the stability of the liquid crystalline phases and appearance of new intermediate phases in some cases.

As a general strategy multi-component mixtures are formulated by doping appropriate chiral dopant in achiral host mixture matrix. Host mixture is usually a mixture of several achiral compounds with wide range of SmC phase which controls the overall temperature range and tilt of the final mixture. The chiral dopant controls the spontaneous polarization, viscosity, helical pitch and switching speed of the final mixture [61-65].

1.5 MOTIVATION OF THE PRESENT WORK

Twisted nematic liquid crystals based displays are presently available in the market with a high viewing angle. The high value of response time (~ms) governing the frame rate, ghost effect and contrast ratio are still a matter for further improvement. The ferroelectric (FLCs) and antiferroelectric liquid crystal (AFLCs)

based display may be the option to solve the problem with their micro-second switching time and that is why these two materials gathered a special interest during last three decades. FLC based displays also encountered several problems - small cell spacing ($1\text{-}2 \mu\text{m}$) to unwind the helix, the problem of mechanical shock due to unstable molecular anchoring at the surface and desired gray scale capability which can only be achieved by indirect methods such as spatial and temporal dithering [66]. The surface stabilized antiferroelectric liquid crystals (SSAFLCs) are the smarter options to build fast response electro-optic devices and displays [67]. These materials have several advantages over the surface stabilized ferroelectric liquid crystals (SSFLCs) such as - inherent DC compensation, gray scale capability, relatively wide viewing angle, driving voltages acceptable for integrated drivers, and no ghost effect, etc. [68]. Due to the tristable switching of these materials, a simple passive matrix driving scheme can be utilized. Using these technologies even big flat panels with video-rate was demonstrated [36, 42]. But still, two major problems encountered in the development of SSAFLC based displays, due to which such displays did not find production commercially. The first one is so-called pre-transitional effect [40, 69]. It is of the dynamic nature and seems to be more important. The second one is poor optical uniformity in off state caused by the existence of microscopic defects and the existence of two preferred orientations of normal to the smectic layer which differ by few degrees from each other. Here surface stabilized orthoconic antiferroelectrics (SSOAFLCs) are appropriate stuff and they can solve the problem of SSAFLCs by their unusual optical properties.

AFLCs are also interesting for the basic studies in soft condensed matter field as these materials have special molecular packing in them and are showing numerous sub-phases (SmC_α^* , SmC_β^* , SmC_γ^* , etc.) with distinct macroscopic properties. So enough scope is here in the study of the fluorinated antiferroelectric liquid crystals for understanding the basic structure-property relations aiming at the improvement of the knowledge domain in the field.

1.6 LIQUID CRYSTAL COMPOUNDS AND MIXTURES STUDIED IN THE DISSERTATION

In the above background, we have selected six fluorinated antiferroelectric compounds for detailed investigation. We have also formulated three mixtures. Out of these six compounds, four are chosen from a homologous series of antiferroelectric compounds with partially fluorinated alkoxy terminal chain and biphenyl benzoate core [70]. The compounds have antiferroelectric phase in a broad temperature range similar to the compounds with partially fluorinated alkanoyloxyalkoxy chain but longer methylene spacer promotes the presence of ferroelectric phase (SmC^*) also. Four members of this series (named as DM0, DM1, DM2, and DM3) structurally differ only by the position and number of lateral fluoro-substitution on the benzoate core. In DM0 there is no fluorination, in DM1 one fluoro-substitution is made at ortho position, in DM2 one fluoro-substitution is made at meta position, and in DM3 two fluoro-substitutions are made at both ortho and meta position positions. We have probed how the properties of the homologues change due to the change of number and position of lateral fluorination at the benzoate core. In order to investigate how the properties of the biphenyl benzoate core-based compounds change when mixed with one another, a few binary mixtures of DM0 and DM3 (having no lateral fluorination and maximum fluorination in core) have also been investigated. It has been observed that the equal weight percent mixture is a eutectic mixture (M3) and this mixture has been studied in detail and the results are compared with those of the pure compounds. After observing the eutectic behaviour in the binary mixture we decided to formulate a mixture of all the compounds DM0, DM1, DM2, and DM3 which resulted in a room temperature AFLC mixture (M6). We have investigated various properties of this mixture in comparison to the pure compounds. Finally, in order to investigate the change of properties of one of the above biphenyl benzoate core-based compounds (DM1) in presence of tiny external particles (nanoscale), a small amount of ($-\text{COOH}$ functionalized) multi-walled carbon nanotubes were doped in it and properties of this nanocomposite have also been studied in detail. We also selected another two antiferroelectric compounds (4F6T and 6F6T) for investigation which structurally differ from the DM series compounds by (i) the number of fluorinated carbon atom in the achiral chain, (ii) instead of alkoxy group in the chain, carbonyl group is attached and (iii) the core is doubly fluorinated terphenyl based instead of biphenyl benzoate.

The compound 4F6T differs from 6F6T only in the number of fluorinated carbon at the achiral chain. 4F6T has 4 fluorinated carbons at achiral chain and 6F6T has 6 fluorinated carbons. We discuss the change of properties of these two compounds due to the major change with respect to the biphenyl benzoate core-based series as well as the change of properties of compounds within the series due to the change of the number of fluorinated carbon atom at the achiral chain. Polarizing optical microscopy, differential scanning calorimetry, X-ray diffraction, frequency domain dielectric spectroscopy and electro-optic techniques have been used to investigate the pure as well as the mixtures. The molecular formulae, phase sequence and transition temperatures of the pure compounds, as well as of the mixtures, are shown in **Table 1.3 and Table 1.4.**

Table 1.3. Molecular structures, phase sequences and transition temperatures of the investigated pure compounds

Name	Molecular formula and transition temperatures of the compounds
DM0	$\text{C}_3\text{F}_7\text{CH}_2-\text{O}-\text{C}_6\text{H}_{12}-\text{O}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\overset{*}{\underset{\text{CH}_3}{\text{CH}}}-\text{C}_6\text{H}_{13} \text{ (S)}$ Cr 61.0 SmC _A * 94.0 SmC* 123.0 SmA* 125.0 I (Heating)
DM1	$\text{C}_3\text{F}_7\text{CH}_2-\text{O}-\text{C}_6\text{H}_{12}-\text{O}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\overset{*}{\underset{\text{CH}_3}{\text{CH}}}-\text{C}_6\text{H}_{13} \text{ (S)}$ Cr 41.0 SmC _A * 75.2 SmC* 103.0 SmA* 103.6 I (Heating)
DM2	$\text{C}_3\text{F}_7\text{CH}_2-\text{O}-\text{C}_6\text{H}_{12}-\text{O}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\overset{*}{\underset{\text{CH}_3}{\text{CH}}}-\text{C}_6\text{H}_{13} \text{ (S)}$ Cr 57.3 SmC _A * 80.5 SmC* 108.0 SmA* 112.2 I (Heating)
DM3	$\text{C}_3\text{F}_7\text{CH}_2-\text{O}-\text{C}_6\text{H}_{12}-\text{O}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\overset{*}{\underset{\text{CH}_3}{\text{CH}}}-\text{C}_6\text{H}_{13} \text{ (S)}$ Cr 63.2 SmC _A * 85.2 SmC* 109.3 SmA* 111.6 I (Heating)
4F6T	$\text{C}_4\text{F}_9-\overset{\text{O}}{\text{C}}(\text{CH}_2)_6-\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_3(\text{F},\text{F})-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\overset{*}{\underset{\text{CH}_3}{\text{CH}}}-\text{C}_6\text{H}_{13}$ Cr 44.6 SmC _A * 55.8 SmC* 68.7 SmA* 85.8 I (Heating)
6F6T	$\text{C}_6\text{F}_{13}-\overset{\text{O}}{\text{C}}(\text{CH}_2)_6-\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_3(\text{F},\text{F})-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\overset{*}{\underset{\text{CH}_3}{\text{CH}}}-\text{C}_6\text{H}_{13}$ Cr 36.0 SmC _A * 64.0 SmC* 72.0 SmC _a * 76.5 SmA* 99.2 (Heating)

Table 1.4. Composition, phase sequences and transition temperatures of the investigated mixtures

M3	DM0 + DM3 (each 50%) Cr 39.8 SmC _A * 86.1 SmC*112.8 SmA* 117.8 I (Heating)
M6	DM0 + DM1+ DM2+ DM3 (each 25%) SmC _A * 81.5 SmC*110.0 SmA* 112.5 I (Heating) <RT SmC _A * 65.0 SmC* 110.0 SmA* 112.0 I (Cooling)
DM1+CNT	DM1 (99.88%) + MWCNT (0.12%) Cr 39.05 SmC _A * 70.0 SmC*102.5 SmA* 103.3 I (Heating) <RT SmC _A * 48.0 SmC* 101.0 SmA* 102.2 I (Cooling)

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