

CHAPTER 9

Conclusions

9.1 Conclusions

The dissertation entitled “*Investigations on the physical properties of some liquid crystalline compounds and multi-component mixtures*” submitted for the degree of Doctor of Philosophy (Physics) of the University of North Bengal embodies the results of experimental investigations on the physical properties of several pure mesogens exhibiting a rich variety of polymorphism using different experimental techniques. The study of the physical properties of fluoro-substituted alkyl terphenyl isothiocyanates as well as fluoro-substituted terphenyl fluorides and chiral orthoconic esters has helped in the identification of suitable materials, where position specific substitutions is found to play a vital role in the optimization of the physical properties with the ultimate objective of promoting themselves as components of multi component mixtures for application in high end devices. Furthermore, as newer and smarter materials have emerged in the field of liquid crystals, study and characterization of such phases with amazing structural morphology as well as inherent anisotropy like the TGB_A , N^* and Blue phases have also been undertaken in this work to understand and explore both the fundamental aspects as well as the structure property relationships that leads to the occurrence of such phases. Moreover, several binary mixtures comprising of a chiral ester exhibiting exotic orthoconic antiferroelectric phases in conjugation with an achiral phenyl pyrimidine component has evoked interesting observations as to the nature of chiral perturbations in an achiral environment.

This thesis comprises of eight chapters. In chapter 1, a brief review of liquid crystal materials, the molecular arrangement within the different mesophases, classification (mainly achiral and chiral nematic and smectic phases) and their commercial applications have been discussed. A description about liquid crystal mixture formulation and their potential applications has also been discussed.

In chapter 2, the relevant experimental techniques and the basic theoretical approaches - Maier-Saupe mean field theory for nematic phase and the Frank elastic continuum theory, concerning liquid crystals have been discussed briefly.

Chapter 3 summarizes the physical characterization of four isothiocyanated and two analogous fluoro substituted terphenyl fluorides from birefringence, dielectric parameters, splay elastic constant, relaxation time and rotational viscosity measurements. The aim of this work was to identify suitable liquid crystalline compounds with low melting point, broad nematic range, large positive dielectric anisotropy and low rotational viscosity, as components of multi-component mixtures for display applications. The replacement of hydrogen atom by fluorine confers the resulting material with unusual and unique properties which allow their use as good precursors in many applications. Several variations of lateral fluorination have been incorporated to the rigid terphenyl core. Compounds with terminal isothiocyanate group exhibit high clearing point even in the presence of a few lateral fluorine atoms, while in the case of fluorine atom in the terminal position, a strong decrease in the clearing point have been observed. Substitution by fluorine atoms in 3,5 positions enhance the values of the birefringence, dielectric parameters, dielectric anisotropy than substitution in 3,3' positions. Fluorine atom in the central 3' position twists the benzene rings, which decreases the π electron conjugation. Compounds with trifluoro lateral substitution have lower birefringence and higher dielectric anisotropy values which is expected. Multiple fluorinations lower the birefringence of the compounds as the laterally substituted fluorine atom pulls the π electrons from the conjugation length along the main molecular axis. Among all the compounds investigated, the bulkier or heavier tri-fluorinated isothiocyanated compounds show the highest viscosity due to higher steric hindrance. To estimate the suitability of a compound in a mixture, Figure of Merit (FoM) has been taken into account. Significantly, higher Figure of Merit has been observed for the laterally fluoro substituted isothiocyanated compounds due to (i) higher values of birefringence and (ii) lower values of rotational viscosity in comparison to the fluoride compounds. Compound with 3,5 fluorine substitution shows marked improvement in its physical parameters as far as its applicability in multi-component mixtures is concerned. However, the operating temperature (at which the FoM is maximum) for this

compound is much higher than room temperature. For room temperature applications, suitable additives should be used during mixture formulation.

Chapter 4 highlights the systematic development of multicomponent nematic mixtures (mixtures **A-D**) from pure liquid crystalline compounds comprising of polar-isothiocyanated biphenyl and terphenyl derivatives which combine the necessary polarity with chemical stability and adequate polarizability. The molar ratios and the eutectic points of all the mixtures (mixture **A-D**) were calculated using the Schröder van Laar equation and the theoretical values of the melting and clearing temperatures were estimated at the eutectic point. This chapter is concerned with the characterization of liquid crystal mixtures containing fluorinated biphenyl/terphenyl ethane derivatives so that the overall display performance may be improved. Mixture **A** consists of one cyclohexylphenyl isothiocyanates and two laterally fluorinated terphenyl isothiocyanates. Mixture **B** is a seven component one, which contains one cyclohexylphenyl isothiocyanates, two biphenyl isothiocyanates along with four laterally fluorinated terphenyl isothiocyanates. Using **B** as a base mixture, it was further modified using dopants of fluoro terphenyl derivatives, resulting in Mixture **C**. Mixture **D** is a fourteen component mixture consisting of bi-phenyl, tri-phenyl, cyclohexyl laterally fluorinated derivatives. Operating at room temperatures, all these mixtures show superior performance with respect to birefringence and viscosity values in comparison to the widely used commercial mixture **E7** (prepared from alkyl, alkoxy cyanobiphenyl and cyanoterphenyls). However they exhibit slightly lower values of the dielectric anisotropy than **E7**, which may easily be modified by doping with alkyl, alkoxy biphenyl and terphenyl derivatives having a lateral fluorine atom. Such additives also effectively eliminate the smectic phases. The values of the birefringence, dielectric anisotropy and splay elastic constant, as well as the rotational viscosity of mixture **D** are of the order of 0.27, 8.57 20pN and 60 mPa.s respectively, which are excellent material parameters and this mixture, may be potentially used in display devices. Additionally, the order parameter and

activation energies (E_a) have also been calculated for all the multicomponent mixtures.

Chapter 5 deals with the detailed comprehensive study on the mesomorphic and structural properties of a chiral lactic acid derivative 4-(1-(octyloxy)-1-oxopropan-2-yloxy)biphenyl-4-yl 4-(decyloxy)benzoate, obtained using polarising optical microscopy, differential scanning calorimetry, optical transmission, x-ray diffraction and dielectric spectroscopy studies. The compound possesses the polar frustrated blue phase II, cholesteric phase, twist grain boundary smectic A (TGB_A) phase and the SmA^* phase. Due to the incompatibility of the cholesteric twist with the smectic layering, the cholesteric–smectic A phase transition is mediated via the TGB_A phase. The diffracted x-ray intensity profile reveals the presence of relatively sharp reflection at small angles ($2\theta \approx 3^\circ$ - 4°) in the TGB_A and SmA^* phase, clearly signifying the layered structure, in comparison to the diffuse ring obtained in the case of the BPII and N^* phases. In the SmA^* phase, the layer spacing (d) values are slightly temperature dependent due to stretching of the aliphatic chains of the molecules. The theoretically calculated length of the most extended conformer in the minimum energy configuration by semi-empirical molecular orbital package MOPAC agrees quite well with the layer spacing values obtained from x-ray diffraction study. The correlation length in the SmA^* phase is much higher than those in the TGB_A and N^* phase, and the transverse correlation lengths diverge near the N^* – TGB_A phase boundary indicating second order phase transition. A small hump related to pre-crystallisation phenomena is observed in the temperature dependent dielectric constant curve near the crystallization point.

Liquid crystals are extremely sensitive materials with respect to any modification of the molecular structure and even a minor change could strongly affect their mesomorphic properties or even their existence. Chapter 6 covers in details the effect of several polar ester linkage groups incorporated in the molecular core of a chiral lactic acid derivative, namely decyl 4-(4-(4-(2-(hexyloxy)propanoyloxy) benzoyloxy)benzoyloxy)benzoate on its structural properties. The existence of four ester groups in this molecule, results in the stable

paraelectric SmA* phase and ferroelectric SmC* phase over a reasonably broad temperature range. A slight discrepancy has been observed in the birefringence values measured on thin (3 μm) and thick (5 μm) planar cell because of differences in surface anchoring energy, surface effect and alignment of the liquid crystal layer of different thicknesses. The values of the spontaneous polarization is relatively high ($\sim 97 \text{ nCcm}^{-2}$ at 70°C) due to the zigzag molecular structure of several (four) ester linkage groups in the molecular core and an additional methylene group near the chiral centre. This molecular geometry also contributes to the large steric hindrance of the chiral centre and increases the viscosity and negatively affects its utilization in devices. The temperature variation of the order parameters *i.e.* the tilt angle and spontaneous polarization, confirms second order nature of the SmC*-SmA* phase transition in this compound. The values of the critical exponent 0.32 and 0.28 determined independently from spontaneous polarization and tilt angle measurements respectively, are found to be quite close to the value of 0.31 as predicted by the three dimensional Ising model. The layer spacing in the orthogonal SmA* phase is more or less constant and it decreases in the SmC* phase with decreasing temperature due to appearance of the tilting. The agreement between the experimental layer spacing (d) values from the x-ray diffraction measurements (41.5 \AA) in the orthogonal SmA* phase with those calculated from semi empirical molecular orbital package MOPAC has been found to be quite good. Moreover, a typical ferroelectric abrupt jump in dielectric anisotropy near the SmA*-SmC* phase transitions has also been observed.

Chapter 7 presents a comparative study of the electro-optical properties of orthoconic antiferroelectric liquid crystals (OAFLC) of some analogues of (S)-MHPOBC using polarization field reversal technique. Compounds with several variations, namely (i) in the position of lateral fluorination in the rigid core and (ii) number of oligo-methylene spacer linkages in the terminal chain, have been studied for the development of liquid crystal materials for application in high end display technology. The high value of spontaneous polarization (P_s) for the investigated compounds is attributed to the presence of the bulky chiral unit,

zigzag ester linkage and polar fluorinated terminal. However elongation of the oligomethylene spacer in the terminal chain and lateral fluorine atoms in the molecular core structure leads to reduction in the value of the spontaneous polarization. All the compounds enter the SmC* phase through a second order transition from the SmA phase. Unsubstituted or monofluoro substituted liquid crystals with relatively low viscosities and transverse dipole moments exhibit the fastest response time ($\sim 150\mu\text{s}$) and low viscosity ($\sim 1\text{Pa}\cdot\text{s}$) in comparison to the difluorinated compounds. Multiple fluorination increases the viscosity of these compound, similar to the results obtained in previous chapters. The “V-shaped” mode or thresholdless switching has been realized for these compounds with high polarization through the strong polar molecular interactions between the liquid crystal and aligning layers of the cell surfaces. The structure property correlation presented for these compounds indicate that fluorination of the aromatic ring has significant effect on the phase behaviour and physical properties of the materials.

The interaction between achiral and chiral liquid crystals has been explored by thermo-microscopic and electro-optical study in chapter 8. Three different binary systems, by mixing an achiral low viscous phenyl pyrimidine liquid crystalline SmC compound with three different orthoconic anti-ferroelectric analogues of (S)MHPOBC exhibiting SmA-SmC*-SmC*_A phase sequence, has been prepared. The purpose of preparing and characterizing these mixtures was to obtain best ferroelectric mixtures with excellent electro-optical performance to be used in fast switching surface stabilized ferroelectric displays. The electro-optical properties of all of the binary liquid crystalline mixtures have been studied by determining crucial physical parameters such as spontaneous polarization, relaxation time, torsional viscosity and surface anchoring energy strength. In these binary mixtures, ferroelectric and antiferroelectric phases were induced. All the physical parameters exhibit a non-additive behavior with respect to the concentration of chiral mesogens due to strong dipole-dipole and/or intermolecular interactions between the polar fluorinated chiral esters and the heterocyclic phenyl pyrimidine compound, along with the polarity derived from the electron-

withdrawing effect of nitrogen atoms in the rigid core. The interactions between such two intrinsically different molecules have been qualitatively explained using Boulder model. According to this model, a chiral compound plays the role of a “passive” guest which adopts a particular conformation that best fits the achiral binding site of the SmC achiral environment. It also may be viewed as a manifestation of molecular recognition via core-core interactions with surrounding achiral molecules. Interestingly, the achiral mesogen reduces the relaxation time of these binary mixtures at the cost of lower P_s . The less inflated viscous heterocyclic pyrimidine achiral compound lowers the viscosity of the binary mixtures. Moreover, the reduction of the spontaneous polarization elongates the pitch length and the system becomes ‘softer’. Additionally, it eliminates the ghost effect which arises due to high spontaneous polarization. Therefore these mixtures have emerged as very fast switching LC mixtures operating at room temperature and are convenient for passive addressing scheme at high multiplexing level and video rate with excellent contrast.

Characterization of the mesomorphic properties of the liquid crystalline compounds is necessary to further improve and update the current understanding of the structure-property relationship in liquid crystalline materials. Such a study is an important prerequisite for the formulation of multi-component mixtures with optimised properties, satisfying the practical demands of the latest technological applications.