

CHAPTER 8

Summary and Conclusions

Summary and Conclusions:

Liquid crystals are very important soft material in the field of material research. With their fascinating physical and electro-optical properties they find application mainly in the display technology as well as in other areas. Antiferroelectric liquid crystals are important class of liquid crystals for their tristate switching, microsecond response, hemispherical viewing angle and no-ghost effect. Moreover, a perfect dark state can be achieved using the orthoconic antiferroelectric liquid crystals as these are uniaxially negative crystal and the optic axis is perpendicular to the glass plates of the cell. Therefore for proper application of these kinds of materials it is very much essential to study their structure-property relationship. These structure-property studies will also help in the understanding of the engineering of the better materials. As no single compounds satisfy the conditions required for display applications, preparing mixture is an alternative means to meet the requirements of the displays. With these aims and objectives we have made detailed investigation on six pure antiferroelectric liquid crystals - **DM0**, **DM1**, **DM2**, **DM3**, **4F6T**, and **6F6T**. The first four compounds are biphenyl benzoate core based (**DM** series) while the remaining two compounds are doubly fluorinated terphenyl core based (**6T** series). We have also investigated in detail three formulated mixtures - a binary eutectic mixture (**M3**) of **DM0** and **DM3** in equal weight percent, a multi-component mixture (**M6**) of equal weight percent of all the **DM** series compounds and a mixture of **MWCNT** and **DM1**. All the nine systems have been studied using POM, DSC, X-ray diffraction, frequency dependent dielectric spectroscopy and electro-optic techniques.

Although the conclusions of these studies have been mentioned while presenting the detailed results in previous chapters in this chapter we summarize below the overall conclusions of the present dissertation. Most of the results have already been published in various scientific journals of international repute, a list of which is given in **Appendix B**.

- All the six pure compounds are found to exhibit antiferroelectric, ferroelectric and paraelectric phases. No change in phase sequence is observed either due to large change in core structure (**DM** series and **6T** series) or due to change in

lateral fluorination in core (**DM** series) or due to increased fluorinated achiral chain length (**6T** series).

- Melting point is found to decrease due to core fluorination at ortho and meta positions (**DM1** and **DM2**) and increasing achiral fluorinated chain length (**4F6T** and **6F6T**), however, for double fluorination in core (**DM3**) it increases. Clearing point also decreases in all the core fluorinated compounds in DM series compared to the protonated core one, while in 6T series it increases with increasing fluorinated chain length.
- Thermal range of the antiferroelectric phase increases in DM1 but decreases in DM2 and DM3 but the range of ferroelectric phase is found to decrease in all the fluorinated compounds. On the other hand, in 6T series compounds thermal ranges of both the phases are found to exhibit odd-even effect.
- All the compounds exhibit quite strong dipole moments. Dipole moment increases with increasing core fluorination but with increasing fluorinated chain length it shows odd-even effect. Fluorinated DM series compounds have higher dipole moments than 6T series compounds.
- The average intermolecular spacing is found to decrease with single fluorination in core, however, it increases with double fluorination in core or with fluorinated chain length.
- Layer spacings in orthogonal SmA* phase increases with single lateral fluorination in core (DM1 and DM2) whereas it is found to decrease with double fluorination in core (DM3) but it is found to increase with fluorinated chain length (6T series). These spacings are less than the optimized molecular lengths in all systems but substantial in DM series implying that the molecules are in different conformations than in *vacuo* condition or the molecules are tilted with azimuthal degeneracy as in de Vries phase or both.
- Temperature variation of layer spacing in SmC* phase shows a parabolic nature near the critical temperature T_c , implying that the paraelectric-ferroelectric (SmA*–SmC*) transition is nearly tricritical in nature in all the systems. Temperature dependence of spontaneous polarization also supports this conclusion.
- All the compounds, fluorinated either in core or in chain or in both, are found, considering their tilts, to be of orthoconic antiferroelectric nature. X-ray tilts are, however, much less as observed in many other systems.

- All the compounds exhibit very large dielectric increment ($\Delta\epsilon$) in SmC* phase but in DM series values are much higher than in 6T series. Maximum value of $\Delta\epsilon$ is found to decrease with single fluorination and increase with double fluorination in DM series compared to the protonated core compound while it decreases with increasing fluorinated chain length in 6T series.
- Goldstone mode and soft mode critical frequencies are much higher in DM series compounds than in 6T series compounds. Critical frequencies of all the relaxation modes (P_L, P_H, GM and SM) are found to decrease with lateral fluorination in DM series compounds whereas in 6T series GM critical frequency shows an odd-even effect and SM critical frequency decreases with increasing fluorinated chain.
- Although SM is observed within SmA* phase in all the DM series compounds, but only when the core is doubly fluorinated (DM3) SM is also observed within SmC* phase near T_c and it shows Curie–Weiss behaviour. On the other hand, both the 6T series compounds exhibit such behaviour.
- Significantly higher field is required for saturation of the spontaneous polarization with increasing lateral fluorination in core and also with increasing fluorinated chain length. However the maximum values of the spontaneous polarization are much higher in DM series compounds compared to 6T series compounds.
- In all systems sub-millisecond response time is observed. However, increasing fluorination in core and increasing fluorinated chain length, result in the slower response of the molecules under a square pulse.
- Antiferroelectric-ferroelectric transition temperature T_{AF} is found to decrease with increasing ac field, decrement rate is faster in longer fluorinated chain molecule.
- A eutectic antiferroelectric mixture (M3) is formed when equal weight percent of the protonated core and doubly fluorinated core compounds DM0 and DM3 are mixed. The mixture shows the same phase sequence (Cr–SmC_A*–SmC*–SmA*–Iso) as in the pure compounds but with increased range of SmC_A* phase. But when equal weight percent of all four DM series compounds are mixed (M6) the thermal range of SmC_A* phase increases further and the phase persists

much below room temperature. Both the mixtures (M3 and M6) retain the orthoconic nature of the antiferroelectric phase of the pure components.

- Properties of both the mixture are not always found to be proportional to the concentration of the pronated core and the fluorinated core components.
- Four collective relaxation modes (P_L , P_H , GM , and SM) are observed in both the mixtures like the pure compounds, however, their critical frequencies are not always proportional to the concentration of the pure compounds. The critical field for the suppression of the P_L and Goldstone modes increases significantly in the mixtures. Also, the GM mode dielectric increment decreases significantly. Like the pure compounds, the hereditary mode is observed in both the mixtures, however, domain mode is observed only in the four-component mixture M6.
- ‘V’ shape variation of soft mode critical frequency and inverse of dielectric increment is exhibited by the four –component mixture M6 like the pure compound DM3, but not by the mixture M3 which although it is a mixture of DM0 and DM3.
- Ferroelectric–paraelectric transition temperature (T_c) of both the mixtures M3 and M6 is found to increase linearly with bias field which could be explained using the Landau model.
- Spontaneous polarizations of both the mixtures are found to be in between those of the pure compounds. Switching time also exhibits similar behaviour and observed to be less than a millisecond.
- When a small fraction (0.12 wt.%) of functionalized multi-walled carbon nano tube is mixed in one of the core fluorinated DM series compound (DM1) the phase sequence does not alter but the phase boundaries are lowered and the stability of the paraelectric and the ferroelectric phases are found to increase but that of the antiferroelectric phase is decreased. Pitch of the helicoidal structure does not change appreciably in the composite, but it is found to increase with decreasing temperature in both the tilted phases in DM1 but an decreasing trend is observed in the SmC^* phase of the composite.
- In the antiferroelectric phase of the composite the in-phase antiferroelectric mode is completely suppressed whereas the absolute values and the ranges of the anti-phase antiferroelectric mode critical frequency (f_{PH}) and the absorption strength (ϵ''_{PH}) are found to decrease. Moreover, decrease of dielectric increment ($\Delta\epsilon_{GM}$) and increase of critical frequency (f_{GM}) of the Goldstone mode are

observed in the composite. Two fold increase of the critical field for suppression of the Goldstone mode in the composite is found, which signifies the helical structure in the nanocomposite is more stable than in the pure compound. Doping of rigid MWCNTs increases the modulus of elasticity of the composite and hence increases SM critical frequency.

- The composite also retains the orthoconic nature of the antiferroelectric phase.
- Spontaneous polarization of the composite is less compared to the pure compound. Most significantly, switching time in the composite is almost half of that of the pure.
- A lower value of conductivity in the composite signifies trapping of impurity ions by the CNTs.

In fine, it is concluded that the nature of core structure, fluorination in the core and chain as well as chain length have pronounced effect in the thermal range of phases and various molecular parameters like dipole moments, layer spacings and tilt angles. These factors also influence significantly the response of the material to an electric field and also their electro-optic behaviour. This study has thrown a significant insight into the structure-property relationship of the materials. That all the materials are having orthoconic antiferroelectric phase and a mixture of four pure compounds have a wide range of antiferroelectric phase far below room temperature with sub-microsecond switching time signify that materials are expected to be useful for formulation of orthoconic antiferroelectric liquid crystal mixture for display applications.