

CHAPTER 7

SUMMARY AND CONCLUSIONS

Now a days liquid crystal technology has a major effect in many areas of science and engineering especially in display technology. For successful applications of liquid crystals, studies on their structure-property relationships are extremely important. These studies also help in synthesizing better materials. Phase behavior and physical properties of fluorinated derivatives are found to be different from their hydrogenous analogues and often give rise to properties suitable for various applications. With this aim and objective various physical properties of a few fluorinated achiral and chiral liquid crystalline materials have been investigated using OPM, DSC, X-ray diffraction, optical birefringence, dielectric spectroscopy and electrooptic methods.

Three laterally fluorinated isothiocyanato terphenyl compounds (**2TP-3'F-4NCS**, **2TP-3'3F-4NCS** and **4TP-3',3F-4NCS**) and six phenyl bicyclohexyl based terminal fluorinated compounds (**3ccp-f**, **3ccp-ff**, **3ccp-fff**, **5ccp-f**, **5ccp-ff** and **5ccp-fff**) have been studied in the achiral system all of which exhibit nematic phase, in some cases also smectic phase. Two partially fluorinated biphenyl benzoate based chiral compounds (**4F3R** and **4F6R**), which exhibit ferroelectric and antiferroelectric phases, have also been investigated. Only one non-fluorinated biphenyl carboxylate based chiral compound (**MPOBC**) have also been studied which shows richly polymorphic behavior viz., four tilted hexatic smectic phases, one tilted synclinic smectic phase, one normal smectic phase along with cholesteric and blue phase.

From the detailed investigations on the first three isothiocyanato terphenyl compounds (**2TP-3'F-4NCS**, **2TP-3'3F-4NCS** and **4TP-3',3F-4NCS**) effect of increasing lateral fluorination and increasing chain length on various physical properties has been determined. It is observed that:

- ❖ With increasing fluorination (**2TP-3'F-4NCS** to **2TP-3'3F-4NCS**) nematic phase stability increases from 68⁰C to 108⁰C, but when chain length is also increased (**2TP-3'F-4NCS** to **4TP-3',3F-4NCS**) increase of thermal stability is less, 68⁰C to 85⁰C.
- ❖ Dipole moments of the molecules also show similar increasing trend, 5.57D to 6.68D to 6.29D as one move from the first to the third compound.
- ❖ Contrary to common perception that NCS compounds do not form dimers, presence of weak antiparallel correlation among the neighbouring molecules in all the three compounds has been observed from X-ray study. Calculated effective values of dipole moments and dipole-dipole correlation factor within nematic phase corroborate the above observation.

- ❖ All the three compounds show positive dielectric anisotropy. With increased lateral fluorination dielectric anisotropy slightly decreases, but it increases when chain length is also increased by two carbon atoms. As a result similar trend is observed in both threshold and driving voltages. Thus the doubly fluorinated ethyl compound is most easily switchable, however driving voltage for all the compounds is suitable for thin TFT based LC display cells.
- ❖ Splay elastic constants of the materials suggest that faster response is expected in the butyl compound compared to ethyl compounds.
- ❖ Flip-flop mode relaxation frequency in the nematic phase decreases with increasing fluorination and chain length while opposite behavior is observed in the smectic phase. Nature of absorption process is Debye type in all cases.
- ❖ All the compounds exhibit high birefringence, highest values being 0.373, 0.357 and 0.333 in the three compounds. Thus with increasing fluorination and increasing chain length the birefringence gradually decreases. These compounds are, therefore, expected to be very suitable for formulating high birefringence nematic mixtures for fast switching displays.

Effect of fluorination and increased chain length on the physical properties of six phenyl bicyclohexyl based terminal fluorinated compounds (**3ccp-f**, **3ccp-ff**, **3ccp-fff**, **5ccp-f**, **5ccp-ff** and **5ccp-fff**) has also been studied. 3-D crystal structure analysis of one of the compounds (**5ccp-fff**) has also been made. It is observed that

- ❖ All the compounds exhibit nematic phase, melting points and phase stability changes considerably with extent of fluorination and chain length.
- ❖ Molecular dipole moments increases from 1.93D to 3.37D with fluorination in both the propyl and pentyl based systems; increment in **f** to **ff** derivatives is more than in **ff** to **fff** derivatives. However, no change is observed with increased chain length.
- ❖ Molecular geometry and conformation, packing in the crystalline state and density, magnitude of molecular dipole moments and its orientation with molecular long axes of **5ccp-fff** differ from those in closely related singly and doubly fluorinated compounds **3ccp-f** and **3ccp-ff**. These differences are probably the cause of the substantial increase of melting point and decrease of nematic range in **5ccp-fff** compared to compounds **3ccp-f** and **3ccp-ff**.

- ❖ The facts that in the nematic phase apparent length of the molecules is more than the most extended molecular lengths, average values of dielectric constants are less than the extrapolated values of dielectric constants in isotropic phase, effective values of molecular dipole moments are less than free molecular dipole moments as well as magnitude of calculated values dipole-dipole correlation factors give conclusive evidence of existence of short range anti-parallel order in all these compounds as was observed in **NCS** compounds.
- ❖ All the compounds show moderately strong positive dielectric anisotropy. Increased fluoro substitution caused increased dielectric anisotropy; however, increased chain length resulted in opposite behavior but in lower degree.
- ❖ Improved switching characteristics (V_{th} and V_d) is observed in **3ccp** series compared to **5ccp** series and increased lateral fluorination resulted further improvement. However, driving voltage for all the compounds is suitable for thin TFT based LC display cells.
- ❖ Values of splay elastic constants suggest that faster response is expected in triply fluorinated compounds and response will be faster than the **NCS** compounds.
- ❖ Like the **NCS** compounds, only one strong dielectric absorption process (flip-flop mode) is exhibited by these compounds which are again almost Debye type.
- ❖ In low temperature region critical frequency decreases sharply from f to ff derivatives but increases from ff to fff derivatives.

From the detailed study on the two partially fluorinated biphenyl benzoate based chiral compounds (**4F3R** and **4F6R**) following points are worth noting:

- ❖ While **4F3R** exhibits only ferroelectric SmC^* phase over a broad temperature range, compound **4F6R** having three additional oligomethylene spacer groups, exhibit both anti-ferroelectric SmC_A^* phase and ferroelectric SmC^* phase.
- ❖ Both the compounds directly goes to isotropic phase from SmC^* phase which is not common in FLCs.
- ❖ Dipole moment of **4F6R** is found to be substantially higher than that of **4F3R** which might be the result of change of molecular conformation due increased oligomethylene spacer group.
- ❖ Clear discontinuities are observed at SmC_A^* - SmC^* transition in **4F6R** in layer spacing, X-ray tilt, dielectric increment and rotational viscosity.

- ❖ Only Goldstone mode relaxation behavior is observed in both the compounds, increase of dielectric strength and critical frequency with temperature has been explained in the light of generalized Landau model. GM is found to be of Cole-Cole type.
- ❖ No soft mode is observed in any case since the compounds directly melt into isotropic phase.
- ❖ The facts that the compounds show quite strong dipole moment, about 45° tilt angle, moderately strong polarization, low viscosity, micro-second range switching and are capable of forming room temperature ferroelectric phase in appropriate host mixture make the compounds suitable from application point of view.

Following conclusions are drawn from the investigation on the only non-fluorinated biphenyl carboxylate based chiral compound (**MPOBC**):

- ❖ Compounds exhibit richly polymorphic behavior from 48°C to 140°C .
- ❖ Within the crystalline and isotropic phase it shows four tilted hexatic phase (SmG^* , SmJ^* , SmF^* , SmI^*), one tilted synclinal phase (SmC^*), one normal smectic phase (SmA^*), cholesteric phase (N^*) and one blue phase (BP^*).
- ❖ Only subtle difference in textures is observed in SmG^* and SmJ^* phases and those in SmF^* and SmI^* . Clear evidence of helicoidal structure in the form of disclination lines is observed in SmI^* and in SmC^* . Blue coloured platelet texture is observed in BP^* phase.
- ❖ Synchrotron X-ray diffraction study nicely depicts the temperature evolution of different smectic phases along with the cholesteric and blue phase in a single compound.
- ❖ Direct evidence of change of tilt direction of the molecules from the edge of the pseudo-hexagonal net (SmF^*) towards its apex (SmI^*) is observed.
- ❖ Correlation lengths, across and within the smectic layers, change discontinuously in hexagonal phases. In the blue phase correlation length along the director increased substantially to 134 nm from 113 nm in cholesteric phase.
- ❖ Clear discontinuities were observed at the transitions of all the phases in d_{001} smectic layer spacing, in X-ray and optical tilt, as well as in dielectric increment.
- ❖ In hexatic phases two relaxation processes are observed - one low frequency process related to phase fluctuation in bond orientational order and one high frequency process related to amplitude fluctuation of the bond orientational order coupled with the polarization and tilt of the molecules.

- ❖ In SmC^* phase Goldstone mode relaxation and in SmA^* phase soft mode relaxation processes are observed. Helicoidal structure in SmC^* phase could be completely unwound at 10V bias.