Abstract

The conventional Twisted Nematic Liquid Crystal Display (TN-LCD's) uses Liquid Crystal materials with positive dielectric anisotropy. However, the greatest drawbacks of the TN-LCD's are their narrow viewing angle, low contrast and slow response times. In contrast, the recently introduced Vertically Aligned mode Liquid Crystal Displays (VA-LCD) combine the vertical alignment technique with nematic liquid crystals having negative dielectric anisotropy, resulting in wide viewing angle, excellent contrast and shorter response time. In VA mode, the name suggests, the liquid crystal molecules are normally aligned at right angles to the substrates, swinging through 90^{o} to lie parallel with the substrates in the presence of an electric field.

A particularly valuable class of materials satisfying the requirements of VA mode technology is the laterally fluorinated bi-phenyls and ter-phenyls. A (2, 3) difluoro substitution on the phenyl ring results in an effective dipole moment perpendicular to the principal molecular axis thus realizing negative dielectric anisotropy ($\Delta\varepsilon<0$) for the liquid crystalline molecule. Moreover, no single liquid crystalline compound can fulfill all the requirements of a display device; multicomponent mixtures with optimum values of material properties are required. The objective of this work is to prepare and characterize several multicomponent mixtures comprising of polar-fluorinated molecules suitable for VA mode application. The aim of this work is to produce materials with wide nematic temperature range, large negative dielectric anisotropy ($\Delta\varepsilon$), low rotational viscosity (γ_1), low values of bend elastic constant (K_{33}) and low values of the optical birefringence (Δn) for their application in VA-LCD's. Several pure liquid crystalline materials with negative dielectric anisotropy have been selected as components of multi component mixtures and their physical properties have been characterized. Bicyclohexane compounds with

low values of the optical birefringence (Δn) have also been characterized with a view to use them in mixtures for lowering the birefringence of the material. This work consists of careful formulation of multicomponent mixtures and the measurement of the dielectric anisotropy, optical birefringence, bend elastic constant and the rotational viscosity of these mixtures. The material properties of these mixtures are to be optimized with respect to improved driving voltages and high quality optical performance so that mixtures with the required specification may be identified for commercial application or patentability of the work. The following are the conclusions summarizing the work done in this thesis.

A. Study of pure compounds:

1. In this work an in-depth study of several liquid crystalline compounds (compound **1-15**) from different experimental techniques has been undertaken.

2. Compound **1** and compounds **3-9** with lateral fluorine substitution posses a higher value of birefringence (0.20-0.28 in the nematic range) while the phenyl bicyclohexane compounds **10** and **11** and the phenyl - cyclohexane compound **12** exhibit a relatively lower birefringence values of around 0.08 – 0.11. Bicyclohexane compounds **14** and **15** show a very low birefringence of the order of 0.03 and 0.08 respectively.

3. It is observed that the dielectric anisotropy ($\Delta\varepsilon$) for compound **9** is around -2 in the nematic phase. Compounds **1**, **3**, **6** and **8** however have a moderately low value of $\Delta\varepsilon$ of about -1. $\Delta\varepsilon$ value for compound **4**, **5** and **7** are slightly higher than -1. Again, $\Delta\varepsilon$ for compounds **10** and **11** are around -2 at the nematic to Sm B phase transition and -6 within the Sm B phase.

4. The K_{33} values vary from 4-16 pN at room temperature for all the laterally fluorinated pure compounds. The γ_1 values for compounds **1**, **3-9** are around 100-120 mPas in the nematic range which is considerably smaller than those obtained for phenyl bicyclohexane compounds **10** and **11** with values of 233 mPas and 322 mPas respectively at the N-SmB phase transition.

5. The terphenyl compounds **1**, **3-9** have improved values of the visco elastic coefficient (γ_1/K_{33}) due to lower values of the rotational viscosity of these materials. Significantly higher Figure of Merit (FoM) (almost ten times or more) are observed for the laterally fluorinated compounds (**1**, **3-9**) compared to bicyclohexane compounds with CH_2-CH_2 linkage group in the core (compounds **10** and **11**).

6. The physical properties of three laterally fluorinated liquid crystalline compounds **1**, **10** and **11**, have been thoroughly studied by different experimental techniques. Orientational Order Parameter ($<P_2>$) values have been determined from the x-ray diffraction and refractive index measurements. Fairly good agreement is observed between the two experimental methods as well as the theoretically calculated values.

B. Formulation and study of several multicomponent mixtures:

Based on the physical properties of single compounds, seven multi component mixtures (mixtures **A-G**) ranging from three component (mixture **A** and mixture **B**) to fifteen component (mixture **G**) have been formulated and their physical characterization has been done.

1. In the tri component mixtures (mixtures **A** and **B**) birefringence results are close to the targeted values for VA mode display devices (around 0.12 and 0.13 respectively) but $\Delta\varepsilon$ values are found too low (~ -1 at around 20°C).

2. To meet the required specifications a five component mixture (mixture **C**) has been prepared whose birefringence values are almost satisfying targeted value (around 0.11) but again the $\Delta\varepsilon$ values are very low.

3. A nine component mixture (mixture **D**) was formulated comprising of all laterally fluorinated bi- and tri-phenyl compounds, which showed a low viscosity (~ 48 mPas at around 20°C) and moderate birefringence (~ 0.18 at around 20°C) and higher values of dielectric anisotropy (~ -2.5 at around 20°C) with a broad nematic range.

4. By introducing two different dopants (laterally fluorinated tolanes) the nine component mixture have been modified into two ten component mixtures (mixtures **E** and **F**) where it was possible to tailor almost all of the physical properties (for a better effect on switching time, threshold voltage and the display contrast), only sacrificing the Δn values.

5. The fifteen component mixture (mixture **G**) gives a reasonable balance among all the required physical properties for a suitable VA display device. Mixtures **D-F** emerged to be the best mixture among all the mixtures studied.

C. Study of the effect of the pretilted cell on different multicomponent mixture:

The effects of 2° and 5° pretilt with respect to normal cell (cell with 0° pretilt) have been thoroughly investigated for all of the multicomponent mixtures (mixture **A-G**). The voltage dependent transmittance curve for the mixture in different pretilted cells (0°, 2° and 5°) has also been compared.

1. At $T = 20^{\circ}C$ the response time decreases to 25% and 35% for mixture **A** for 2° and 5° cells respectively compared to 0° pretilt. On the other hand, at the same temperature for **B**, the reductions in these values are 16% and 35% respectively.

2. At T_{NI}-T= $63^{\circ}C$ (i.e. $T = 20^{\circ}C$), the response time for the mixture decreases to 22% and 41% for 2° and 5° respectively, compared to zero pretilt. On the other hand, at the same temperature the V_{th} values are decreased by 5% and 9% respectively.

3. It has been found that when 2° pretilted cells are used, the relaxation time for mixture **D**, **E** and **F** are decreased by 6%, 14% and 11% respectively and for 5° pretilted cell the same values are reduced by 14%, 18% and 47% respectively for mixtures **D**, **E** and **F**. Similar behaviour is also found for V_{th} values of these mixtures. It is observed that the V_{th} values for mixture **D, E** and **F** is reduced by 5%, 18% and 12% for 2° pretilted cell and for 5° pretilted cell the same values are reduced by 10%, 16% and 13% respectively.

4. The response time for the mixture decreases to 14% and 44% for 2^{o} and 5^{o} respectively, On the other hand, it is found that at the same temperature the V_{th} values are decreased by 6% and 11% respectively.

D. Study of mesomorphic and structural properties of some liquid crystals possessing a bicyclohexane core:

1. In this work the results of refractive indices and density measurements on seven alkenyl bicyclohexane compounds of which five compounds show only nematic phase while other two compounds possessing smectic B phase which is precursor of nematic phase has been presented. The refractive indices as well as the density data have been used to determine the Orientational Order Parameter ($<P_2>$) using the standard Vuks isotropic model and have also been compared with the theoretical mean field values.

2. Optical Transmission (OT) method has also been employed to obtain a high resolution (accuracy~10^{-6}) measurement of the temperature dependences of the optical birefringence (Δn), which provides a macroscopic measure of the anisotropy of the liquid crystalline phase, and can also, be considered as a measure of the orientational ordering. The optical birefringence data obtained from optical transmission method have been compared with the same as obtained from thin prism technique.

3. Interestingly, the high resolution Δn data obtained from temperature scanning measurement of optical birefringence are quite successful in characterizing the transitional anomaly associated with the nematic-isotropic phase transition. For the investigated compounds, the values of the critical exponent β related to the limiting behavior of the nematic order parameter close to the N-I transitions, are found to be close to 0.25 and thus are in well accordance with the tricritical hypothesis and also excludes the possibility of any higher β values.

4. Additionally, the dielectric permittivities parallel and perpendicular to the molecular long axis throughout their mesomorphic range of the seven pure

liquid crystalline compounds has also been measured. The structure property relationship of these compounds has also been discussed.