CHAPTER IV

GRAPHENE OXIDE INDUCED HOMEOTROPIC ALIGNMENT IN FERROELECTRIC LIQUID CRYSTALS

In this chapter, the studies based on uniform and defect free homeotropic (HMT) alignment of negative dielectric anisotropic ferroelectric liquid crystal (FLC) has been described. One can achieve HMT alignment by the treatment of silane over the surfaces of substrates of FLC samples. In contrast, doping of graphene oxide (GO) into FLC material favours for a good quality HMT alignment without any surface treatment of the substrates. The observed HMT alignment has been confirmed by dielectric and optical studies.

4.1 INTRODUCTION

Ferroelectric liquid crystals (FLCs) are the most promising materials which can be used in various display devices due to their high speed, better optical contrast and fast response to external stimuli such as electric field, magnetic field, temperature and pressure, etc. [1, 2]. Noticeable investigations have been carried out extensively in order to understand the complex phase transition from ferroelectric (Sm C*) to paraelectric (Sm A*) phase of FLCs [3-6]. Among all FLCs, a special class of FLC with considerably wide range of Sm A* phase, is very interesting due to its ultra fast response and non-layer shrinkage [7-13]. These FLCs are known as electroclinic liquid crystals (ELCs) and described on the basis of symmetry arguments by Garoff and Meyer [7, 8].

Thereafter, Andersson et al. put forward the possible application of such type of liquid crystals (LCs) [13]. ELCs are remained the topic of academic interest for about a decade. Detailed discussion on ELCs has been given in the first chapter of present thesis (Chapter I).
The liquid crystalline state is anisotropic owing to the ordering of the constituent molecules; therefore their alignment with respect to the applied electric field affects their dielectric and electro-optical properties. The alignment of the FLCs is extremely important both for elucidation of the molecular processes as well as for practical applications because a good alignment layer provides high optical contrast. In an aligned sample, the director points, on an average, in the same direction over the entire sample. There are mainly three configurations of alignments, namely, homogeneous (HMG), homeotropic (HMT) and hybrid configurations. The detail description of all these alignments is given in Chapter II of present thesis. The orientation of the molecules on the surface is characterized by the pretilt angle (θ, angle between molecules to the plane of the surface) and the anchoring energy. Depending on the molecular alignment angles in case of HMG, θ will be 0°, in case of HMT, θ will be π/2 while in case of tilted or hybrid alignment, θ will lie in between 0° to π/2 [14]. However, the nature of alignment required differs in different geometries depending on the display mode used. In twisted nematic (TN) or surface stabilized ferroelectric liquid crystal (SSFLC) displays; HMG alignment is required whereas HMT alignment is useful in applications as liquid crystal displays (LCDs) for high information display devices, large area LCD TVs, and digital medical imaging [15, 16]. Negative dielectric anisotropy LCs have recently seen extensive use in flat panel display applications, especially in the vertically aligned mode since such a structure has good contrast combined with fast switching times [17].

4.1.1 HMT alignment in LCs by surface treatment

In HMT alignment, all of the long molecular axes are perpendicular to the substrate. The surfaces of the substrates such as glass, oxides, and metals exhibit the ability to align LC molecules vertically [18]. It is reported that the HMT alignment of LC is favored when the surface is hydrophobic and has a lower polar surface energy [19, 20]. The pretilt angle increases as the polar surface energy of the alignment film decreases, thus the weak polar surface energy plays an important role in the HMT alignment of LC [20]. To achieve HMT alignment, the glass substrates are treated
with the surfactant materials such as hexadecyltrimethyl-ammonium-bromide (HTAB), N,N-dimethyl-n-octadecyl-3-aminopropytrimethoxysilyl chloride (DMOAP), silane, lecithin, etc. [21, 22]. The molecules of such surfactants tend to align themselves perpendicular to the substrate and thus impart the HMT alignment to LC molecules. Kahn has demonstrated the importance of physicochemical forces, e.g., vander waals, hydrogen bonding and dipolar forces that play an important role in the alignment of molecules [23]. The deposition of the silane layer and large alkyl side chain alcohols onto the indium tin oxide (ITO) layer makes the surface hydrophobic and also decreases the surface energy value which is attributed to the long alkyl chain in the silane molecule [24]. Apart from these methods, Hiroshima et al. proposed rotational oblique evaporation of silicon monoxide (SiO) in order to obtain HMT alignment [25-26]. Matsumoto et al. proposed that tetrachloro-µ-hydroxo-µ-carboxylatodichromium (III) complexes could be used to induce HMT alignment [27]. The HMT alignment of LCs using fluorinated diamond like carbon thin films is an example of such techniques [28]. The alignment achieved in all above cases propagated from the substrate surface to the bulk of the LC and hence is clearly dependent on the surface treatments. Cheng et al. have succeeded to achieve vertical alignment by adding an appropriate dopant into LC material in contrast to the surface contact treatment techniques. They explored the possibility of favorable HMT alignment of LCs having large negative dielectric anisotropy ($\Delta\varepsilon$) by the addition of dopant material possessing a longitudinal dipole and therefore a positive $\Delta\varepsilon$ in LCs [29].

4.1.2 Nanomaterials induced HMT alignment in LCs

The effect of addition of various nanomaterials into LCs has been studied by various groups around the world for observing improvements in performance of LCs based display and non-display devices. A little amount of nanomaterials into LC materials has improved many features of the latter in the form of frequency modulation response, better optical contrast, non-volatile memory effect, faster electro-optic response, low driving voltage and enhanced photoluminescence [30-34]. Addition of different type of nanoparticles (NPs) provides a way to align LC molecules by a non-
contact technique or without any surface treatment of the substrates. The NPs of polyhedral oligomeric silsesquioxane (POSS), induced HMT alignment in nematic liquid crystals (NLCs) with positive dielectric anisotropy [35]. The electro-optical properties of POSS NPs induced vertically aligned LC cells were found similar to the conventional HMT aligned cells. It has also been discussed that the aligning capability induced by POSS is due to adsorption of POSS on the inner surfaces of the substrates and also influenced by doping concentration of POSS [35, 36]. The physical properties of FLCs are quite different from those of the NLCs due to the differences in the degree of order, the molecular arrangement and the presence of a permanent dipole moment. It is for this very fact, that nematic phases have been studied very extensively in both the HMT and HMG state [37-40] compared to few studies for the HMT alignment in FLCs [41, 42].

Now a days, graphene and graphene oxide (GO) are the interesting nanomaterial for dynamic research studies. The ease of synthesizing GO and its solution processing compatibility make it attractive for large area applications including transparent conductors [43-46], electrical energy storage devices and polymer composites, etc. [47]. In 2008, Blake et al. used graphene to fabricate electrodes for the LC device and observed excellent performance with a high contrast ratio [48]. In the beginning of 2010, Safavi and Tohidi designed the LC-Graphite composite electrodes and were found these electrodes perfect for the application of electric field in different electrochemical and biosensing applications [49]. GO is an intriguing nanomaterial and shows very high anisotropic morphology. Becerril et al. evaluated the potential of highly reduced GO thin films as transparent conductors and proposed a possible route for addressing the LC devices [43]. Till now graphene and GO have mainly been used in the fabrication of electrodes and applied in the form of thin film but doping of GO in LCs is rarely reported in literature. It is for the first time, GO nanomaterial was doped in ELCs [50].

In this chapter, we described in detail the techniques to achieve perfect HMT alignment. The silane layer over the surface of ITO coated glass substrate induced HMT alignment in the studied ELC material [51] while by adding GO into ELC material we can achieve a perfect HMT alignment without any surface treatment of the substrate. After applying a bias voltage HMT alignment can be converted in to
HMG alignment. Optical and dielectric studies allowed us to confirm the HMT alignment (geometry). These results will provide a fascinating tool to align FLC materials in HMT manner with and without surface treatment and such alignment have important implications for modern LCD technology.

The current chapter also describes the effect of doping of GO on the physical parameters of the ELC material.

4.2 EXPERIMENTAL DETAILS

GO used in the present study was synthesized by Hummer’s method [52]. Hummer et al. prepared GO by using a mixture of sulphuric acid (H₂SO₄), sodium nitrate (NaNO₃) and potassium permanganate (KMnO₄). Only the purification step has been replaced with washing of products step with known concentration of nitric acid (HNO₃). One can remove the impurities of other metal ions and enhance the oxidation of graphite by this replacement. The product was thoroughly washed with distilled water and at the end, a golden yellow powder of GO nanomaterial was obtained. The structural characterization of GO was carried out in detail by powder x-ray diffraction (XRD), Fourier transform infrared (FTIR) and atomic force microscopy (AFM) [53]. AFM images of GO nanomaterial showed layering morphology having thickness of ~25 nm consisting of each stack thickness of ~5 nm.

Sample cells for the dielectric relaxation processes and electro-optical studies were prepared by using highly conducting (10-18 Ω/□) indium tin oxide (ITO) glass substrates. Two types of sample cells were prepared. In first type cells, we treated two electrodes by dipping into the silane (phenyl trichlorosilane : toluene in the ratio of 1 : 100) solution for 6-7 minutes, washed in isopropanol to remove any adsorbed silane molecules, baking was performed at 90 °C for 20 minutes and finally gently rubbed (~10-12 strokes) with velvet cloth. In second type cells, both the electrodes were left untreated (i.e., neither the polymer nor silane was coated or rubbed) and they were called untreated cells. The morphology of the alignment layer is of great consequence for the achievement of the desired orientation of the LC molecules. The glass substrates were assembled facing the electrodes to each other, in the form of cells maintaining a uniform thickness by using Mylar spacers [54]. The filling of cells has been done at isotropic temperature of the material.
In the present study, we used a commercially available ELC material (BDH 764 E) having phase sequence as follows:

\[
\text{Cryst.} \xrightarrow{-7^\circ C} \text{Sm C*} \xleftarrow{28^\circ C} \text{Sm A*} \xrightarrow{73^\circ C} \text{N} \xleftarrow{89-92^\circ C} \text{Iso.}
\]

where, Cryst. is the crystalline phase, Sm C* is chiral smectic C phase, Sm A* is the chiral smectic A phase and Iso. is the isotropic phase of studied ELC material, respectively.

A small amount (0.1-0.2 wt %) of GO was dispersed in the ELC material at room temperature and then the composition was introduced into the LC sample cells in isotropic phase of the ELC material by means of capillary action.

The molecular and collective dynamic dielectric processes were investigated by broadband dielectric spectroscopy in an electrically shielded parallel plate capacitor using impedance analyzer 6540A (Wayne Kerr, U.K.) in the frequency range of 20 Hz to 1 MHz and the probe amplitude for the dielectric measurement was fixed at 0.5 V.

The optical micrographs (i.e. textures) observations of sample cells with different bias voltages have been recorded using high-resolution crossed polarizing microscope (AX-40, Carl Zeiss, Germany) [Chapter II]. The material constants such as spontaneous polarization (Ps) and rotational viscosity (\(\eta\)) have been determined by using an automatic liquid crystal tester (ALCT, Instec, U.S.A.). The temperature controller (JULABO F-25 HE) equipment with temperature stability of \(\pm 0.01^\circ C\) was used for controlling the temperature of the sample cell. The sample holder was kept insulated from the external sources (electrical and thermal).

### 4.3 RESULTS AND DISCUSSION

In the present study, the HMT configuration in sample cell filled with ELC material has been achieved either by silane treatment over the surface of substrate or by adding GO into ELC material without any surface treatment. In HMT configuration, molecules are aligned perpendicular to the ITO coated glass substrates. The first section of this chapter is dealing with HMT alignment achieved by silane coating over the surface of substrate while second section of the chapter is focussed on HMT alignment induced by GO doping into ELC material.
4.3.1 Analysis of alignment in ELCs by surface treatment

In this section, we are describing the HMT configuration achieved by silane treatment over the surface of ELC samples. The optical and dielectric observations confirmed the HMT configuration and after applying a bias voltage such HMT alignment can be converted in to HMG alignment. The experiments have been carried out on both, HMT aligned and planar or HMG converted (by applying dc bias), sample cells.

4.3.1.1 Optical observations

The optical micrographs of surface treated ELC samples recorded by using polarizing microscope to confirm the alignment configuration have shown in Figs. 4.1(a-d). The texture in Fig. 4.1(a) confirms a perfect HMT alignment because no light transmission occurs through the sample cell and hence a dark field of view appears under the crossed polarizers.

Figure 4.1: Optical micrographs of HMT aligned ELC material in Sm C* phase under (a) no bias (b) 10 V (c) 20 V, and (d) 25 V (which changes the orientation from HMT to HMG configuration).
Surprisingly, on applying a bias of 25 V in Sm C* phase, one can obtain a HMG aligned state [Fig. 4.1(d)] which was confirmed by the changes in the transmission as seen by the rotation of the cell under the crossed polarizers. Figs. 4.1(a)-(c) show the textural observation of the HMT aligned sample. After applying 10 V bias, there is no change in texture [Fig. 4.1 (b)] while by applying 20 V bias, there is a little transmission of light as shown in Fig. 4.1 (c). It is worth to notice here that the planar state was preserved even after removing the field up to very high temperature (about 65°C). Hence the alignment observed in silane treated surfaces is not only in HMT geometry but also it changes into HMG configuration on the application of a significant field in the Sm C* phase. In order to explore such effect in the Sm A* phase, the cell was further heated up to the isotropic phase (90°C) and then cooled slowly to retrieve the HMT state. At a temperature of 38°C, i.e., in the HMT aligned Sm A* phase [Fig. 4.2(a)], we observed a transition to the planar state on application of 55 V [Fig. 4.2(b)]. Even after removal of the field, the cell remained in planar orientation. Chen et al. have described a device geometry using inter digital electrodes that enables the electrically driven reorientation of Sm A* layers from HMG state to HMT state and back again [41].

Figure 4.2: Optical micrographs of HMT aligned ELC material in Sm A* phase under (a) no bias, and (b) 55 V (which changes the orientation from HMT to HMG configuration).
The observance of dark state is probably due to the expansion of strains and a balanced torque from electric field, in the cells which align the LC molecules perpendicular to the substrate instead of aligning along the rubbing direction and forcing the smectic layers normal to be tilted by some angle. The surface anchoring energy of the orthogonal boundary alignment layers imply that the surface effects do play a role in obtaining a perfect HMT alignment.

4.3.1.2 Dielectric observations

Dielectric spectroscopy is a powerful method to study dipolar ordering and molecular dynamics of collective and non-collective behavior of molecules. This technique also provides an insight into molecular dynamics of various cell configurations (HMT/HMG). Therefore, a study of temperature and frequency dependent dielectric response of ELCs is worthwhile to examine the molecular dynamics of different phases. The dielectric spectra of FLCs in the Sm C* phase for HMG alignment, in general, shows two collective relaxation modes, i.e. Goldstone and soft mode [55-57]. The Goldstone mode appears in the Sm C* phase and the soft mode dominates over the Goldstone mode near transition (Sm C* to Sm A*) temperature. The principal molecular reorientations, i.e. the rotation around the long molecular axis give separate relaxation regions falling within the microwave frequency range (3 GHz to several GHz) [58, 59].

The frequency-temperature dependence of the complex dielectric permittivity qualitatively can be explained by the well-known Debye’s equation as given by:

\[ \varepsilon^*(\omega) = \varepsilon_\infty + \sum_{i=G,S} \frac{(\varepsilon^i_\infty - \varepsilon^i_\omega)}{1 + (i\omega\tau_i)^{-\alpha_i}} \]

(4.1)

where, \( \alpha \) stands for the distribution parameter. G & S stands for Goldstone and soft mode respectively. The real and imaginary part can be separated out easily from the complex function by the relation:

\[ \varepsilon^*(\omega) = \varepsilon'(\omega) - i \varepsilon''(\omega) \]

(4.2)

where, \( \varepsilon' \) denotes the real part of the complex dielectric permittivity, \( \varepsilon'' \) is the imaginary part of the permittivity and \( \omega \) is the angular frequency of applied electric field (Ref. Chapter II for more details).
Generally, in HMG aligned samples, where we applied an electric field perpendicular to the molecular director, the dielectric permittivity ($\varepsilon_\perp$) is very high [3, 60]. In HMT configuration, however, the dielectric spectrum exhibits absorption peaks related to the rotation around short axis and in HMG alignment the re-orientation of the long molecular axis around the short axis falling in the radio (20 kHz-30 MHz) and microwave frequency range, respectively [59]. These relaxation processes are non-collective modes. In HMT alignment, with electric field applied parallel to the molecular director, contribution of the dielectric permittivity is denoted by $\varepsilon_\parallel$ and the values of $\varepsilon_\parallel$ are relatively lower than their $\varepsilon_\perp$ counterpart [60]. Thus, the values of $\varepsilon^*$ allow us to differentiate between the two alignments configurations provided other circumstances remain the same.

The variation of $\varepsilon_\parallel$ as a function of frequency (20 Hz – 1 MHz) at different temperatures (15°C – 45°C) in the HMT aligned sample, is shown in Fig. 4.3(a). It is observed that the values of $\varepsilon_\parallel$ vary between ~5.5 and 6, even though a wide temperature range has been studied, pointing to the fact that cell is indeed in the HMT configuration.

![Figure 4.3](image)

**Figure 4.3:** Dielectric permittivity ($\varepsilon_\parallel$) in the HMT-aligned cell of ELC material as a function of frequency (a) under no bias for the temperature range 15 – 45°C, and (b) at room temperature with different bias voltages (0-20V).
Also, it can be seen from this figure that the $\varepsilon_{||}'$ component exhibits a low-frequency dispersion region around few kHz, which is associated with the well-known molecular rotation around the short axis and such reorientation appears only when the measuring electric field excites the longitudinal part of the permanent dipole moment of molecules [61]. Figure 4.3(b) shows the variation of dielectric permittivity ($\varepsilon_{||}'$) with frequency at room temperature for different bias voltages. It is clear from Fig. 4.3(b) that the value of $\varepsilon_{||}'$ does not suppress even at higher values of applied voltages which suggesting the alignment to be in HMT geometry and further confirms that the contribution to the permittivity is a result of the excitation of the longitudinal component of dipolar moment, \textit{i.e.}, molecular orientation around short axis. This is so because, neither the permittivity ($\varepsilon_{||}'$) shows high value in the low-frequency region (in view of the Goldstone mode strength in planar alignment) nor it falls to a low value on applying a bias value up to 10 V (in view of the suppression of Goldstone mode).

Figure 4.4 shows the absorption curve showing the frequency dependence of dielectric loss factor (tan $\delta$) in the temperature range 15 - 45°C for HMT aligned

![Figure 4.4: Frequency dependence of dielectric loss factor (tan $\delta$) measured in the temperature range 15 - 45°C in the HMT aligned sample cell of ELC material.](image-url)
sample cell. It shows the existence of a single relaxation process that depends on temperature and presents relaxation frequencies of about ten to hundreds of kHz. This implies that the dielectric relaxation process connected with rotation around the short axis is a thermally activated process.

To ascertain the activation behavior of molecular processes of various phases, the temperature dependence of relaxation frequency ($\nu_R$) is plotted in Fig. 4.5. It represents the well-known Arrhenius–type behavior governed by the equation [61]:

$$\nu_R = \nu_0 \exp\left(\frac{-E_a}{k_BT}\right)$$

(4.3)

where, $\nu_R$ represents the relaxation frequency, $E_a$ is the activation energy of LC phase, $T$ is the absolute temperature and $k_B$ is the Boltzmann’s constant.

Figure 4.5: Arrhenius plot of the relaxation frequency ($\nu_R$) in the HMT aligned cell of ELC material. Dashed line is the linear fit obtained for Sm C* and Sm A* phases.

In the studied sample, we observed that the Arrhenius plot is linear in the Sm C* as well as in the Sm A* phase implying that the activation process remains same throughout. The low activation energy of about 39 kJ mol$^{-1}$ K$^{-1}$ is due to the easier movements of the molecules around short axis.
By applying of a dc field of 25 V (using an external dc power supply), we observed a transition from the HMT to the HMG state in the Sm C* phase as shown in Fig. 4.1(d). The dielectric studies of on field induced state confirmed that this state is indeed the HMG state. Figure 4.6(a) shows the dielectric permittivity ($\epsilon'_\perp$) as a function of frequency for HMG configuration at different temperatures under no bias application in which $\epsilon'_\perp$ is very high for lower frequencies and falls near Sm C* to Sm A* transition temperature. The high value of $\epsilon'_\perp$ for lower frequencies in Sm C* phase is attributed to the well-known phase fluctuations, i.e., the Goldstone mode.

![Figure 4.6](attachment:image.png)

**Figure 4.6:** Dielectric permittivity ($\epsilon'_\perp$) in the “field-induced state” of ELC material as a function of frequency (a) under no bias for the temperature range 15–45°C, and (b) at room temperature with different bias voltages (0-20V).

On application of successive bias field (0-20 V, using an impedance analyzer) in this field induced state, one can observe a significant change and suppression of $\epsilon'_\perp$ values as shown in Fig. 4.6(b). The jump in the dielectric permittivity ($\epsilon'$) value from ~6 (HMT alignment) to ~120 (“field-induced state”), shows the fact that the transition in the alignment configuration is in fact from the perpendicular (HMT) to nearly parallel (HMG) orientation of the molecules with respect to the electrodes. Figure 4.7 shows the variation of $\nu_R$ as a function of inverse of absolute temperature under the application of 10 V bias in the field induced HMG aligned sample cell.
A linear best fit, using Eq. 4.3, in the region of Sm C* and Sm A* phases, results into activation energies ($E_a$) as 17.34 KJ/mole-K and 74.58 KJ/mole-K, respectively. The value of $\nu_R$ is constant near transition temperature in the Sm C* phase. This is attributed to the phason fluctuation and random modes near transition temperature [62]. Each phase of LCs is uniquely represented by one activation energy. However, in our studies no significant change in the relaxation frequency ($\nu_R$) has been observed at the phase transition. In general, the bias application suppresses the phason mode (Goldstone mode) and the value of $\nu_R$ falls near transition temperature and one can observe the soft mode. However, in present studied material, it is observed that the value of $\nu_R$ maintains a constant value near transition under 10 V bias and Goldstone mode is suppressed only partially in this case causing it to be difficult to observe the soft mode in the Sm C* phase near transition temperature even by applying a strong bias [63].

Figure 4.7: Arrhenius plot of $\nu_R$ in the field-induced HMG aligned cell of ELC material. Dashed line is the linear fit obtained for Sm C* and Sm A* phases.
4.3.1.3 Dielectric anisotropy

From dielectric observations it has been confirmed that the value of \( \varepsilon'_{\perp} \) remains clearly higher than \( \varepsilon'_{\parallel} \) in the entire frequency range, which indicates a negative dielectric anisotropy in the studied sample (BDH 764E).

The dielectric anisotropy (\( \Delta \varepsilon \)) can be calculated by the following relation between \( \varepsilon'_{\parallel} \) and \( \varepsilon'_{\perp} \):

\[
\Delta \varepsilon = \varepsilon'_{11} - \varepsilon'_{\perp}
\]  

(4.4)

It is difficult to determine the dielectric anisotropy (\( \Delta \varepsilon \)) of FLC materials, especially in the low frequency region where Goldstone mode is dominant in the planar state. In view of this, \( \varepsilon'_{\parallel} \) and \( \varepsilon'_{\perp} \) acquired at 10 kHz and 100 kHz under no bias and after applying 10 V bias is plotted as a function of temperature, which is shown in Figs. 4.8(a) and (b), respectively. As can be observed, \( \varepsilon'_{\perp} \) is comparatively higher than \( \varepsilon'_{\parallel} \) component in the entire temperature range. This difference is due to the very high negative dielectric anisotropy of the studied sample.

Figure 4.8: A comparison of the dielectric permittivity (\( \varepsilon'_{\perp} \): HMG state; \( \varepsilon'_{11} \): HMT state) as a function of temperature for different frequency values (10 and 100 kHz) under (a) no bias, and (b) 10 V bias for silane treated sample cell.
In Fig. 4.8(a), a peak in the \( \epsilon_{\perp} \) component (10 kHz) is observed near the Sm C* to Sm A* transition temperature, which is due to the contribution from soft mode in the field induced planar state. In Fig. 4.8(b) it is observed that, on application of a bias voltage of 10 V, the peak in \( \epsilon_{\perp} \) [Fig. 4.8(a)] is suppressed in the same temperature regime. It is clear from the figure that the material under study has a high negative dielectric anisotropy (−4) as compared to the very low value of dielectric anisotropy in conventional FLCs (~ 0.2-1) [64].

It is well-known that LC molecules, can possess permanent or induced dielectric moments both along (parallel component, \( p_{||} \)) and across (transverse component, \( p_{\perp} \)) the long axis of the molecules [61]. Thus, on application of electric field, the molecule tends to orient in a manner such that the stronger of either the components lies along the electric field [65]. Knowing how the molecules respond to the applied electric field, it is thus understandable that since in the present case \( \epsilon_{\perp} \) is greater than \( \epsilon_{||} \), the molecules tend to orient perpendicular to the field or in other words, \( p_{\perp} \) tends to orient along the field. It is for this reason that we could observe a transition from the HMT state to the HMG state on application of a bias of 25 V in the Sm C* phase and similarly in the Sm A* phase. Moreover, since the transverse component, \( p_{\perp} \) is stronger than \( p_{||} \), the strong coupling of electric field with \( p_{\perp} \) in the ELC does not allow switching back from HMG to HMT state in either of the phases (Sm C* and Sm A*).

Hence, these investigation provides a simple way of acquiring a perfect HMT alignment using silane which never been obtained earlier in the Sm C* phase of ELCs and the transition from HMT to HMG state has been understood in view of the high negative dielectric anisotropy. The attainment of such perfect HMT alignment for an ELC has substantial potential and advantage over the existing use of nematic based devices because of their faster response time.

### 4.3.2 Analysis of alignment in ELCs by doping GO nanomaterial

In this section, we are describing the HMT alignment observed by doping GO nanomaterial into ELC material even without any surface treatment (neither polymer nor silane) of the substrates. The optical and dielectric observations confirmed the
HMT configuration. The HMT alignment can be converted to HMG alignment by applying a significant bias voltage. The experiments have been carried out on virgin sample cell in HMT configuration and same cell converted into HMG configuration by applying a bias voltage.

4.3.2.1 Optical observations

In order to confirm the HMT configuration in GO doped ELC sample, it was initially investigated using polarizing microscope. The optical micrographs of GO added untreated sample cell of ELC at different bias voltages in Sm C* phase, are shown in Fig. 4.9.

![Figure 4.9: Optical micrographs of HMT aligned sample cell of ELC material doped with GO nanomaterial in Sm C* phase under (a) no bias (b) 10 V (c) 20 V, and (d) 30 V (which changes the orientation from HMT to HMG configuration).](image)
From Fig. 4.9(a), it is clear that the cell having HMT configuration, shows perfect dark state under crossed polarizers at 0 V bias. The dark state remains unaffected even if we rotate the sample cell under crossed polarizers. Now after applying a bias of 30 V in the Sm C* phase, we obtained a HMG configuration [Fig. 4.9(d)] which has been confirmed by the changes in the transmission as seen by the rotation of the cell under the crossed polarizers. However, the cell does not retain its mono domain orientation in the HMG state, which could be hindrance for its use in good contrast display applications. It is worth to be noted here that once the sample goes in the HMG configuration then it can not go back to the HMT configuration which means that the transition from HMT to HMG configuration is not reversible. HMT alignment on the untreated substrates could be possible, when the surface energy (due to the intermolecular interaction among LC molecules) is more than the substrate surface energy. However, after the bias field application the non-uniformity in the bright state might be due to the reduction of LC surface energy as compared to substrate surface energy.

### 4.3.2.2 Dielectric observations

Dielectric spectroscopy is very effective tool to detect stochastic reorientation of collective molecular dipole moment processes particularly in 1 Hz to 1 MHz frequency domain. Figures 4.10(a) and (b), reveal the real part of $\varepsilon'$ in HMT aligned (in virgin sample) and HMG aligned (aligned by dc electric field) samples. HMT alignment is the result of filling the GO doped ELC material in the sample cell having untreated ITO coated glass substrates. The molecular alignment has been found vertical in virgin sample cell, therefore, the value of $\varepsilon'$ in low frequency domain is less as compared to the HMG aligned sample, which has shown in Fig. 4.10(a). The decrease in $\varepsilon'$ value is due to the low dielectric strength along the long molecular axis. The HMG alignment was achieved by applying dc electric field of 30 V, as can be seen in Fig. 4.10 (b). Its corresponding $\varepsilon'$ curve of HMG aligned sample as a function of frequency shows very high value of $\varepsilon'$ as compared to HMT aligned sample.
Figure 4.10: Dielectric permittivity ($\varepsilon'$) as a function of frequency with respect to temperature for ELC material doped with GO in (a) HMT aligned and (b) field induced HMG aligned sample cells.

Figure 4.10(b) shows the permittivity ($\varepsilon'_{\perp}$) as a function of frequency at different temperatures without any external bias application in which $\varepsilon'_{\perp}$ is very high for lower frequencies and falls near Sm C* to Sm A* transition temperature. The high value of $\varepsilon'_{\perp}$ for lower frequencies in Sm C* phase is attributed to the well-known mode due to phase fluctuations, i.e., Goldstone mode.

Figure 4.11 shows the behavior of $\varepsilon'$ with respect to frequency at room temperature for GO doped ELC material in both HMT aligned sample [Fig. 4.11(a)] and field induced HMG aligned [Fig. 4.11(b)] samples, at different bias voltages. It is clear from the Fig 4.11(a) that the value of $\varepsilon'_{||}$ does not get suppressed even at higher values of applied voltages suggesting the alignment to be in HMT configuration and the low value of $\varepsilon'_{||}$ is a result of the excitation of the longitudinal component of dipolar moment, i.e., molecular orientation around short axis. In field induced state, one can observe a significant change and suppression in $\varepsilon'_{\perp}$ values by applying the successive bias fields as shown in Fig. 4.11(b), and this can be attributed to quenching of the Goldstone mode.
Figure 4.11: Dielectric permittivity ($\varepsilon'$) as a function of frequency with respect to different applied voltages for ELC material doped with GO in (a) HMT aligned and (b) field induced HMG aligned sample cells, at room temperature.

Figure 4.12 shows the frequency dependence of dielectric loss factor (tan $\delta$) in the temperature range 15 – 60°C for HMT aligned ELC sample doped with GO. From the graph, we observed a single relaxation process in HMT aligned cell that depends strongly on temperature and this relaxation process connected with rotation around the short axis while in HMG converted sample cell, we observed more than one relaxation processes.
Figure 4.12: Frequency dependence of dielectric loss factor (tan δ) measured in the temperature range 15 – 60°C in the HMT aligned sample cell of ELC material doped with GO.

The detailed study of dielectric relaxation behaviour in field induced HMG aligned sample of GO doped ELC material is presented in next chapter of thesis (Chapter VI).

4.3.2.3 Dielectric anisotropy

Figure 4.13 shows the dielectric permittivity versus temperature for both dielectric components, HMG (ε⊥) and HMT (ε∥), for frequencies 10 KHz and 100 KHz. The value of ε⊥ remains higher than ε∥ in the entire frequency range in GO doped ELC material as in silane treated surface of substrate.

The difference between the ε of HMG aligned (ε⊥) and HMT aligned (ε∥) samples is due to the very high negative dielectric anisotropy of the studied material. In Figure 4.13, due to the presence of soft mode a peak in the ε⊥ component (10 kHz) is observed near Sm C* to Sm A* transition temperature in the field induced HMG state. It is clear from the figure, that the material under study has a high negative dielectric anisotropy (~ − 4).
4.3.3 Effect of doping of GO nanomaterial on the physical parameters of ELCs

In this section, the effect of GO nanomaterial on the physical parameters of the ELC material (BDH 764E) has been discussed. The effect of GO nanomaterial on the material constants has shown in Fig. 4.14. Figure 4.14 (a) shows a little increment in the values of spontaneous polarization ($P_s$) of GO doped ELC sample in Sm C* phase and minimization of spontaneous polarization ($P_s$) near 30°C is the indication of transition before 30°C. Figure 4.14(b) shows increment in the values of rotational viscosity ($\eta$) of GO doped sample and drops to minimum at 30°C while in pure it drops to minimum at 27°C which is a general behavior of ELC materials and this could happen because of the highly electroclinic nature of ELC material near transition temperature.
Figure 4.14: Behavior of (a) spontaneous polarization ($P_S$) and (b) rotational viscosity ($\eta$) with temperature for both GO doped and pure ELC sample cells.

This can also reflect the effect of anchoring on the surface substrate without any alignment layer. The conversion from HMT to HMG configuration is not perfect due to the vertical anchoring of ELC molecules with ITO substrate through GO molecules. The possible interaction of oxide-oxide (graphene and ITO) and the affected molecular ordering may result vertical anchoring.

Furthermore, another measurement for comparison of substrate attachment with ELC has been carried out on the ITO substrate coated with nylon 6/6 and rubbed with velvet cloth for proper HMG alignment of ELC molecules. It is to examine whether the vertical alignment is due to ITO surface anchoring of molecules or any bulk induced effect. Figure 4.15 shows the relevant textures of planar alignment of GO doped ELC material filled in the treated sample cell, i.e., the attachment of ELC material is mediated by nylon 6/6 layer. The dark and bright state has been obtained in virgin sample cell, as shown in Figs. 4.15(a) and (b).

This exhibits the effect of GO in bulk and not on the surface. The major differences have been observed in an untreated sample where there is a direct exposure of ITO to GO doped ELC sample.
This means that the vertical alignment in untreated sample substrates is only due to the interaction of GO and ITO components. GO works as an order-affecting agent, which affects the viscosity of ELC and makes it easier to be aligned along the GO molecules attached to the ITO surface in vertical direction. Hence, GO interacts with ITO layer and supports the ELC molecules to align in the direction of GO molecules.

4.4 CONCLUSIONS

A perfect HMT alignment has been observed in ELC material by using two methods. In first method, ITO coated glass substrates are treated with silane and followed by rubbing. In second method by adding the GO nanomaterial in ELC material, we achieved a perfect HMT alignment without any surface treatment. We proposed that the reason behind such good vertical alignment without any surface treatment is the consequence of coupling between ELC molecules and ITO film mediated by GO nanomaterial. On application of high bias voltage, we can convert HMT configuration into HMG configuration in both the cases and this transition from HMT to HMG state has been understood in terms of the high negative dielectric anisotropy. Furthermore, the achievement of such perfect HMT alignment of an ELC material has provided substantial prospective and the technique can be adopted for various dynamic studies of ELC materials.
References


