5.1 Introduction

The study of ferroelectric liquid crystals (FLCs), a class of materials first discovered just fifteen years ago, has developed into a rapidly growing multidisciplinary field involving physicists, electrical and computer engineers, and chemists. Problems of both fundamental scientific interest and a more practical nature are being addressed, as research teams work towards an improved understanding of the physics and chemistry of FLCs, as well as developing devices such as flat panel computer displays and components of sophisticated optical computing systems based upon the technology. Chiral compounds are able to form liquid crystals with structures related to those of non-chiral materials but with different properties. The cholestric (or twisted chiral nematic) and blue phases are non-ferroelectric whereas the chiral smectic phases exhibit ferroelectric properties.

Due to their low symmetry, the chiral smectic phases, are able to exhibit spontaneous polarization and piezoelectric properties[1-4]. In the chiral nematic (Cl or Nt or N*) phase the director varies in direction throughout the medium in a regular way and displays a continuous twist along the optic axis leading to a helical structure. It is due to the twisted or helical structure, the Nt phase possesses special optical properties, which make it very useful in practical applications. All the chiral smectic (Sm C*, Sm I* and Sm F*) and chiral crystal smectic (Sm J*,SmG*, Sm K* and Sm H*) phases have tilted structure. The Sm C*, Sm I* and Sm F* phases have been found to exhibit ferroelectric properties. Among these three mesophases, the Sm C* has been the focus of a lot of attention during the past two decades. It is the least ordered and the least viscous, and has potential applications in fast-switching, high-contrast and large-viewing angle displays [5,6].

Because of the a spatially modulated layered structure in FLCs, the molecular director precesses helicoidally while going from one layer to another successive layer maintaining a constant tilt angle [7,8].
Figure 1. Helielectric structure of Sm C* phase

An electric field applied perpendicular to the helix, unwinds it giving rise to linear electro-optic effects. The strong coupling between applied electric field \( E \) and the polarization \( P \) of the molecules makes these materials interesting for use in fast sub-microsecond electro-optic switching devices [6]. Chiral smectic C* materials [1] are improper Ferro electrics, i.e. the permanent polarization is governed by the director tilt angle, which is the order parameter. Because of this, an external electric field can induce a director tilt which results in a polarization proportional to the field above the SmC*-SmA* transition (electroclinic effect) [9]. The electro-clinic effect also exists in the SmC* phase: an electric field enhances the director tilting, thus increasing the permanent polarization.

The coupling between an electric field and the molecular tilt is known as Electro-Clinic (EC) effect. The EC-effect is analyzed through symmetry arguments [10,11] and is explained in terms of coefficients of Free energy [12–14] expansion. The concept of EC-effect is further developed for its applicability in electro-optic (EO) devices.

Study of dielectric properties play major role to analyze the Ferroelectric liquid crystal and to use it for technical application [15, 16]. Their use in devices demands measurements of certain physical parameters like dielectric parameters, electro-optic responses, surface properties etc. Dielectric investigations of ferroelectric liquid crystals (FLC) extracts useful
information regarding the molecular and relaxation processes of these materials and gives a measure of parameters like dielectric strength, relaxation frequency etc. But on investigations of LF dielectric relaxations in LC phases in the domain of frequency and dielectric strength provide [17,18] invaluable information regarding the response of dipole moment to the external field. Thus, its response would be preferentially optimized in the devices.

Various dielectric studies on the commercially available FLCs reveal the existence of two dielectric relaxations in homogeneously aligned samples in SmC* phase and quenching of one mode called the Goldstone mode in the vicinity of SmC* - SmA transition [19]. These modes appear due to the fluctuation of order parameter and rotation of molecule around the long molecular axis [20, 21].

5.2 Results and Discussion
5.2.1 Textures and phase transition temperatures

The textural observations of the compound (S)-(−)-2-Methylbutyl 4'-(4''-n-alkanoyloxy benzoyloxy) biphenyl-4-carboxylates (S-MB-nB-BC where \( n = 16 \) and 18) made through POM have shown enantiotropic behavior. Typical texture exhibited by Smectic C* phase presented in plate 5.1 and Smectic A phase is shown in plate 5.2

Plate 5.1. Sm C* phase for S-MB-16B-BC.
Plate 5.2. Sm A phase for S-MB-18B-BC

**TABLE1. Data of phase transition temperatures \( T_c \) (K) and Enthalpy by POM, DSC**

<table>
<thead>
<tr>
<th>compound</th>
<th>Method</th>
<th>Details of Phases, Transition Temperatures ( T_c ) (K) and Enthalpy ( \Delta H ) (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n=16</td>
<td>POM [present]</td>
<td>Heating Cr→337→SmC*→385.4→SmA→426.2→Iso</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cooling Cr(_1)→325.4→Cr(_2)→333.7→SmC*→375.4→SmA→425.8→Iso</td>
</tr>
<tr>
<td></td>
<td>POM &amp; DSC[22]</td>
<td>Heating Cr→337→SmC*→385.4→SmA→426.2→Iso</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cooling Cr(_1)→325.4→Cr(_2)→333.7→SmC*→375.4→SmA→425.8→Iso</td>
</tr>
<tr>
<td></td>
<td>LF Dielectric</td>
<td>Cooling Cr(_1)→325.4→Cr(_2)→333.7→SmC*→375.4→SmA→425.8→Iso</td>
</tr>
<tr>
<td>n=18</td>
<td>POM [present]</td>
<td>Heating Cr→346.3→SmC*→385→SmA→425→Iso</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cooling Cr(_1)→335.9→Cr(_2)→341.5→SmC*→377.5→SmA→424.8→Iso</td>
</tr>
<tr>
<td></td>
<td>POM &amp; DSC[22]</td>
<td>Heating Cr→346.3→SmC*→385→SmA→425→Iso</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cooling Cr(_1)→335.9→Cr(_2)→341.5→SmC*→377.5→SmA→424.8→Iso</td>
</tr>
<tr>
<td></td>
<td>LF Dielectric</td>
<td>Cooling Cr(_1)→335.9→Cr(_2)→341.5→SmC*→377.5→SmA→424.8→Iso</td>
</tr>
</tbody>
</table>

Values in [ ] indicate enthalpy Cr= Crystal; SmC=Smectic C*; SmA= Smectic A; Iso=Isotropic

Thus, the observed LC phase variance exhibited by S-MB-nB-BC i.e., SmC*, is confirmed as enantiotropic in nature. The phase transition temperatures recorded through POM in heating and cooling runs are presented in Table 5.1. The thermal spans of LC phases observed for S-MB-nB-BC in heating scan are found to slightly differ from those observed in cooling scan.
However, the hierarchy of occurrence is found to remain invariant. The data obtained from POM and DSC [22] is in good agreement.

*Phase Transitions by Dielectric constant $\varepsilon$ and Loss Factor $\tan\Delta(T)$:*

The S-MB-$n$B-BC cell is connected to the L.C.R meter is operated at a fixed frequency of 100 kHz and triggered by 1Vp-p oscillating signal under the bias–off condition. and the readings of Dielectric constant and loss factor $\tan\Delta(T)$ exhibited by sample (at the temperature) of interest are recorded in all phases of S-MB-$n$B-BC in the cooling run.. The observed temperature variation for Dielectric constant, loss factor $\tan\Delta(T)$ are presented in Figure 5.2. The peaks in Dielectric constant and the valleys in loss factor $\tan\Delta$ are identified as phase transition temperatures. The observed values of phase transition temperatures exhibited by S-MB-$n$B-BC during the LF dielectric study (in cooling run) are presented in Table 5.1. The phase transition temperatures determined by LF dielectric method are found to agree with the values determined by POM, DSC [22]. Increasing trend of dielectric constant in the vicinity of a phase transition infers the increasing dipolar correlation pertaining to the on-coming phase structure. However, it could be evinced by the present LF dielectric method. Hence, the LF dielectric method is argued to be capable of detecting even the second (continuous) order transitions, involving the marginal structural changes.

![Figure 5.2 (a)](image-url)
5.3 Low frequency Dielectric studies:

The low frequency (1Hz to 1MHz) dielectric dispersion is measured as variation in capacitance $C$ and loss factor $\tan\Delta$ at different specified temperatures in different LC phases during the cooling scan of S-MB-$n$B-BC where $n = 16$ and 18. The capacitance $C(\omega)$ and loss factor $\tan\Delta(\omega)$ are recorded at the temperature of interest in all LC phases exhibited by S-MB-$n$B-BC. The variation of $C(\omega)$ and $\tan\Delta(\omega)$ is presented in Figure 5.1 In the wake of the temperature invariant capacitance exhibited by the empty cell ($\sim 38.99\text{pF}$) the relative permittivity $\varepsilon'(\omega)$ (or $\varepsilon_r$) is estimated by

$$\varepsilon'(\omega) = \frac{C}{38.99} = \varepsilon_r(\omega) \quad (5.1)$$

The dielectric loss $\varepsilon''(\omega)$ is estimated by

$$\varepsilon''(\omega) = \varepsilon_r \ast \tan\Delta \quad (5.2)$$

However, by the dielectric dispersion in LCs is given [23, 24, 29] by

$$\varepsilon*(\omega) = \varepsilon_\infty - \{(\Delta\varepsilon)/(1 + [j\omega\tau]^{1-\alpha})\} \quad (5.3)$$

Where, $\Delta\varepsilon = [\varepsilon_\infty - \varepsilon_\omega]$ is the Dielectric Strength, estimated by extrapolating $\varepsilon''$ on to the $\varepsilon_r$ axis.

$\tau = \text{the Relaxation Time given by } 1/f_R$

$\omega = 2\pi f$ and

$\alpha = \text{the distribution parameter reflecting upon the degrees of}$
Freedom exhibited by the phase in any LC phase structure.

Figure 5.1. (a) Variation of capacitance and loss factor with temperature
(b) Variation of capacitance with frequency in empty cell

The dielectric constant (\(\varepsilon'\)) at different frequencies is calculated using equation (1). Its variation as a function of frequency (f) for the FLC compounds is presented in figure 5.3 at different temperatures. Both compounds are found to exhibit the decreasing trend of \(\varepsilon'\) at low frequencies, while it is low to marginally vary at higher frequencies. Marginalized variation of \(\varepsilon'\) at high frequency range reflects upon the dominant response of orientational fluctuations in the low frequency region as characteristic feature of LC state of matter. Dielectric constant (\(\varepsilon'\)) is decreased gradually with increasing frequency and increased with the increase of temperature. The high
value of dielectric constant in liquid crystal phase is interpreted as originating in the fluctuations of the azimuthal angle of the molecular long axis in the helicoidal structure which is called Gold stone mode. At high frequency the dielectric constant found to be small because of the decrease of Gold stone mode contribution. The high value of dielectric permittivity has been found at low frequencies due to the large spontaneous polarization in liquid crystal compound.

Figure 5.3. Frequency dependence of dielectric constant $\varepsilon'$ for (a) S-MB-16B-BC and (b) S-MB-18B-BC at different temperatures.
The dielectric loss exhibited by the FLCs in the vicinity of SmC* and SmA phases are estimated by equation 5.2 at different temperatures are presented in figures from 5.4 to 5.5. From the figure 5.4 it is observed that the dielectric loss is decreased with decreasing temperature, and at particular temperature there is cross over region is observed, from that temperature onwards there is a reverse trend is followed i.e. the dielectric loss is increased with decreasing temperature in both the compounds. The cross over temperature is observed as 363K (n=16) and 368 K (n=18). In all the cases loss peak accompanied by the Arrhenius shift are found [25-28] to be characteristic of different and distinct orientational relaxation mechanisms involved in dipolar reorientation process. The frequency corresponding to the peak value of $\varepsilon''_{\text{max}}$ (or Tan$\Delta_{\text{max}}$) is identified as the relaxation frequency $f_R$. In all the cases the relaxation frequency follows the Arrhenius behavior, the relaxation frequency is shifted towards the lower frequency side as the temperature decreases. A careful observation of variation in $\varepsilon''(\omega)$ with frequency also reveals the non-symmetric response of LC phases, i.e., about the $\varepsilon''_{\text{max}}$. The non-symmetric response of loss $\varepsilon''$ (or Tan$\Delta$ about its maximum value) with the increasing frequency in turn suggests for an off-centered dielectric dispersion [28, 29] in the all phases.
Figure 5.4: Frequency dependence of dielectric loss for (a) S-MB-16B-BC and (b) S-MB-18B-BC at different temperatures.
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(b) H.T.mode of SmC* in S-MB-16B-BC

(c) L.T.Mode of SmC* in S-MB-18B-BC
Figure 5.5: Frequency dependence of dielectric loss for (a) L.T mode (b) H.T. mode of S-MB-16B-BC, (c) L.T mode (d) H.T. mode of S-MB-18B-BC at different temperatures
Comparing to the observed capacitance value in SmA and SmC* phase region are presented in figure 5.6. $\tau_\varepsilon$ is found to attain maxima values $\sim 4.25 \times 10^4$ and $4.5 \times 10^4$ ppm/$^\circ$C for $n=16$ and 18 samples. The observed maximum $\tau_\varepsilon$ centered in the vicinity of KHz for both samples inform low frequency susceptibility of the samples in the entire range of the liquid crystal phases. At higher frequencies, the temperature coefficient dielectric constant is noticed rather to low frequencies in both compounds which are shown in figure 3. As the $\tau_\varepsilon$ conveys a combination of thermal and dielectric response of the sample the resulting $\tau_\varepsilon$ reveals the frequency response of FLC during the liquid crystal phase structure change. It is observed that $\tau_\varepsilon$ is maximum around 100 to 1000 Hz for these samples which represents the existence of orientational polarization of liquid crystal molecule with temperature.

**Cole Cole plots:**

In order to analyze the observed LF dielectric response and to investigate the two distinct (time scale wise) modes of relaxation behavior, the data of $\varepsilon''$ and $\varepsilon_r$ viz., the LF dielectric dispersion (ie., in all LC phases exhibited by S-MB-$n$B-BC for both LF and HF relaxations) is presented as Cole-Cole plots in Figure. The data of LF dielectric parameters corresponding to the LF relaxation modes, viz., Relaxation frequency $f_R$, loss maximum

---

**Figure 5.6 Frequency dependence of thermal coefficient of dielectric constant $\tau_\varepsilon$ for (a) S-MB-16B-BC and (b) S-MB-18B-BC**

![Graph showing frequency dependence of thermal coefficient of dielectric constant for different samples.](image-url)
\( \varepsilon'' \) max, dielectric strength \( \Delta \varepsilon \), distribution parameter-\( \alpha \) and activation energy \( E_a \) are estimated from the Cole-Cole plots and reduced temperature plots (Figure 5.7). The data of LF dielectric parameters for S-MB-nB-BC is presented in Table 5.2, with the expected values. The \( \varepsilon_o \) and \( \varepsilon_\infty \) are determined from Cole-Cole plots as extrapolated values of Cole-Cole arc-line of \( \varepsilon'' \), which intersects with \( \varepsilon_r \) axis. The point of intersection towards the LF side is read as \( \varepsilon_o \) and that at HF side is read as \( \varepsilon_\infty \). An overview of the Cole-Cole plots in the LF relaxations reveals a greater temperature shift of \( \varepsilon_r \) in the LF end (ie., through \( \varepsilon_o \)) in all the phases. The observed large temperature shift of \( \varepsilon_o \) speaks out the relative dielectric susceptibility (\( \Delta \varepsilon=[\varepsilon_o-\varepsilon_\infty] \)) of S-MB-nB-BC structure in the LF kHz region. These are presented as Cole-Cole plots in Figure 5.6 a,b,c d and e respectively. The specified trend of \( \alpha \)-parameters in equation 5.3 (in the Cole-Cole plots of SmA and SmC* in phases) speaks out the freezed degrees of freedom with decreasing temperature during the process of dipole reorientation to external field. The low frequency end \( (\varepsilon_o) \) of dispersion plot is found to change its value with decreasing temperature while its high frequency end \( (\varepsilon_\infty) \) remains almost constant. This trend of dispersion process throws light on the relative susceptibility of liquid crystal dipole at lower frequency end, while a helix super structural order sets in with decreasing temperature. It is observed that the temperature variation in relaxation frequency \( (f_R, \text{corresponding to peak value in loss}) \) follows Arrhenius shift as shown in Figure 5.7, they reflect the increasing strength of rotational potential barrier experienced by the liquid crystal dipole with decreasing temperature.

The Cole-Cole plots are found (Table 5.2) to yield an increasing \( \alpha \) values with the decreasing temperature for all the phases in both the compounds. The increasing \( \alpha \) parameter value reflects upon the relatively confined frame of the dipole with decreasing temperature, it is also noticed that the observed increasing dielectric increment \( \Delta \varepsilon \) with the decreasing temperature is effectively influenced by the low frequency end of the observed dispersion during the LF mechanisms exhibited by all the phases in both the
compounds. This trend of relative permittivity $\varepsilon_r$ being more susceptible to lower frequency dielectric field infers the characteristic liquid crystalline response more pronounced at lower frequencies.

(a)

(b)
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Figure 5.7: Cole Cole plots for SmA, SmC* of S-MB-nB-BC

Activation energy

An overview of LF dielectric data (Table 5.2) for S-MB-nB-BC reveals that the $f_R$ follows a shift with a temperature in all the LC phases. This shift in $f_R$ is suggestive of Arrhenius behavior in the LF relaxation. The potential barrier experienced by an LC phase structure during its orientation (to the applied field) is estimated by drawing (Figure 5.8) the corresponding reduced temperature plots. The activation energies (Table 5.2) observed for LC phases of S-MB-nB-BC. These values are in good agreement with the reported values[31]
Figure 5.8: Variation of relaxation frequency with inverse temperature for (a) S-MB-16B-BC and (b) S-MB-18B-BC at different phases.

Table 5.2: Data of dielectric loss maximum, dielectric strength and Distribution parameter in different phases of S-MB-nB-BC

<table>
<thead>
<tr>
<th>$n$</th>
<th>Phase</th>
<th>Temperature (K)</th>
<th>Relaxation frequency ($f_R$) (Hz)</th>
<th>Dielectric strength $\Delta \varepsilon$</th>
<th>Max. loss $\varepsilon''_{max}$</th>
<th>Distribution Parameter $\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>SmA [1.25 eV]</td>
<td>418</td>
<td>2.080</td>
<td>113.05</td>
<td>61.96</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>408</td>
<td>1.959</td>
<td>113.60</td>
<td>52.04</td>
<td>0.226</td>
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<tr>
<td></td>
<td></td>
<td>399</td>
<td>1.714</td>
<td>115.239</td>
<td>50.63</td>
<td>0.261</td>
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<tr>
<td></td>
<td></td>
<td>389</td>
<td>1.591</td>
<td>116.86</td>
<td>47.08</td>
<td>0.296</td>
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<td></td>
<td></td>
<td>379</td>
<td>1.469</td>
<td>117.95</td>
<td>44.25</td>
<td>0.349</td>
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<tr>
<td></td>
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<td>373</td>
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<td>152.53</td>
<td>56.24</td>
<td>0.191</td>
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<td>368</td>
<td>1.220</td>
<td>144.65</td>
<td>55.34</td>
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<td>361</td>
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<td>59.01</td>
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<td>1.224</td>
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<td>162.82</td>
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<td>0.244</td>
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<tr>
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<td></td>
<td>359</td>
<td>0.489</td>
<td>165.6</td>
<td>44.86</td>
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<tr>
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<td>0.244</td>
<td>168.99</td>
<td>45.85</td>
<td>0.296</td>
</tr>
</tbody>
</table>

[ ] represents activation energies.
5.3. Conclusions:

From the present study it may be concluded that:

The phase transition temperatures and phases in ferroelectric liquid crystals of \((S)-(\cdot)-2\text{-Methylbutyl 4'}-(4''-n\text{-alkanoyloxybenzoyloxy)}\) biphenyl-4-carboxylates (where \(n=16\) and 18) are studied the occurrence of SmC* and SmA in chiral FLCs can be detected by POM. Low frequency Dielectric parameters studied as a function of temperature can be used to determine the phase transitions temperatures in FLCs The low frequency relaxations in SmC* phase observed as the Goldstone mode responds at few Hz. High frequency relaxation mode, is the around the soft mode relaxation process occurring at high frequency region, is related to the reorientation of the longitudinal molecular dipole moment to the field. From this it was found that the goldstone mode dispersion in SmC* phase is similar to the soft mode dispersion in SmA phase regarding the temperature variation of dielectric strength. The variation of dielectric strength (\(\Delta\varepsilon\)) with temperature is found to be effectively mediated through the low frequency dipole response, a relative observation of soft mode relaxation in SmA and goldstone mode in SmC* throw light on relatively rapid change in \(\Delta\varepsilon\) With temperature in SmA phase due to the higher susceptibility.
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