Chapter 5

Dielectric investigations in a bent-core/calamitic blend exhibiting a novel columnar-calamitic phase sequence.

Overview
This chapter describes static and dielectric dispersion experiments carried out on the binary mixture of the system discussed in the two previous chapters. Static dielectric as well as dispersion measurement of the real and imaginary parts of the permittivity was carried out using a wide frequency range impedance analyzer. Dielectric spectroscopy data analyzed in detail in terms of the generalized Havriliak-Negami expression, show the presence of a soft mode relaxation in the vicinity of the orthogonal B1 phase (B1_{OPAF2}) – tilted B1 phase (B1_{TPAF}) transition with the relaxation frequency of the mode exhibiting a behavior similar to that seen for the calamatic smectic A-smectic C* phase transition. Mean field coefficients determining the soft mode behavior as well as the thermal variation of the tilt angle have been determined.

Results are published in

5.1 Introduction

The molecular dynamics of bent-shaped compounds is known to be quite complicated in comparison with those for the calamitic ferroelectric liquid crystal (FLC) and antiferroelectric liquid crystal (AFLC) materials. With this view dielectric investigations have been carried out on the bent-core system, which is a valuable tool for a complete characterization of the nature of the yet-to-be-fully-understood phases exhibited by the bent-core systems. The dielectric studies can provide rich information about the reorientation dynamics of the molecules, any short range correlation, if present and the dynamics of polar ordering in the medium.

5.1.1 Dielectric constant

The complex dielectric constant is given by $\varepsilon^* (\omega, T) = \varepsilon' (\omega, T) + j \varepsilon ''(\omega, T)$, where $\omega=2\pi f$ is the angular frequency of the applied electric field and $T$ is the temperature of the system. In general several relaxation mechanisms, each of which is connected to a characteristic eigen frequency $f_i$, are contributing to $\varepsilon^* (\omega, T)$. In the case of ferroelectric liquid crystals, Sm-C* phase we expect two relaxation modes connected to the reorientation of the director, two polarization modes, and at least one mode connected to the electronic properties of the medium. For each mode, at a given temperature, the contribution to the dielectric constant decreases with increasing frequency of the field, from the low-frequency value ($f \ll f_i$) to zero, which is the value adopted when the frequency of the applied electric field is so high ($f \gg f_i$) that the mode cannot follow the electric field.
The difference between the low- and high-frequency contribution of the mode to the total dielectric constant is called the dielectric strength of the mode and will be denoted $\Delta \varepsilon (T)$.

### 5.1.2 Dielectric Spectroscopy

Dielectric spectroscopy (DS) is a powerful technique that can be used to study the confinement effect on the dynamic behavior of liquid crystals (LCs). It probes the relaxation due to the reorientations of polar molecules in the sample. Broad band dielectric spectroscopy can be applied for investigations of the dynamic behavior of liquid crystals in the isotropic, nematic, and smectic phases. DS measurements are performed using a broadband dielectric spectrometer based on the Schlumberger Technologies 1260 Impedance/Gainphase Analyzer, Novocontrol Broad Band Dielectric Converter with an active sample cell and Hewlett Packward 4194A Impedance Analyzer. For bulk LCs, the dielectric relaxation process is of Debye type, which has a single relaxation time.

Debye function is used to describe the relaxation process:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau}$$

Where $\omega$ is the circular frequency ($\omega = 2\pi f$) of the alternating field, $\varepsilon_s$ is the static permittivity, $\varepsilon_\infty$ is the permittivity at infinite frequency, and $\tau$ is the macroscopic relaxation time.

For confined LCs, relaxation processes are of non-Debye type, which have a distribution of relaxation times.
In such cases Havriliak-Negami expression is used. The data obtained by dielectric spectroscopy measurements was analyzed in detail in terms of the generalized Havriliak-Negami expression, a brief explanation is given;

**Havriliak–Negami relaxation** is an empirical modification of the Debye relaxation model, accounting for the asymmetry and broadness of the dielectric dispersion curve. The model was first used to describe the dielectric relaxation of some polymers, [10] by adding two exponential parameters to the Debye equation:

The Havriliak-Negami function is used to analyze the dielectric spectra quantitatively:

\[
\varepsilon^* = \varepsilon_\infty + \sum_j \frac{\Delta \varepsilon_j}{1 + (i2\pi f \tau_j)^{1-\alpha_j}^{1-\beta_j}} - i \frac{\sigma}{2\pi \varepsilon_0 f^n}
\]

Where \(\varepsilon_\infty\) is the high-frequency limit of the permittivity, \(\Delta \varepsilon_j\) is the dielectric strength, \(\tau_j\) is the mean relaxation time, and \(j\) is the number of the relaxation process. The exponents \(\alpha_j\) and \(\beta_j\) describe the symmetric and asymmetric distribution of the relaxation times. The term \(i(\sigma/2\pi \varepsilon_0 f^n)\) accounts the contribution of conductivity \(\sigma\), with \(n\) as the fitting parameter. In the case of pure ohmic conductivity \(n = 1\). If electrode polarization also contributes to the imaginary part of dielectric permittivity \(\varepsilon''\), then \(n\) is less than 1.
5.1.3 Dielectric Relaxation

Apart from the molecular modes, the SmC* and SmA phases exhibit collective dielectric behavior, which have attracted more attention, owing to the fact that the dielectric parameters of these modes, such as the strength and relaxation frequency can be related to properties like polarization, pitch, tilt angle etc. These collective relaxation modes are referred to as the *Soft mode* (occurring in the $10^3$ - $10^6$ Hz range) and the *Goldstone mode* (10 - $10^3$ Hz range) [1-4]. While both the modes are present in the SmC* phase only the soft mode is observed in the SmA phase. Here we briefly discuss the origin of both the modes. In order to describe the ferroelectric Sm-C* phase one generally introduces 2 two-component order parameters. Thus, the dielectric response of the system consists (apart from the usual electronic contribution) of four modes—two high-frequency polarization modes and two modes of lower frequency connected to the relaxation of director fluctuations [5]. The two latter modes are commonly denoted as the soft mode and the Goldstone mode. These two low frequency director relaxation modes are related to the two components; the amplitude and the phase of the tilt order parameter. In the Sm-A phase the system exhibits two degenerate modes—one high-frequency polarization mode and one (soft) mode of lower frequency connected to the relaxation of director fluctuations. In the present system which is studied in detail a single relaxation mode in kHz region is observed for two smectic phases; two such modes are obtained in the $B_{1OPAF2}$ and the tilted columnar phases.
**Goldstone mode**

The change in the symmetry from D\(_\infty\) to C\(_2\) across A-C\(^*\) transition can be viewed as a continuous breaking of the symmetry group. In such cases according to the Goldstone theorem [6] a symmetry recovering mode called the Goldstone mode will appear in the low temperature phase. Since the presence of helix in the C\(^*\) phase recovers uniaxial symmetry in the A phase, so the Goldstone mode is associated with distortion of the helix. Because of the macroscopic nature of the helix, the relaxation frequency of the GM is small (10\(^2\) - 10\(^3\) Hz). For the same reason the strength of the GM is very large. Note that in the SmA phase the two modes become doubly degenerate. In present case transformation from tilted banana B1 phase (B1\(_{TPAF}\)) to tilted calamatic phase (SmC\(^*\)) phase GM appears.

**Soft mode**

Historically speaking, it was Raman and Nedungadi [7], see also [8] who were perhaps the first to observe the existence of soft modes (SM) in the vicinity of structural phase transitions, although the term ‘soft mode’ itself was introduced by Cochran [9] to describe the inelastic neutron scattering results in BaTiO\(_3\). The diminishing of the resistance of the system or “softening” to any structural changes is responsible for the observed behavior. The reason for the presence of the soft mode in the SmA phase is easy to comprehend. In the SmA phase the molecules are aligned in a direction parallel to the layer normal. The stability of this structure is
governed by an elastic constant, which keeps the long molecular axis parallel to the smectic layer normal.

As the system approaches $T_c$, the SmA - SmC* transition temperature, the elastic constant controlling the tilt fluctuation gets soft. Thus the fluctuation amplitude increases drastically with the susceptibility diverging at $T_c$ and the associated frequency becoming very small. This mode can also exist in the SmC* phase, but generally observed close to $T_c$. In the present case the transition from the columnar phase $B1_{OPAF2}$ with upright molecules to that with tilted molecules is accompanied by the softening of relaxation frequency connected with the tilt.

The data analyzed bring out the feature that in the two smectic phases and the highest temperature there is a single relaxation mode in the kHz region; two such modes are obtained in the orthogonal banana $B1$ phase ($B1_{OPAF2}$) and the tilted columnar phases.

This chapter also discusses an application of the Landau Ginzburg theory (developed for the SmA-SmC* situation) to the temperature-dependent softening of the relaxation frequency across the orthogonal columnar-tilted columnar banana $B1$ phase ($B1_{OPAF2}$-$B1_{TPAF}$) transition. It is indeed interesting to see that the Landau coefficient which contains temperature dependence of the order parameter governing the softening of the mode of the calamatic SmA-SmC* transition, and the columnar-tilted columnar ($B1_{OPAF2}$-$B1_{TPAF}$) phases studied here are in the same range.
5.2 Experimental Set up

The liquid crystal cell used for the electrical and electro-optic work consisted of a pair of optically flat glass plates with a thin film of indium-tin oxide (ITO) coating (from Donnelly Applied Films Corporation, USA), separated by PET spacers of known thickness, and glued together. The cell gap, typically in the range of 10-12 μm, was determined using an interferometric technique by employing a UV-vis spectrometer (Lambda 10, Perkin Elmer). For the electrical studies, the required planar alignment of the molecules was achieved by spin coating (coating unit: Single Wafer Spin Processor, Laurell Technologies Corporation, Model WS-400A-6NPP/LITE) the inside surfaces of the glass plates, prior to cell assembly, with a pre-polymer (PI-Kit, E-Merck) film that was cured at 300 °C for 3 hours to yield in situ polymerization of the pre-polymer, and subsequently rubbed unidirectionally. The sample was filled into the cell by capillary action in the isotropic phase to avoid any flow-induced alignment of the molecules. Slow cooling (rate of 0.1 °C) of the sample from the isotropic phase to the desired temperature in the mesophase yielded uniform planar orientation of the molecules.

The details of the materials used are mentioned in chapter 3. The structures and the transition temperatures of the materials used are shown below.
Figure 5.1: Molecular structure of (a) achiral bent core (PHDBB), (b) chiral rod-like compound (C2-116)
Measurement is carried out on a mixture of 25% by weight of the compound PHDBB in C2116. The phase sequence of this mixture which is being observed based on Optical polarizing microscope, X-ray diffraction measurements and polarization measurements mentioned in chapters 3 and 4 respectively is SmA - B1OPAF1 – B1OPAF2 – B1TPAF – SmC*, where O, P, T, and AF stand for orthogonal, polar, tilted and antiferroelectric respectively. The phases B1OPAF1 and B1OPAF2 are distinguished by the XRD measurements, the only change in the values of lattice parameter was observed. In this chapter, the investigation is done on the dynamics associated with the phase transition from orthogonal lamellar to orthogonal columnar to tilted columnar phase. The set-up used for the dielectric measurement is shown in Figure 5.2. The cell fabricated as mentioned above, results in a parallel plate capacitor, with the ITO coating acting as the electrode surface.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHDBB</td>
<td>Iso 176°C B2 ~100°C Cr</td>
</tr>
<tr>
<td>C2-116</td>
<td>Iso 163°C SmA 96.4°C Sm C* ~89°C Cr</td>
</tr>
</tbody>
</table>

*Table 1: Transition temperatures of bent core (PHDBB) and chiral rod-like compound (C2-116)*
Figure 5.2: Schematic representation of the experimental setup used for dielectric measurements
The capacitance and dielectric loss measurements were done using a variable frequency impedance analyzer (Hewlett Packard 4194A) interfaced to a PC using the IEEE 488 bus. The dielectric constant of the sample was determined by the ratio of the cell capacitance measured with and without the sample. Temperature-dependent measurements were performed using a temperature controlled chamber (Mettler FP82) whose programmer (FP90) was connected to the PC through the serial port (RS-232). The data collection and control of the experiment was handled by a user-written program in Visual Basic.

Frequency-dependent dielectric relaxation data was analyzed using a commercially available program, WinFit (Novocontrol, Germany), which provides a convenient user interface to model the relaxation process by incorporating various parameters, which will be discussed in a later section.

5.3 Results and Discussion

Static measurements

The thermal variation of the permittivity $\varepsilon$ for the planar geometry obtained at a probing frequency of 100 Hz applied along the substrate normal is shown in Figure 5.3. The SmA- $B_{1\text{OPAF}1}$ transition is marked by a step like increase that, considering the negative anisotropy of the system, indicates an enhancement of the anisotropy. The $B_{1\text{OPAF}1}$-$B_{1\text{OPAF}2}$ transition is marked by a large increase in the permittivity.
With further decrease in temperature, a plateau-like region is reached, before a large decrease in $\varepsilon$ at the $B_{1\text{OPAF2}}$-$B_{1\text{TPAF}}$ transition; the rate of decrease diminishing significantly upon the appearance of the SmC*.

**Dispersion measurements**

Over the temperature studied, $\varepsilon$ exhibits frequency-dependent characteristics, presenting one/two relaxations in the frequency range 20 Hz – 1 MHz. For lower frequency measurements and analysis, Novocontrol Broadband Dielectric convertor in combination with a Solarron SI 1260 gain phase analyzer with frequency range $10\mu$Hz – 32MHz is being used.

*Figure 5.3: Temperature dependence of the permittivity at a frequency of 100 Hz applied perpendicular to the director direction.*
The temperature dependence of the relaxation parameters, frequency ($f_R$) and the dielectric strength ($\Delta \varepsilon$) associated with the relaxation, are shown in Figure 5.4. and 5.5 respectively. Throughout the B1 phases a high frequency relaxation was observed whose $f_R$ value changed from 300 kHz to 20 kHz as the temperature was lowered, and is basically monotonic but for a small increase at the transition to the lower temperature OPAF phase. On the other hand, the strength of the relaxation, $\Delta \varepsilon$, exhibits small, but clear changes at both the transitions between the columnar phases.

Figure 5.4: The temperature dependence of the relaxation parameter; relaxation frequency in the different mesophases. The data shown as filled symbols correspond to the polar ordering of the bent-core molecules, whereas the open symbols represent the soft mode (connected with tilting of the molecules) in the $B1_{OPAF}$ and $B1_{TPAF}$ phases, and the Goldstone mode in the $SmC^*$ phase.
Figure 5.5: The temperature dependence of dielectric strength in different mesophases. The data shown as filled symbols correspond to the polar ordering of the bent-core molecules, whereas the open symbols represent the soft mode (connected with tilting of the molecules) in the B1_{OPAF} and B1_{TPAF} phases, and the Goldstone mode in the SmC* phase.
Figure 5.6: The temperature variation of the dielectric strength of the high frequency mode alone on an enlarged scale bringing out clear changes at the SmA-B1_{OPAF1}-B1_{OPAF2}-B1_{TPAF}-SmC* transitions (indicated by vertical lines).
The origin of this relaxation is not very clear to us, although two possibilities exist. Considering the frequency range involved it could be the relaxation of the director about the short axes of the molecules. However, the fact that the alignment of the molecules is planar and that the signature of the relaxation is not seen in the calamitic SmA and SmC* phases casts a doubt on this interpretation.

The second possibility is that the relaxation arises from the polar ordering of the molecules. A support for this argument comes from the feature that the dielectric strength of the relaxation reaches a maximum in the B1OPAF1 phase (fig. 5.6) but reduces on approaching the smectic phases at the high as well as low temperature sides.

The temperature dependence of $f_R$ can be described by an Arrhenius behavior with an activation energy of 65 and 74 kJ/mol in the B1OPAF1 and B1OPAF2 phases respectively. The second relaxation, at lower frequencies, making its appearance in the B1OPAF2 phase presents more interesting results. While its $f_R$ exhibits a sharp decrease with temperature the strength shows a concomitant increase; both the parameters reach an extremum at the transition to the phase with the tilted molecules (B1TPAF) at which point their thermal variation is reversed. Upon transformation to the SmC* phase the temperature dependence of these parameters becomes very weak, and is typical of the Goldstone mode. On the other hand, the strong decrease (linear in temperature in the B1OPAF2 phase) in $f_R$ resembles the behavior of the soft mode, seen in the SmA phase existing above a chiral smectic C phase. It should be borne in mind that tilt gets introduced at the B1TPAF phase itself, and therefore the true softening feature of this mode should be occurring on approaching the B1TPAF
phase from above. Owing to the non-availability of any explicit theoretical model, we use the standard Landau–Ginzburg expression [5] for the SmA-SmC* transition to analyze the mode softening in the B1_{OPAF2} phase. According to this model, the temperature dependence of the soft mode is given by

\[ f_s = \frac{a (T - T_c) + K q_o^2}{2 \pi \eta_s} \]  

Here ‘a’ is the Landau coefficient that contains explicitly the temperature dependence of the order parameter, the tilt angle. \( T_c \) is the transition temperature from the orthogonal to the tilted phase, \( K \) is an elastic term, \( q_o \) is the wavevector of the helix at the transition, and \( \eta_s \) is the rotational viscosity associated with the soft mode. Preliminary inspection shows that the \( f_R \) data in the vicinity of the \( B1_{OPAF2} \) to \( B1_{TPAF} \) transition that the frequency depends linearly on temperature.

Figure 5.7: shows the fitting of the soft mode frequency (in the \( B1_{OPAF2} \) phase) to the Landau model expression (eq. 1) discussed in the text.
Thus we can safely assume that $\eta_s$ has a very weak dependence on temperature, and thus the right hand side of expression (1) is essentially an equation for a straight line. With this in the background, we fitted the data to a straight line and the fitting shown in figure 5.7 is quite good. The slope of this straight line yields $a/(2\pi\eta_s)$. Taking a typical value of $\eta_s = 1$ Pa s [11, 1], ‘a’ is determined to be $7.3 \pm 0.2$ kJm$^{-3}$K$^{-1}$. This value is about an order of magnitude lower than certain early reports on ferroelectric rod-like liquid crystals [11-16], but is comparable to those reported more recently [17-19].

Figure 5.8: The tilt angle variation with temperature in the titled $B1_{TPAF}$ phase obtained by considering that the molecules tilt in a rigid-rod-like fashion.
It is indeed interesting to see that the Landau coefficient that controls the softening of the mode is in the same range for the SmA-SmC* transition, and the columnar-tilted columnar (B1OPAF2-B1TPAF) studied here. In view of this feature we fitted the temperature-dependent tilt angle \( \theta \) in the B1TPAF (see Fig.5.8) phase to a power-law,

\[
\theta \propto (T_c - T)^\beta
\]

where \( T_c \) is the B1TPAF-B1OPAF2 transition temperature, and \( \beta \) is the critical exponent connected with the temperature dependence of the order parameter, \( \theta \). The fitting yields a value of \( \beta = 0.41 \pm 0.01 \), which is in line with the values observed for the SmA-SmC (SmC*) transition, and if the arguments that are used for the SmA-SmC transition are applicable for the present case, suggest the influence of a tricritical point that may be in the vicinity in some parameter space.

5.4 Conclusion

The temperature-dependent fixed frequency data of the permittivity showed marked changes across calamitic to columnar transition. The dielectric spectroscopy measurements showed softening of relaxation frequency (connected with tilt) across the transition from the columnar phase with upright molecules to that with columnar phase of tilted molecules. The temperature dependence of this frequency has been explained using the same Landau model that is employed to describe such a phenomenon in systems having a direct smectic A-smectic C* transition. These studies thus show that tuning of the chiral and polar interactions can be realized with proper choice of the molecular components.