CHAPTER IV

OPTICAL MICROSCOPIC TEXTURAL STUDIES

ABSTRACT

The liquid crystalline mesogens are characterized by optical polarizing microscopic studies. Various orthogonal and tilted liquid crystalline phases are identified by their characteristic optical texture. With the aid of computer software these textures, which vary with temperature, are recorded, retrieved and analyzed. Also, the thermal textural phase variances of the No.m compounds are discussed.
4.1 INTRODUCTION

Liquid crystals, when cooled from isotropic melt to lower temperature, passes through different phases which can be optically identified as exciting colorful textures [101] by polarizing microscopic studies. It is prudent to mention that the orthogonal and tilted classification of the phases can be experimentally recorded through this technique. Thus not only the phase variance but also the thermal spans of the individual compounds can be evaluated by this tool.

4.2 ORTHOGONAL PHASE ORDERING

The best understood smectic phases are the smectic A, C, and B phases [1,2]. All three phases appear to have one common feature, viz. one degree of translational ordering, resulting in a layered structure. As a consequence of this partial translational ordering, the smectic phases are much more viscous than the Nematic phase.

4.2.1 SMECTIC A ORDERING

With in the layers of a smectic A mesophase the molecules are aligned parallel to the layer normal and are uncorrelated with respect to center of mass position [5], expect over very short distances. Thus, the layers are individually fluid, with a substantial probability for inter-layer diffusion as well. The layer thickness, determined from x-ray scattering data, is essentially identical to the full molecular length. At thermal equilibrium the smectic A phase is optically uniaxial due to the infinite-fold rotational symmetry about an axis parallel to
the layer normal. A smectic representation of smectic A order is shown in plate 4.2.

4.2.2 SMECTIC B ORDERING

Plate 4.4 depicts Smectic B phase. In addition to the layered structure, x-ray scattering data [8] indicate ordering of the constituent molecules with in the layers of the smectic B phase. Hence, the layers are no longer fluid, in contrast to the smectic A and C phases. However, the mechanical properties of the smectic B phase are quite different from those that would be expected for a material having full 3-dimensional order; thus, it can be conclude that the ordering, whatever its detailed nature, cannot be of the sort familiar in solids. It has been reported that the smectic B phase may in fact be a plastic crystal [8] which would be very interesting as it would provide the first opportunity to investigate both disordered crystal and ordered fluid mesophases in a single material (for any polymorphous smectic substance having a smectic B phase). This model is not the only one possible for the smectic B phase, however. It could also be that this phase is composed of a collection of 2-dimensional solid layers coupled by very weak forces, such that the layers could slip over one another quite easily [9] Smectic B phase can be either biaxial or uniaxial depending upon whether or not there is a finite tilt angle.

4.2.3 NEMATIC ORDERING

Plate 4.5 shows the equilibrium structure of the Nematic phase. As in the Cholesteric phase, lack of long range translational order imparts fluidity to the
Nematic phase. On a local scale, it is evident that Cholesteric and Nematic ordering are very similar. However, on a larger scale the Cholesteric director n follows a helix [2] of the form

\[ n_x = \cos (q_0 z + \phi) \]

\[ n_y = \sin (q_0 z + \phi) \]

\[ n_z = 0 \]

where both the direction of the helix axis z in space and the magnitude of the phase angle \( \phi \) are arbitrary. Thus the structure of a Cholesteric liquid crystal is periodic with a spatial period given by

\[ L = \frac{\Pi}{|q_0|} \]

The sign of \( q_0 \) distinguishes between left and right helices and its magnitude determines the spatial period. When \( L \) is comparable to optical wavelengths, the periodicity results in strong Bragg scattering of light. If the wavelength of the scattered light happens to be in the visible region of the spectrum, the Cholesteric phase will appear brightly colored.

It is interesting to note that a Nematic liquid crystal is really nothing more than a Cholesteric with \( q_0 = 0 \) (infinite pitch). In fact, the two are subclasses of the same family, the distinction being whether the equilibrium value of \( q_0 \) is identically zero, or finite. If the constituent molecules are optically inactive, i.e. are super imposable on their mirror image, then the mesophase will be Nematic. If, on the other hand, the constituent molecules are optically active, i.e. are not super imposable on their mirror image, then the mesophase will be Cholesteric (expect if the molecule and its mirror image are present in precisely
equal amounts, i.e. a “racemic” mixture, in which case the mesophase will again be Nematic).

Finally, a comment on nomenclature is in order. Cholesteric liquid crystals get their name historically from the fact that the first materials that were esters of cholesterol. It would be useful to continue identifying as “Cholesteric” those mesophases whose constituent molecules are derivatives of cholesterol, and to use the term “chiral Nematic” to identify mesophases formed by optically active, non-steroidal molecules.

4.3 OPTICAL TEXTURES OF 80. SERIES

The compounds, 80.12 and 80.16 of the present nO.m series exhibit di-variant phase sequence [104,105]. The observed phases are smectic A and smectic B. Smectic A is identified with characteristic focal-conic texture and the appearance of transient transition bars across focal-conic fans depicts smectic B phase. Plate 4.1 depicts fully grown smectic A phase from isotropic while plate 4.2 illustrates the smectic B phase grown from Smectic A.

4.3.1 PHASE SEQUENCES IN 80. HOMOLOGOUS SERIES

In this homologous series, compounds studied are 80.12 and 80.16. These compounds exhibit [104, 105] di phase variance namely smectic A and smectic B which are classified [101] as orthogonal phases. On cooling from isotropic melt the phase sequence of various compounds are given below

i) \textbf{80.12}\n
Isotropic \(\rightarrow\) Smectic A \(\rightarrow\) Smectic B \(\rightarrow\) Crystal

ii) \textbf{80.16}\n
Isotropic \(\rightarrow\) Smectic A \(\rightarrow\) Smectic B \(\rightarrow\) Crystal
Table 4.1 Transition temperatures of 8O. Homologous series

<table>
<thead>
<tr>
<th>nO.m</th>
<th>Phase Transition</th>
<th>Polarizing Microscopic Studies (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8O.12</td>
<td>Isotropic – Smectic A</td>
<td>76.10 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Smectic A- Smectic B</td>
<td>68.50 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Smectic B – Crystal</td>
<td>37.10 ± 0.01</td>
</tr>
<tr>
<td>8O.16</td>
<td>Isotropic – Smectic A</td>
<td>86.10 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Smectic A- Smectic B</td>
<td>65.90 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Smectic B – Crystal</td>
<td>44.70 ± 0.01</td>
</tr>
</tbody>
</table>

The transition temperatures of 8O. homologous series obtained by polarizing microscopic study are given in Table 4.1.

From the optical thermal microscopic studies it is inferred the following points:

1) In the 8O.12 liquid crystal compound the isotropic to Smectic A transition temperature is found to be at 77.13°C, while Smectic A to Smectic B transition occurred at 68.73°C and Smectic B transformed to crystal at 37.21°C. Thus the mesogenic thermal span, which is the difference between the isotropic and crystal temperatures, is computed to be 39.92°C.
2) The 80.16 mesogen had its isotropic to Smectic A phase transition temperature at 85.70 °C, while the Smectic A transformed to Smectic B at 65.83 °C. The crystallization is observed at 43.68 °C. Thus the mesogenic thermal span is about 44 °C.

4.4 OPTICAL TEXTURES OF 4O. SERIES

The compounds, 4O.12 and 4O.16 of the present nO.m series exhibit trivariant phase sequence [104, 105]. The observed phases are Nematic, smectic A and smectic B. Nematic phase is identified [92,101] by the characteristic finger print texture of Nematic drop lets. Smectic A is identified with characteristic focal-conic texture and the appearance of transient transition bars across focal-conic fans depicts smectic B phase. Plate 4.3 depicts fully grown Nematic phase from isotropic

4.4.1 PHASE SEQUENCES IN 4O. HOMOLOGOUS SERIES

In this homologous series, compounds studied are 4O.12 and 4O.16. These compounds exhibit tri phase variance [104,105] namely Nematic, smectic A and smectic B which are classified as orthogonal phases[101]. On cooling from isotropic melt the phase sequence of various compounds are given below:

i) 4O.12  Isotropic $\rightarrow$ Nematic $\rightarrow$ Smectic A $\rightarrow$ Smectic B $\rightarrow$ Crystal

ii) 4O.16  Isotropic $\rightarrow$Nematic $\rightarrow$ Smectic A $\rightarrow$ Smectic B $\rightarrow$ Crystal
<table>
<thead>
<tr>
<th>nO.m</th>
<th>Phase Transition</th>
<th>Polarizing Microscopic Studies (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4O.12</td>
<td>Isotropic – Nematic</td>
<td>66.10 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Nematic - Smectic A</td>
<td>53.30 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Smectic A – Smectic B</td>
<td>52.60 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Smectic B – Crystal</td>
<td>33.60 ± 0.01</td>
</tr>
<tr>
<td>4O.16</td>
<td>Isotropic – Nematic</td>
<td>63.15 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Nematic - Smectic A</td>
<td>61.55 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Smectic A – Smectic B</td>
<td>54.21 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Smectic B – Crystal</td>
<td>50.16 ± 0.01</td>
</tr>
</tbody>
</table>

The transition temperatures of 4O. homologous series obtained by polarizing microscopic study are given in Table 4.2.

From the optical thermal microscopic studies the following points are inferred:

1) In the 4O.12 liquid crystal compound the isotropic to Nematic transition temperature is observed to be at 66.10°C, while Nematic to Smectic A transition occurred at 55.30°C, Smectic A to Smectic B transition is at 52.60 °C while Smectic B transformed to crystal at 33.60°C. Thus the
mesogenic thermal span, which is the difference between the isotropic and crystal temperatures, is computed to be 32.50°C.

2) The 4O.16 mesogen had its isotropic to Nematic phase transition temperature at 63.15 °C, while the Nematic transformed to Smectic A at 61.55 °C. The formation of Smectic B from Smectic A is observed at 54.21 °C. The crystallization is observed at 50.16°C. Thus the mesogenic thermal span is about 13 °C.

4.5 TILTED PHASE ORDERING

In this class of smectic phase, the long axis of the molecules which is referred as director makes an angle to the layer normal.

4.5.1 SMECTIC F PHASE

Tilted phases with in-plane hexatic order are classified [70,101] as Smectic F phase. In this hexagonal arrangement with in the smectic planes the molecules can tilt along two distinct directions with respect to hexagonal lattice. If the molecules are tilted towards a corner it is generally known as Hex I phase which is referred as Smectic F phase.

4.5.2 SMECTIC G PHASE

In smectic G phase the molecules arrangement with in smectic plane possesses long range PO and BOO [21].

In the present investigation, it is observed that nO.m compounds under investigation possess mono, di and tri phase variance. The tilted phases observed are Smectic F and Smectic G.
4.6 PHASE SEQUENCES IN 150. HOMOLOGOUS SERIES

In this homologous series, compounds studied are 150.8, 150.10, 150.12 and 150.16. The compounds 150.8, 150.10 and 150.12 exhibit mono phase variance namely smectic F, which is classified as tilted phase [21,92, 101,104,105]. The compound 150.16 exhibits [104] di phase variance namely Smectic F and Smectic G, which are classified as tilted phase. Textural observation of broken focal conic [92] is attributed to the Smectic F phase. In Smectic G phase is identified [21] with smooth colored mosaic texture. Plate 4.4 depicts Smectic F phase grown from isotropic, plate 4.5 depicts Smectic G phase grown from smectic F.

On cooling from isotropic melt the phase sequence of various compounds are given below:

i) **150.8**
   Isotropic $\rightarrow$ Smectic F $\rightarrow$ Crystal

ii) **150.10**
    Isotropic $\rightarrow$ Smectic F $\rightarrow$ Crystal

iii) **150.12**
     Isotropic $\rightarrow$ Smectic F $\rightarrow$ Crystal

iv) **150.16**
    Isotropic $\rightarrow$ Smectic F $\rightarrow$ Smectic G $\rightarrow$ Crystal
Table 4.3: Transition temperatures of 150. homologous series

<table>
<thead>
<tr>
<th>nO.m</th>
<th>Phase Transition</th>
<th>Polarizing Microscopic Studies (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15O.8</td>
<td>Isotropic – Smectic F</td>
<td>82.50 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Smectic F – Crystal</td>
<td>40.90 ± 0.01</td>
</tr>
<tr>
<td>15O.10</td>
<td>Isotropic – Smectic F</td>
<td>84.70 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Smectic F – Crystal</td>
<td>44.30 ± 0.01</td>
</tr>
<tr>
<td>15O.12</td>
<td>Isotropic – Smectic F</td>
<td>83.90 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Smectic F – Crystal</td>
<td>44.10 ± 0.01</td>
</tr>
<tr>
<td>15O.16</td>
<td>Isotropic – Smectic F</td>
<td>91.20 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Smectic F – Smectic G</td>
<td>87.30 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Smectic G – Crystal</td>
<td>65.90 ± 0.01</td>
</tr>
</tbody>
</table>

The transition temperatures of 15O. homologous series obtained by polarizing microscopic study are given in Table 4.3.
The phase diagram of 15O. series is depicted in figure 4.1. It can be observed that as the carbon number increases in the homologous series, smectic F phase is quenched by a higher ordered smectic G phase. However, in the last compound of the series, 15O.16 both the phases co-exist, though the thermal span of the smectic F phase is only about 4°C. From the optical thermal microscopic studies it is inferred the following points:

1) In the 15O.8 liquid crystal compound the isotropic to Smectic F transition temperature is found to be at 82.5°C, while smectic F transformed to crystal at 40.9°C. Thus the mesogenic thermal span,
which is the difference between the isotropic and crystal temperatures, is computed to be 41.6°C.

2) In 15O.10 compound, the isotropic to Smectic F phase transition temperature is observed at 84.7°C and the smectic F to crystal temperature is at 44.3°C. The mesogenic thermal span of this compound is 40.4°C.

3) In 15O.12 mesogen, the isotropic to smectic F phase is found to be at 83.9°C, while the crystal is formed at 44.1°C. For this compound the liquid crystalline thermal span is calculated to be 39.8°C.

4) The last compound of the 15O. homologous series, 15O.16 exhibits two transitions. The isotropic to smectic F transition is at 91.2°C, smectic F to Smectic G transition is observed at 87.3°C while the smectic G transformed to crystal at 65.9°C. The mesogenic thermal span is computed to be 25.3°C.

From the above data it can be inferred that in the 15O. homologous series as the alkyl carbon chain increased from 8 to 16 the mesogenic thermal span decreased from 41.6°C in 15O.8 to 25.3°C in 15O.16. It is not surprising to note that in this series the isotropic temperatures increased from 82.5°C in 15O.8 to 91.2°C in 15O.16.

It can be concluded that as the alkyl carbon atoms increased the mesogenic thermal span decreases remarkably while the isotropic temperatures increase marginally.