CHAPTER 6
PHOTOACOUSTIC INVESTIGATIONS OF PHASE TRANSITIONS
IN LIQUID CRYSTALS

6.1 DIFFERENT THERMAL TECHNIQUES EMPLOYED FOR THE
IDENTIFICATION OF PHASE TRANSITIONS IN LIQUID
CRYSTALS:

i. INTRODUCTION:

Photoacoustic Spectrometer (PAS), Thermal Microscopy (TM) and
Differential Scanning Calorimeter (DSC) are the normally employed thermal
instruments for the identification of mesophases and the associated phase transition
temperatures. In the present investigation, the author has employed the "computer
based photoacoustic spectrometer" developed by him for identification of phase
transition temperatures of certain liquid crystals belonging to $nO.m$ compounds,
benzoic acids and hydrogen bonded complexes. The liquid crystal systems selected
for the present study are provided by the "Centre for Liquid Crystal Research and
Education, Nagrajuna University, Nagarjuna Nagar, Guntur". The detailed
description of the design and development of this instrumentation system is
presented in Chapter 2 of this thesis and the standardization of the instrumentation
is described in chapter 5.

The results obtained by him through this technique are compared with the
results obtained with TM and DSC measurements.

ii. Thermal Microscopy:

Liquid crystalline compounds are birefringent and exhibit different optical
textures for different phases under crossed polars. Hertel Reuss (Super Pan II)
polarizing microscope is used for identifying the textures of different phases of the
liquid crystalline compounds. With the help of heating block (hot stage INSTEC, USA), the textures of different phases are observed.

The hot stage from INSTEC, USA with a temperature accuracy of ±0.1°C is employed for the identification of the liquid crystalline phases and phase transition temperatures. The liquid crystalline phases are characterized by the observation of optical textures exhibited by a thin film of liquid crystal placed between the crossed polars, in comparison with the characteristic textures.

iii. Differential Scanning Calorimeter:

The transition temperatures and the enthalpies associated with phase transitions of the crystalline and the liquid crystalline phases of the compounds are determined using a Perkin Elmer DSC-7 differential scanning calorimeter.

6.2 SAMPLE HANDLING AND PRECAUTIONS:

The samples are kept in a crucible of 7mm diameter and 1.5mm depth (Perkin Elmor DSC-7 crucibles). The samples as such give very low amplitude photoacoustic signal because of their low optical absorbivity. Hence, methylene blue is added to all the sample to enhance the photoacoustic signal amplitude. And it is observed in DSC that the addition of methylene blue has no effect on the phase transitions of the samples\(^1\). All the phase transition plots are obtained after adding a pinch of methylene blue to the samples. The experiment is repeated twice for each sample to test the repeatability of the results. The following precautions are taken to obtain the efficient PA signal.
i. Prior to insertion of the sample, the cavity of the PA cell is cleaned and dried with the acetone.

ii. The silicon O-rings are properly aligned to avoid the possible leaks.

iii. Glass windows are cleaned with acetone and kept highly transparent.

iv. The laser beam is perfectly aligned so that it will not give any spurious reflections inside the chamber and generate noise.

v. Cavity is perfectly capped.

vi. The cell is kept on a vibration free platform.

6.3 PHASE TRANSITION STUDIES ON nO.m COMPOUNDS:

The large amount of the data available in literature shows a well known "Benzylidene Aniline liquid crystal systems popularly known as nO.m" compounds, where \( n \) and \( m \) denote the alkoxy and alkyl chain numbers respectively. The carbon chain number can be varied from one to sixteen to obtain a variety of liquid crystals which exhibit different phase sequence variants. The ease in the synthesis, the exhibition of different liquid crystalline phases at and around ambient temperature and the presence of subtle polymorphism make these systems ideal not only for testing the fabricated PAS experimental setup but also for identifying the different phase transition temperatures present in new systems, as the case with the other thermal techniques like thermal microscopy (TM) and differential scanning calorimetry (DSC).

The lower homologues exhibit the high temperature nematic and orthogonal smectic-A phases while the higher homologues show only the tilted phases like smectic-F and smectic-G phases with simultaneous quenching of the orthogonal phases. However, the compounds with the intermediate alkoxy and alkyl chain numbers exhibit the orthogonal as well as tilted phases. The compound N-(p-n-pentyloxybenzylidene)-p-n-hexylaniline, 50.6 show the maximum phase variant in
this series namely, nematic, smectic-A, smectic-C, smectic-B, smectic-F and smectic-G phases (NACBFG). The details of the phase transition studies carried out by the author on this compound are described in the forthcoming sections. The significance of the \( nO.m \) compounds is also realized from the wide phase selectivity under moderate working temperatures. Apart from this, these materials show high chemical and thermal stability under repeated thermal scans. This experimental viability of these compounds, motivated the author to undertake the phase transition studies on the selected \( nO.m \) compounds listed below, whose structures are presented in Fig.6.1.

i. \( \text{N-(p-n-pentyloxybenzylidene)-p-n-butylaniline (50.4)} \)

ii. \( \text{N-(p-n-pentyloxybenzylidene)-p-n-hexylaniline (50.6)} \)

iii. \( \text{N-(p-n-pentyloxybenzylidene)-p-n-nonylaniline (50.9)} \)

iv. \( \text{N-(p-n-decyloxybenzylidene)-p-n-nonylaniline (100.9)} \)

v. \( \text{N-(p-n-dodecyloxybenzylidene)-p-n-dodecylaniline (120.12)} \)

vi. \( \text{N-(p-n-hexadecyloxybenzylidene)-p-n-hexadecylaniline (160.16)} \)

The characteristic amplitude and phase behaviours of different compounds along with the corresponding transition temperatures are depicted in Table-6.1.

The compound-wise discussion on the phase variants and the corresponding transition temperatures observed by photoacoustic spectrometer developed by the author is presented in foregoing sections. A comparison of the results obtained through photoacoustic spectrometer with differential scanning calorimeter for selected compounds is also discussed in this section. As some of the compounds are enantiotropic in nature, the characteristic phase transition graphs during cooling cycle could not be obtained for them.
Fig. 6.1 Structures of nO.m compounds
i. Compound 5O.4:

The amplitude and phase variations with temperature from PAS technique developed by the author for compound 5O.4 are presented in Fig.6.2. The compound 5O.4 exhibits nematic, smectic-A and smectic-G (NAG) phase variants. However, Fig.6.2 shows weakly resolved isotropic to nematic and smectic-G to crystalline transition only. In view of the large change in amplitude at A to G interface at higher temperatures NA transition could not be resolved in the present case. As the phases of 5O.4 compound are enantiotrophic in nature, the transition graph during the cooling cycle could not be detected. On the other hand, DSC thermogram presented in Fig.6.3 shows only isotropic to nematic liquid crystal and smectic-G to crystal transitions. It is worth mentioning here that the second order phase transition corresponding to nematic to smectic-A is not resolved in the DSC thermogram. However, this transition is observed from the photoacoustic measurements. Results of the PAS, TM and DSC studies on 5O.4 compound are consolidated in Table 6.1.

ii. Compound 5O.6:

The amplitude and phase variations with temperature from PAS technique developed by the author for the compound 5O.6 are presented in Fig.6.4. The 5O.6 compound is unique in nO.m series as it exhibits maximum phase variants viz., nematic, smectic-A, smectic-C, smectic-B, smectic-F, smectic-G (NACBFG). The variation includes both first and second order transitions. Both amplitude and phase variations studied through the PAS technique developed by the author facilitate to identify all the phase transitions except smectic-C to smectic-B transition. It is expected in view of large amplitude change from smectic-C to smectic-B compared to smectic-A to smectic-C. On comparison with DSC thermogram, it is interesting to note that the PAS studies could resolve the second
Fig. 6.2 N-(p-n-pentyloxybenzylidene)-p-n-butylaniline (50.4)
50.4 - heating

Fig. 6.3 DSC Thermogram
Fig. 6.4 N-(p-n-pentyloxybenzylidene)-p-n-hexylaniline (50.6)
Fig. 6.5 DSC Thermogram
order smectic-A to smectic-C and smectic-G to smectic-F transitions. While these transitions could not be observed from DSC thermograms as can be seen from Fig.6.5.

The above results, provide a substantial evidence of the sensitivity and significance of PAS technique in detecting the weak first order and second order phase transition over the other techniques viz. the DSC and TM. The results of the PAS, TM and DSC studies on 50.6 compound are consolidated in Table 6.1.

iii. Compound 50.9:

A glance at Fig.6.6, which representing the variation of amplitude and phase with temperature for 50.9 compound observed through PAS technique developed by the author reveals well resolved phase transitions which exhibits nematic, smectic-A and smectic-B (NAB) phases sequence. This figure also shows that the all the phase transitions could not be identified exclusively with amplitude or phase studies alone. Hence, it is necessary to consider both amplitude and phase transitions curves for identification of all the transitions, as is evident in the present case of 50.9 compound. For example, the NA transition, which is suppose to be a weak first order transition is identified with the phase change rather than amplitude. Further, it is observed in this compound that the trend in the phase variation to the amplitude variation is found to be opposite at all transitions, which is contrary to the observation made in other compounds of the same homologous series. The transition temperatures observed in PAS study are found to be in reasonable agreement with the DSC profiles as shown in Fig.6.7. The results of the PAS, TM and DSC studies on 50.9 compound are consolidated in Table 6.1.
Fig. 6.6 N-(p-n-pentyloxybenzylidene)-p-n-nonylaniline (50.9)

Temperature / °C
iv. Compound 100.9:

Fig. 6.8 represents the variations of amplitude and phase with temperature in both heating and cooling cycles observed through PAS technique developed by the author. The compound 100.9 shows direct smectic-A transition from isotropic state on cooling. The compound exhibits smectic-A, smectic-C, smectic-B and smectic-G (ACBG) phase variants. The amplitude variation resolved all the phase boundaries except, the second order A to C transitions unlike in the case of 50.6. This may be due to narrow thermal ranges of both smectic-A and smectic-C phases. The results of the PAS, TM and DSC studies on 100.9 compound are consolidated in Table 6.1.

v. Compound 120.12:

The compound 120.12 is a higher homologous of nO.m compounds, where all high temperature phases such as nematic and smectic-A are quenched with the onset of smectic-F phase. The compound 120.12 exhibits smectic-F and smectic-G (FG) phase variants as can be seen from Fig.6.9 and Fig6.10 for heating and cooling cycles show almost identical behaviour. In the PAS measurements carried out through the technique developed by the author both on heating and cooling cycle respectively show the phase transitions from isotropic to smectic-F. However, in case of 120.12 the smectic-F to smectic-G boundary could not be resolved. The DSC thermograms of 120.12 is represented in Fig.6.11 in which both isotropic to smectic-F and smectic-F to smectic-G transitions could be resolved. The results of PAS, TM and DSC studies on 120.12 compound are presented in Table 6.1.
Fig. 6.8 N-(p-n-decyloxybenzylidene)-p-n-nonylaniline (100.9)
Fig. 6.9 N-(p-n-dodecyloxybenzylidene)-p-n-dodecylaniline (120.12)
Fig. 6.10 N-(p-n-dodecyloxybenzylidene)-p-n-dodecylaniline (120.12)
Figure 6.11 DSC Thermogram
vi. Compound 160.16:

The compound 160.16 is also a higher homologous of \( nO.m \) compounds, where higher temperature phases such as nematic and smectic-A are also quenched with the onset of smectic-F phase. This compound exhibits smectic-F phase variant as can be seen from Fig.6.12 and Fig.6.13 for heating and cooling cycles respectively in PAS technique developed by the author. Further, it is interesting to observe in case of 160.16 compound that the phase variations are in opposition to variations in amplitude both at isotropic to smectic-F and smectic-F to crystalline transitions. The results of the PAS, TM and DSC studies on 160.16 compound are consolidated in Table 6.1.

6.4 THE SALIENT FEATURES OBSERVED IN THE STUDIES ON \( nO.m \) COMPOUNDS:

i. The 50.6 compound exhibits phase variants of nematic and smectic phases like A,C,B,F,G (NACBFG) which is the basis for all \( nO.m \) homologous series. The PAS technique developed by the author could resolved all the phases including second order transitions such as smectic-A to smectic-C and smectic-F to smectic-G, which could not be observed in the differential scanning calorimeter technique.

ii. In the compounds studied in \( nO.m \) series the phase has no simple relation with the amplitude variations at the isotropic to first liquid crystalline transitions whereas they follow at all other phase transitions. This is contrary to the observations made in the case of 40.\( m \) compounds of \( nO.m \) series (where the phase variations show opposite tendencies to the amplitude variation at the isotropic to first liquid crystal transitions).
Fig. 6.12 N-(p-n-hexadecyloxybenzylidene)-p-n-hexadecylaniline (160.16)
Fig. 6.13 N-(p-n-hexadecyloxybenzylidene)-p-n-hexadecylaniline (160.16)
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iii. In the case of 120.12, inspite of repeated scan rates the phase boundary between smectic-F to smectic-G could not be detected through the present PA technique. This may be due to the low thermal span of smectic-F phase.

6.5 PHASE TRANSITION STUDIES ON BENZOIC ACIDS AND HYDROGEN BONDED COMPLEXES:

The synthesis and characterization of hydrogen bonded complexes formed with a combination of mesogenic and non-mesogenic systems has attracted the scientists in the field of liquid crystals. Due to the characteristic nature of self assembling capability, the formation of hydrogen bonded complexes and the presence of non-mesogenic moiety exert influences on the physical properties as well as on the liquid crystalline behaviour. The compounds chosen for the present study are listed below, whose structures are presented in Fig.6.14.

i. p-n-hexyloxybenzoic acid (HBA)
ii. p-n-nonyloxybenzoic acid (NBA)
iii. p-n-hexyloxybenzoic acid : p-hydroxy methyl benzoate (HBA:HMB)
iv. p-n-nonyloxybenzoic acid : p-hydroxy methyl benzoate (NBA:HMB)
v. p-n-decyloxybenzoic acid : p-hydroxy methyl benzoate (DBA:HMB)
vi. p-n-decyloxybenzoic acid : 1,3-dihydroxy benzene (DBA:DB)
vii. p-n-dodecyloxybenzoic acid : 1,3-dihydroxy benzene (DDBA:DB)

The transition temperatures along with the phase variants are incorporated in Table 6.2.

Fig. 6.14 Structures of Benzoic acids and Hydrogen bonded complexes
The compound-wise discussions on the phase variants and the corresponding transition temperatures observed by photoacoustic spectrometer developed by the author are presented in the foregoing sections. Comparisons of the results obtained through PAS with the results obtained through DSC for selected compounds are also discussed in the following section. As some of these compounds are enantiotropic in nature, the characteristic phase transition plots during cooling cycle could not be obtained for them.

**i. Compound HBA :**

The amplitude and phase variations with temperature from PAS technique developed by the author for compound HBA are presented in Fig.6.15 and Fig.6.16 for heating and cooling cycles respectively. The compound HBA exhibits nematic phase variant. The amplitude and phase variations in both heating and cooling cycle resolved all the transitions. This behaviour of HBA compounds is similar to that exhibited by 40.6 compounds where the phase variation is in opposition to the variation of amplitude during isotropic to nematic transition, while it is in phase with the variation at all other phase transitions. The results of the PAS, TM and DSC studies on HBA are consolidated in Table 6.2.

**ii. Compound NBA :**

The amplitude and phase variations with temperature for the compound NBA carried out through PAS technique developed by the author are presented in Fig.6.17 and Fig.6.18 for the heating and cooling cycles respectively. This compound NBA exhibits nematic and nematic to smectic-C (NC) phase variants. The amplitude and phase variations during both heating and cooling cycles could resolve all the phase transitions viz. nematic and smectic-C. In addition, the compound NBA exhibits opposite trends in phase amplitude variations during
Fig. 6.15 p-n-hexyloxybenzoic acid (HBA)
Fig. 6.16 p-n-hexyloxybenzoic acid (HBA)
Fig. 6.17 p-n-nonyloxybenzoic acid (NBA)
Fig. 6.18 p-n-nonyloxybenzoic acid (NBA)
isotropic to nematic transition, whereas, it shows similar trends at all transitions. The results of the PAS, TM and DSC studies on NBA are consolidated in Table 6.2.

iii. Compound HBA:HMB:

The amplitude and phase variations with temperature through PAS technique developed by the author for the compound HBA:HMB are presented in Fig.6.19 and Fig.6.20 for heating and cooling cycles respectively. The compound HBA:HMB exhibits nematic to smectic-G during heating cycle distinctly. Whereas, a broad nematic to smectic-G (G+N) could only be observed during cooling cycle. This clearly shows that it is not possible to resolve all the transitions through exclusive study of anyone of the heating and cooling cycles alone. Hence, it is necessary to study both the cycles for completely resolving all the transitions. Further, unlike the case of pure alkoxy benzoic acids, the phase variations are found to follow the amplitude variations at all other transitions including isotropic to nematic. The observation of thermogram shown in Fig.6.21 reveals two transitions nematic and smectic-G are prominently observed in heating cycle whereas a single transition (N+G) is observed in cooling cycle. This confirms the ability of PAS to detect all the transitions observed in DSC. The results of the PAS, TM and DSC studies on HBA:HMB are consolidated in Table 6.2.

iv. Compound NBA:HMB:

The amplitude and phase variations with temperature for the compound NBA:HMB observed through PAS technique developed by the author are presented in Fig.6.22 and Fig.6.23 for heating and cooling cycles respectively. The compound NBA:HMB exhibits, nematic and nematic to smectic-G phase
Fig. 6.19 p-n-hexyloxybenzoic acid : p-hydroxy methyl benzoate (HBA:HMB)
Fig. 6.20  p-n-hexyloxybenzoic acid : p-hydroxy methyl benzoate (HBA:HMB)
Figure 6.21 DSC Thermogram
Fig. 6.22 p-n-monyloxybenzoic acid : p-hydroxy methyl benzoate (NBA:HMB)
Fig. 6.23 p-n-nonyloxybenzoic acid : p-hydroxy methyl benzoate (NBA:HMB)
transitions during heating cycle while it exhibits nematic and combined C+G transitions during cooling cycles. The phase variations are opposite to the amplitude variations at transition G where as it is following at the other transitions during heating cycle. However, the phase variations are exactly following the amplitude variations during cooling cycle. Further, the smectic-C transition is monotrophic and the data reported in literature on this compound shows the inducement of smectic-G phase which is not present in the alkoxybenzoic acids. The results of the PAS, TM and DSC studies on NBA:HMB are consolidated in Table 6.2.

v. Compound DBA:HMB:

The amplitude and phase variations with temperature for the compound DBA:HMB observed through PAS technique developed by the author are presented in Fig.6.24 and Fig.6.25 for heating and cooling cycles respectively. The compound DBA:HMB exhibits, isotrope to nematic and nematic to smectic-G phase variants during heating cycle. However, it exhibits isotrope to nematic and a nematic to broad C+G transitions are observed in cooling cycle. The phase variations are exactly following the amplitude variations both in heating and cooling cycles. The results of the PAS, TM and DSC studies on DBA:HMB are consolidated in Table 6.2.

In the case of HBA:HMB the nematic to smectic-G transition could not be resolved in the cooling cycle. The same is the case with smectic-C to smectic-G transitions in other two compounds in cooling cycle. Further, unlike the case of pure alkoxy benzoic acids, the phase transitions is in phase with amplitude at all transitions including isotropic to nematic transitions.
Fig. 6.24 p-n-decyloxybenzoic acid : p-hydroxy methyl benzoate (DBA:HMB)
Fig. 6.25 p-n-decyloxybenzoic acid : p-hydroxy methyl benzoate (DBA:HMB)
vi. Compound DBA:DB:

The amplitude and phase variations with temperature for the compound DBA:DB through the PAS technique developed by the author is presented in Fig. 6.26 for heating cycle. The compound DBA:DB exhibits, nematic, smectic-A and smectic-G (NAG) phase variants. In this study all the transitions NAG could be resolved. The phase variations are exactly opposite to the amplitude variations. The results of the PAS, TM and DSC studies on HBA are consolidated in Table 6.2.

vii. Compound DDBA:DB:

The amplitude and phase variations with temperature for compound DDBA:DB is presented in Fig. 6.27 for heating cycle. The compound DDBA:DB exhibits, nematic and smectic-A (NA) phase variants. In this study all the transitions (NA) could be clearly resolved. The phase variations are exactly opposite to the amplitude variations. The results of the PAS, TM and DSC studies on HBA are consolidated in Table 6.2.

The phase relation to the amplitude with temperature in DBA:DB and DDBA:DB is opposite to that observed in the above three hydrogen bonded complexes.
Fig. 6.26 p-n-decylxycarboxylic acid : 1,3-dihydroxy benzene (DBA:DB)
Fig. 6.27 p-n-dodecyloxybenzoic acid : 1,3-dihydroxy benzene (DDBA:DB)
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6.6 THE SALIENT FEATURES OBSERVED IN THESE STUDIES ARE:

i. PAS measurements on benzoic acids HBA and NBA clearly could resolve all the phases present in the compounds.

ii. The inducement of Smectic-G phase in all hydrogen complexes either with Methyl benzoate or resorcinol is identified from these measurements.

iii. In the case of HBA and NBA, the phase variations show opposite tendencies to the variations of amplitude at isotropic to nematic transitions while at all other transitions the phase variations follow the amplitude variations.

iv. The interesting observation in all these cases is that the phase variations follow the variations of amplitude at all transformations including isotropic to first liquid crystalline transformation except in the case of \( nO.m \) compounds and benzoic acids.

The results of the photoacoustic measurements carried out with the instrumentation system developed by the author establish the suitability of the instrument as a reliable tool for the photoacoustic studies.
REFERENCES