CHAPTER VI

SUBSIDIARY MATTER
6.1 SOLID POLYMORPHS OF p-azoxyanisole (PAA).

(a) INTRODUCTION:

The nematic liquid crystalline material p-azoxyanisole (PAA) has received considerable experimental and theoretical attention in the past. It is the simplest and first member of the classic series of 4,4'-di-n-alkoxyazoxybenzene, having chemical structure:

\[
\text{CH}_3\text{O} - \quad \text{N} = \quad \text{N} - \quad \text{CH}_3
\]

Arnold\(^1\) was the first to carry out the precision calorimetry of this series of liquid crystals. Later on a number of workers (listed in the review article by Birlall and Johnson\(^2\)) made the phase transition studies in PAA but they (with the exception of Chow et al\(^3\)) did not found the existence of different solid phases before going to the nematic phase. Here we report a detailed phase transition studies which reveal some hitherto unknown phases of PAA along with the heat of transition (\(\Delta H\)) and transition entropies (\(\Delta S\)) for various transitions.

(b) EXPERIMENTAL:

A differential thermal analysis (DTA) apparatus was
used for recording the phase transition with precession. The DTA apparatus was specially designed to study the liquid crystalline phase transitions and it can be programmed for different heating and cooling rates. The heat of transition (\( \Delta H \)) was calculated by measuring the area of the transition peak by means of a planimeter. The thermal optical microscopy (TOM) was employed to verify the result of DTA. It is essentially a Zeiss polarising microscope equipped with a regulated hot stage to examine a thin section of PAA on a cover slide. The DTA and TOM apparatus are discussed in detail in chapter III.

The spectroscopic grade PAA sample (purity 99.9%) was procured from M/s E. Merck, Germany and it was used as such. For studying the effect of impurity on the phase transitions, a number of PAA samples of different purity were prepared by externally adding the known amount of p-methoxybenzaldehyde as an impurity to the pure PAA sample.

(C) RESULTS AND DISCUSSIONS:

We started with the room temperature solid (SI) phase of PAA and the DTA plot was obtained during heating.
cycle (Fig. 6.1a) with a heating rate 5°K/min. It shows two clearly marked endothermic peaks, one at 380.0°K constituting a phase transition from solid I to nematic phase (SI-I transition) and the other at 406.9°K for a transition from nematic to isotropic phase (I-I transition). The DTA behaviour when isotropic liquid was cooled is shown in the Fig. 6.1b which consists of three exothermic peaks corresponding to I-II (at 406.9°), N-Solid II (at 365.8°K) and solid II - solid I (at 335.6°K), transitions. Thus, a new solid phase (solid II or SI) emerges from nematic phase at a fixed temperature which subsequently converts to solid I at a lower temperature. It was also found that SI-II transition temperature depends on the thermal history of the sample. The presence of two solid phases was confirmed by X-ray. The solid textures of SI and SI are shown in Fig. 6.2a and 6.2b respectively. The high temperature solid II phase is characterised by big, flat, birefringent platelets which break into smaller ones to give SI phase at the SI-II transition. This type of behaviour is also reported by Chow and Martine and they concluded that the purity of the sample plays an important role for observing the two solid phases during cooling. This is contrary to observations of other workers possibly due to the use of not so pure samples.
Fig. 6.1: DTA traces of PAA
To check on this point, the thermal behaviour of a 
deteriorated sample (93.0%) was studied and it shows only 
one solid phase during cooling (Fig.1d) in agreement with 
earlier workers. If SII phase is directly heated, it passes 
into nematic phase at a lower temperature, 377.6°C (Fig.1e) 
then SII-SI transition temperature.

A slow DTA sweep is generally used to discriminate 
against the pretransitional effects if the transitions are 
sharply defined (Hoyer and Kovari). The Fig.6.1e shows the 
thermal behaviour during the slow heating cycle (heating rate 
1°/min). The slow heating rate results in an additional 
peak shouldering the main peak at SI-SII transition. The first 
peak is ascribed to SII-SII transition and second peak stands 
for SII-SI transition. Hence the high temperature, metastable 
solid II phase can exist in various mixtures with solid I 
phase even at room temperature. The observation of a poorly 
marked endothermic peak just before the N-I transition 
indicates some pretransitional thermal behaviour.

The sample was quenched from isotropic melt with a 
rage greater than 30°C/min. to study the effect of nucleation 
rate on the formation of solid phase. As a result of rapid 
quenching, a new solid phase (SIII) was detected which
Fig. 6.2 Photomicrographs of different solid phase of MA (a) SI phase (b) SII phase (c) SIII phase
Magnification x 160
transforms into room temperature solid (SI) phase at
250.7°K. This SIII-SI transition is depicted by a very low
peak of fusion in Fig.6.1f along with usual SI-III and III-I
phase transitions. The PM sample was also quenched in TMD
apparatus under exactly similar conditions and the
photomicrograph of the new solid (SIII) phase thus obtained
is shown in Fig.6.2c. The SIII phase is marked with lumines
texture which breaks into smaller platelets of SI phase at
SIII-SI phase transition.

The effect of impurity in PM sample on the appearance
of monotropic SII phase during cooling was investigated separately.
The DTA plots during cooling for PM samples of different
purity was obtained and shown in Fig.6.3. The SII phase was
observable in the three samples having purity 99.9%, 99.8% and
99.7% while it was absent in the samples having purity 99.6%
and 99.5%. It was also noted that the values of heat of
transition (∆H) and transitions temperatures of III-SII and
SII-SI transitions are not much affected by the percentage of
impurity. Thus the minimum purity required for the detection
of the monotropic SII phase in the PM sample is 99.7% and
it is absent in the samples having less purity.

The transition temperatures heat of transition (∆H)
and transition entropy (∆S) for various transitions are listed
in Table 6.1.
Fig. 6.3 DTA plots during cooling cycle for HMA samples having purity -

(a) 99.9%  (b) 99.8%  (c) 99.7%  (d) 99.6%  (e) 99.5%.
(3) Conclusion

Three solid phases of PH were detected using DTA and TMA. The solid I (SII) phase is stable at room temperature whereas solid II (SII) phase is a high temperature, monotropic solid. The observation of SIII phase during cooling is linked with the purity of PH material and the minimum purity required for it is 30.7%. It was also found that SII phase gives nematic mesophase at a lower temperature than SII phase and it can exist with SII phase even at room temperature in various mixtures. The formation of the third, metastable solid III (SIII) phase depends on high quenching rate. The sequence of phase transition is summarized below:

\[ \text{SII} \rightarrow \text{SIII} \]

Rapid quenching
TABLE 4.1

Heats of transition, transition entropies and transition temperatures of various phases of \( \text{FA} \)

<table>
<thead>
<tr>
<th>Transition</th>
<th>Transition Temperature ( (^\circ \text{C}) )</th>
<th>( \Delta H ) (Cal./mol.)</th>
<th>( \Delta S ) (Cal./mol/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SI - N</td>
<td>383.0</td>
<td>7273</td>
<td>19.74</td>
</tr>
<tr>
<td>N - I</td>
<td>406.3</td>
<td>181</td>
<td>0.44</td>
</tr>
<tr>
<td>N - III</td>
<td>365.3</td>
<td>7180</td>
<td>19.63</td>
</tr>
<tr>
<td>III - SI</td>
<td>335.6</td>
<td>1040</td>
<td>3.10</td>
</tr>
<tr>
<td>III - N</td>
<td>377.5</td>
<td>5710</td>
<td>15.13</td>
</tr>
<tr>
<td>III - III</td>
<td>250.7</td>
<td>25</td>
<td>0.10</td>
</tr>
</tbody>
</table>

SI  Solid I

SII Solid II

SIII Solid III

N  Nematic
6.2 CHOLESTERYL ACETATE

(A) INTRODUCTION

The number of solid phase exhibited by Cholesteryl acetate (CA) has been studied by a number of workers. Kofler was the first to study it and proposed three different forms. Chistyakov suggested the existence of only two forms. Ferrell et al. reported two endothermic DTA peaks for samples recrystallized (a) from ethanol, and (b) from melt and found that the latter gives three endothermic DTA peaks. However, a rapidly quenched melt shows two solid forms upon heating. Davis et al. observed neither multiple transitions nor mesophase in a CA sample highly purified with n-pentanol. Price and Wendorff carried out density and x-rays measurements of a CA sample purified with n-pentanol and detected three solid phase SI, SII and SIII in a once melted CA sample. SI is formed directly upon cooling from the isotropic liquid phase and behaves reversibly up to the melting point. SII is formed by cooling the cholesteric phase and transforms reversibly to SIII around 40°C. They also found that the density of SIII phase is slightly less than SII phase whereas the density of SI is greater than that of SIII phase but less than SII phase. They also determined the d-spacings for all
once-melted solids which were slightly different from that of solution crystallized sample.

(B) EXPERIMENTAL:

The DTA and TMA apparatus employed in the experiment has been already discussed in 6.1 (B).

The CA and n-pentanol of spectroscopic grade was supplied by T/s G. Merck, Germany. The sample was further recrystallized from n-pentanol and dried at 60°C in vacuum. For TMA studies, the CA is deposited on glass slide from the concentrated n-pentanol solution and then the cover slip is placed on it. This thin section of the CA sample was vacuum dried at 60°C to remove the n-pentanol.

(C) RESULTS:

Cholesteryl acetate recrystallized from n-pentanol undergoes a broad endothermic solid-solid transition at 74°C and fusion at 114°C. This behaviour is shown by the first DTA run in Fig.6.4a. The solid-solid transition is irreversible (as shown by an additional DTA run attached to Fig. 6.4a) and it is characteristic of the solution used for
recrystallization\textsuperscript{7,8}. For example, in our studies it occurs at about 75°C for the n-mentanol crystallized CA samples whereas for the ethanol crystallized samples give rise to the same transition at 81-87°C as studied by Davis et al\textsuperscript{8}. The solution crystallized, irreversible phase (before mark \textsuperscript{7} Fig.6.4a) is marked by crystalline rods in 70°C shown by photomicrograph 6.5c. This transforms into another solid phase after transformation at 74°C and finally melts at 114°C. The photomicrograph 6.5b has been taken at the instant of fusion at 114°C.

If CA sample is not heated to very high temperature above melting point for a long time, it usually crystallizes from isotropic liquid to a solid phase at 110°C (see EVA record Fig.6.4b) in the form of fibers as shown in Fig.6.5c. This fiber like solid obtained from isotropic melt was designated as solid I (SI) phase by Price et al\textsuperscript{9}. On reheating, the SI phase directly gives isotropic liquid at 118°C as shown in thermogram 6.4c.

It is customary to quench the molten CA sample with a high rate for inducing a monotropic cholesteric phase in it but we found success in inducing the cholesteric phase in CA by annealing the isotropic melt at a high temperature
Fig. 6.3 DTA traces of different solid polymorphs of cholesteryl acetate.
for a long time. The Fig.6.4d gives the thermal behaviour during cooling of CI sample given such a heat treatment. A large supercooling is observed and the cholesteric phase appears at 92°C which is marked by a small, additional peak shouldering to the main peak of cholesteric-solid transition. The cholesteric phase persists for very small temperature span of approximately 2°C before going to solid phase and therefore it is very difficult to photograph the texture of cholesteric phase. The solid phase obtained at 30°C by cooling the cholesteric phase shows entirely different texture from SI phase marked by small needle-like texture shown in Fig.6.5d in TMM studies and Price et al named it SII phase. The SII phase transforms into another solid at about 40°C which resembles with the SIII phase of Price and Bendroff. The solid III-solid II transition is reversible and it is displayed on reheating also (Fig.6.4e). The solid III phase is characterized by spherulite texture with well defined cross in TMM as shown in Fig.6.5e and sometimes a spherulite texture with poorly defined cross is also observed.

It has been found that the appearance of monotropic cholesteric phase depends upon both time and temperature at
Fig. 6.5 Textures of different solid phases of cholesteryl acetate.
(a) solution dependent irreversible solid phase
(b) first fusion at 114°C (c) SI phase
(d) SII phase (e) SIII phase; (f) meta stable SIV phase. Magnification x 160
which the CA sample is annealed. This is confirmed by the DTA experiments conducted in two parts shown in Figures 6.7 and 6.6. In the first part, the CA sample in the DTA cell has been annealed for a constant time period of 1 hour at four different temperatures namely 125°C, 135°C, 140°C and 150°C. The cholesteric mesophase is exhibited only for the heat treatments done at the temperatures, 140°C and 150°C. The results of experiment is depicted in the Fig.6.6. In the second part of the experiment, the annealing is performed for three different time periods namely 15, 30 and 45 minutes keeping the temperature constant at 140°C. The cholesteric mesophase is observed for the annealing time period of 30 and 45 minutes only as shown in the Fig.6.7. Thus it is sufficient to anneal the CA sample at 140°C for 30 minutes to get a cholesteric phase during cooling cycle. It has also been noted that less time is required if annealing temperature is kept higher.

The effect of rapid quenching on the formation of solid phase has been investigated by cooling down the molten CA sample with a rate 30°C/min. The flow of cholesteric phase has been observed, marked by iridescent colors due to light
FIG. 6.6 EFFECT OF ANNEALING ON THE CA SAMPLE FOR 1 HOUR AT DIFFERENT TEMPERATURES GIVEN IN THE GRAPH.
FIG 6.7 EFFECT OF ANNEALING ON THE CA SAMPLE AT 140°C FOR DIFFERENT TIME PERIOD MENTIONED IN THE FIGURE.
scattering while quenching. A new spherulitic solid is obtained shown in photomicrograph Fig.6.5f which will be called solid IV (SIV) in this paper and it was found to be stable at room temperature for a long time SIV phase transforms into another solid at 33°C which is shown by a poorly marked endothermic peak in Fig.6.4f. The solid phase obtained at 83°C is nothing but SI phase as it has fibre-like texture shown in Fig.6.4e and it ultimately disappears into isotropic liquid with a wide pre-melting.

(D) DISCUSSION:

It is concluded from the above discussion that the cholesteryl acetate exhibits four solid phases namely SI, SII SIII and an irreversible solid phase characteristic of the solvent used for recrystallization. Kunihisa et al.12 carried out the x-rays analysis of various solid polymorphs of cholesteryl acetate and found that all of them possess monoclinic unit cell and the four forms of cholesteryl acetate are due to small changes in enthalpy which results in various packing orders in the bulk space of lattice imperfections. The purity of cholesteryl acetate used by
us was 99.7% mol and it exhibits four solid polymorphs mentioned above.

It is obvious from our experiment that cholesteric mesophase can also be induced by special heat treatment to the isotropic melt in addition to the rapid quenching. The appearance of the monotropic cholesteric phase in C7 is dependent on both temperature and time and it is sufficient to hold on the CA sample 140°C for half an hour.

As a result of rapid quenching of isotropic melt, a new spherulitic solid phase (SIV) has been obtained. The SIV solid phase is stable at room temperature for a long time and it transforms into solid I (SI) phase at 85°C. The SIV-SI transition involves very small heat of transition.

The transition temperature and heat of transition (AH) for various transition are listed in Table 6.2.
<table>
<thead>
<tr>
<th>Transition</th>
<th>Transition temperature °C</th>
<th>ΔH Cal./gm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irr. transition</td>
<td>74.2</td>
<td>4.6</td>
</tr>
<tr>
<td>S1 - I (First run)</td>
<td>114.2</td>
<td>11.3</td>
</tr>
<tr>
<td>I - S2</td>
<td>111.6</td>
<td>9.3</td>
</tr>
<tr>
<td>S2 - I</td>
<td>116.2</td>
<td>9.8</td>
</tr>
<tr>
<td>S21 - I</td>
<td>113.6</td>
<td>9.8</td>
</tr>
<tr>
<td>I - Ch</td>
<td>92.0</td>
<td>0.13</td>
</tr>
<tr>
<td>Ch - S21</td>
<td>90.0</td>
<td>3.6</td>
</tr>
<tr>
<td>S211 - S211</td>
<td>40.0</td>
<td>0.4</td>
</tr>
</tbody>
</table>

S1  Solid I  
S21  Solid II  
S211  Solid III  
I    Isotropic  
Ch   Cholesteric
6.3 CRYSTALLINE STATES AND MESOPHASES OF n-(p-
HEXYLOXYBUNZIDENE)-p-r-TOU1IDENE (HBT).

(1) INTRODUCTION

n-(p-Hexyloxybutzilene)-p'-toluidene abbreviated
as HBT has been extensively studied by Schodur\textsuperscript{13} but his
measurements of ultrasonic velocity, density and magnetic
susceptibility were concentrated around nematic-isotropic
liquid (N-I) transition. It was later on found that very
pure samples of HBT exhibit a highly ordered smectic phase
during cooling. Hilde et al\textsuperscript{14} made the x-rays analysis of
smectic phase and found that it belongs to S-type. However,
Leibfetter et al\textsuperscript{16} 's recent x-rays investigation confirms
it to be of S-type. In the present study, this smectic phase
is carefully examined by TGA and DSC and it is found to be
of S-type which transforms into S-type at a lower temperature.
The nature of solid-smectic B, smectic S-smectic E and
smectic B-nematic along with the thermal data of various
transitions are presented below.

(B) EXPERIMENTAL

The crystalline states and mesophases of HBT were
detected and analysed by a combination of DTA and TGA as
discussed earlier.
The NFT sample was supplied by M/s E. Merck, Germany and it was further purified by repeated recrystallisation by ethanol and benzene separately. It was then vacuum dried by keeping it in isotropic liquid phase.

(C) RESULTS AND DISCUSSIONS:

The DTA experiment was carried out with the freshly crystallised sample and the first DTA run during heating cycle is shown in Fig. 6.8a which consists of two endothermic peaks at 58°C and 74°C corresponding to solid-nematic (S=N) and nematic-isotropic (N-I) transitions respectively. The same experiment was repeated in TDM apparatus and the solid phase (shown in photomicrograph 6.9a) passes into nematic liquid at 58°C, which is marked by threaded, Schlierene texture shown in Fig. 6.9b. The nematic liquid ultimately transforms into isotropic liquid at 74°C, which appear as dark texture under crossed polarizers.

Quite a different behaviour was observed during cooling of the NFT sample. Four exothermic peaks appear in DTA run shown in Fig. 6.8b. The four exothermic peaks corresponds to isotropic-nematic (I-N), nematic-smectic-B (N-Sb), smectic B-high temperature solid, S'(Sb-S) transitions
at 74°C, 52°C, 43°C and 39°C respectively. The MBT material
is cooled in T0: apparatus from isotropic liquid phase, the
nematic phase separates in the form of characteristic droplets
(Fig.6.9c) at 74°C and it gives rise to smectic-3 phase at
52°C. The smectic 3 phase emerges from threaded nematic
texture in the form of characteristic small rods called
'betonates' as shown in Fig.6.9d. These rods extend along
their breadth to give the mosaic texture of smectic-3 phase
(shown in photomicrograph 6.9e). The smectic phase transforms
into a solid phase at 43°C which was checked by nondisplacebility
of the cover slip. The optical texture (photomicrograph 6.9f
of solid phase obtained by cooling the smectic-3 phase is
quite different from that of room temperature solid (S-phase)
shown in Fig.6.9g and hence it is named S'-phase in our
discussions.

On careful observation of the DTA plots, it was found
that the base line slightly shifts downward (indicating the
appearance of a small peak) at 45°C as shown in the Fig.6.8b.
The detection of the small peak at 45°C was found to link with
the transformation of the mosaic texture of S3 phase (Fig.6.9e)
to a gross mosaic texture (Fig.6.9h). In our opinion, this
gross mosaic texture is of smectic-H phase and the shift in
DTA base line at 45°C is due to smectic S-smectic H transition
Fig. 6.8  DTA runs of liquid crystals HBT.
which involves negligible heat of transition (ΔH) and hence entropy of transition (ΔS). Thus the $S_B - S_H$ transition is of second order and the same prediction was made by Weyr and McMillan about $S_B - S_H$ transition.

If smectic-$B$ ($S_B$) phase is directly heated instead of allowing it to pass into $S'$ solid phase, it gives rise to nematic phase at a higher temperature, $63^\circ C$ and nematic phase gives isotropic liquid phase at $74^\circ C$ at the last. This behaviour is marked by two endothermic peaks in the ET. run 6.8c. On the close observation in TEM apparatus at smectic $B$-nematic transition, the boundaries of $S_B$-domains in the mosaic texture was found to become the disclination lines of the chilereance texture of nematic phase. It leads to the conclusion that the molecules have both translational and orientational order in the $S_B$ phase and out of these only orientational order persists in the nematic phase because the disclination lines in liquid crystals are analogous to the dislocation in solids and the orientation of the nematic molecules abruptly changes across these lines.

The microphotograph shown in Fig.6.8g has been taken just at $S_B - S'$ transition. It is obvious from it that the high temperature solid $S'$ starts forming with deterioration
Fig. 6.9 Optical textures of different Crystalline states and mesophases of HMT.
(a) room temperature (§) phase (b) nematic phase (c) isotropic-nematic transition (d) $S_B$-$N$ transition (e) mosaic texture of $S_B$ phase (f) high temperature solid ($S'$) phase (g) $S_B$-$S'$ transition (h) gross mosaic texture of $S_H$ phase
of the boundaries of the domain-like texture of $S_p$. In the crystalline solid phase the alkyl chains have very little disorder or no disorder at all and both rotational and translational coupling are strong but on the other hand, the alkyl chains are disordered in $S_p$ and $S_1$ phases and translational coupling is much weaker than rotational coupling. It has already been discussed that the molecules are highly ordered inside the $S_B$ domains and obviously the zig-zag alkyl tails touches the boundaries of the mosaic texture. Therefore the deterioration of domain boundaries and formation of solid $S'$ is obviously due to coupling of extended alkyl chains of the molecules lying in adjoining domains. The freedom of movement of alkyl chains in $S'$ phase is restricted as a result of this interaction.
**Table 6.3**

Transition temperatures, $\Delta H$ and $\Delta S$ values for various phase transitions in HET.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Transition</th>
<th>Transition temperatures $\theta_C$</th>
<th>$\Delta H$ kCal/mole</th>
<th>$\Delta S$ Cal./mole/$^\circ$K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$S \rightarrow N$</td>
<td>58.0</td>
<td>4.00</td>
<td>12.18</td>
</tr>
<tr>
<td>2.</td>
<td>$N \rightarrow I$</td>
<td>74.2</td>
<td>0.27</td>
<td>0.76</td>
</tr>
<tr>
<td>3.</td>
<td>$N \rightarrow S_B$</td>
<td>61.0</td>
<td>1.89</td>
<td>4.92</td>
</tr>
<tr>
<td>4.</td>
<td>$S_B \rightarrow S'$</td>
<td>43.5</td>
<td>0.77</td>
<td>2.45</td>
</tr>
<tr>
<td>5.</td>
<td>$S' \rightarrow S$</td>
<td>39.0</td>
<td>1.83</td>
<td>5.86</td>
</tr>
</tbody>
</table>

$S$: Solid (room temperature)  
$I$: Isotropic liquid  
$S'$: High temperature solid  
$S_B$: Smectic B  
$N$: Nematic
REFERENCES


