Chapter 4

Diminution of the Ordering in Plastic and Liquid Crystalline Phases by Confinement

Overview

X-ray and calorimetric studies have been performed on a compound exhibiting plastic and liquid crystalline phases confined in a nanoporous (Anopore) membrane. The results show that the features are drastically affected by confinement and also the orientation of the molecules in the Anopore membranes. In the untreated membrane, where the molecules are aligned parallel to the pore axes, there is a significant diminution in the correlation length corresponding to the positional order of the plastic phase. In contrast, in the case where the molecules lie in the plane of the membrane, a new phase is induced. Structural possibilities for the induced phase are discussed. These findings are expected to open up a new path to understand the melting phenomenon, especially that occurs in lower dimensions.

4.1 Introduction

Understanding the behavior of finite-sized systems is important in many areas of science both from theoretical and experimental point of view. In particular, the influence of the size of the system on phase transitions, for example, freezing and melting [1-4] has received interest for more than a century. The interest in confined systems is because such studies have raised fundamental questions, challenging the known static and dynamic behaviors. The differences between the confined cases arise due to the competition between the intrinsic length scale driving the phase structure or dynamics, and the finite size of the system. The length scale imposed externally by the confining geometry can cause two major effects. The first is the cutoff or finite size effect, owing to which neither the static or the dynamical correlation length can grow larger than the maximum pore size, resulting in perhaps the breakdown of scaling and universality [5, 6]. The second is the surface effect, caused by the enhancement in the surface-to-volume ratio due to the additional surface of the confining medium [2, 7, 8].

Liquid crystals are especially suitable for work on confined geometries because:

1. They exhibit a variety of phases with different degrees of orientational or translational order,

2. The involved transitions are second-order or at best weakly first-order,

3. They are soft materials presenting strong competition among elastic, surface, and external field forces,

4. Their response to perturbations induced by the confining matrix is pronounced and long ranged without any chemical interactions.

The first investigation of confined liquid crystals dates back to the early 1900s when interest in the macroscopic properties of bulk liquid crystals was still in its infancy. Lehmann [9] successfully suspended supramicrometre nematic liquid crystal droplets in
a viscous isotropic medium. By studying the birefringent textures with optical polarizing microscopy he concluded that the specific director configuration within the spherical confining cavity depends on the liquid crystal material and the angle at which the liquid crystal molecules are anchored to the isotropic fluid interface. Since then a number of studies have been conducted on liquid crystals under confinement [For recent review articles on the subject see Ref 10 and 11]. Several ways to achieve restricted geometries have been reported: confining the material in capillary tubes, polymer dispersions, vycor glass, silica aerogel, to name a few. What concerns us in this chapter is the prefabricated geometry, wherein the liquid crystalline material is filled into a confining matrix prepared before hand. Certain commercially available membranes, such as Millipore, Synpor, Nuclepore and Anopore have proved to be popular for the purpose. Details of the morphology of these membranes can be found in literature [12]. In the present study, we have employed Anopore membranes, the details of which are given in the next section.

The nematic (N) liquid crystal possess orientational order but no positional order. The smectic A (SmA) phase on the other hand is described as a “one-dimensional (1D) solid and 2D liquid”, which implies that the molecules are positionally ordered along one direction, forming layers, but the orientation of the molecules within the layer is liquid-like. In the SmA phase, both positional order and bond orientational order are short ranged. The latter kind of order, is geometric in nature and defined through the orientation of the imaginary line joining two adjacent molecules. If it is long ranged but the positional order is still short ranged, a hexatic phase is realized. If both types of order are long ranged, the system is in the crystal B (CrB) phase. The CrB phase differs from a true crystal in one important aspect, viz., the molecules have the freedom of rotation about their long axis. Such phases, in which the positions of the molecules are fixed but their motion is not arrested are classified as plastic crystals. Hence CrB phase is a 3D solid with some degree of orientational freedom for the molecules and thus a plastic crystal. Tilted forms of the CrB phase are also known. A schematic representation of the molecular arrangements in
Figure 4.1: Schematic diagram depicting the arrangement of the molecules in the layer plane of (a) SmA and (b) CrB phases.

The SmA and CrB phases is shown in Figure 4.1. The transition from SmA to N phase can be regarded as a 1D melting and that from CrB to SmA as a 2D melting process. In materials exhibiting the CrB-SmA transition, the effect of reduced dimensionality has been investigated using free-standing films (FSF) and confining the sample in a network made of silica particles. In the latter measurements [13, 14] the only changes observed upon confinement were the lowering of the transition temperatures and a slight broadening of the calorimetric peaks. The FSF experiments showed a more attractive feature, viz., layer-by-layer transition, wherein the freezing from the SmA phase takes place in multiple steps,
the number of which depends on the film thickness. In this chapter, results of X-ray and calorimetric studies performed on a sample exhibiting the CrB-SmA transition confined in Anopore membrane are described.

4.2 Experimental Section

The compound chosen is butyloxybenzilidene-octylaniline (40.8), used as received from Frinton lab. It exhibits N, SmA and CrB mesophases. Its molecular structure and transition temperatures are given below.

\[
C_4H_9O-\begin{array}{c}
\bullet \\
\bullet
\end{array}CH=N-\begin{array}{c}
\bullet \\
\bullet
\end{array}C_8H_{17}
\]

178 °C N 63.5 °C SmA 48.5 °C CrB 33 °C Cr

Figure 4.2: The molecular structure and transition temperatures of the compound, 40.8 used here.

As mentioned in the Introduction, a convenient way of creating a restricted geometry situation is to confine the material in a porous membrane. Among the membranes which can be used for the purpose of present studies and available commercially, Anopore is the most suitable and better than others in many ways. For example, the Millipore and Synpor membranes have a large distribution of the pore sizes with interconnected cavities. In Nuclepore membranes the cavity walls are not smooth, but corrugated. Pore density is also lower for these membranes. On the other hand, Anopore membranes are made from an inorganic aluminium oxide matrix using an electrochemical anodizing process in which the anodizing voltage controls the pore size. Since the process is electrochemical, conditions can be precisely controlled and a reproducible pore structure with narrow pore size distribution and high pore density is obtained. These membranes have highly parallel cylindrical pores with a large surface to volume ratio, which is important from the view point of the
present studies. Also, in comparison with other types of membranes, the Anopore membranes do not have the complications of pore blockage and connectivity effects. A further feature is that the cavity surface is amenable to surface treatment, a point that we have exploited here. These membranes are commercially available from Whatman Corp., USA under the trade name Anodisc with a diameter 13 mm and pore size 0.2 μm having 50% porosity and density of pores as $10^9 \text{ cm}^{-2}$. Scanning electron microscope photographs of an Anopore membrane are shown in Figure 4.3. For filling the sample into the membranes,

![Figure 4.3](image)

Figure 4.3: (a) Cartoon depicting the porous structure of the Anopore membrane (taken from Ref [15]). Scanning Electron Microscope photographs showing (b) the top view of a 0.2 μm Anopore membrane and (c) a cross-sectional view which shows 0.23 μm latex microspheres retained on the membrane surface, indicating the precision in the diameter (taken from Ref [16]).

the membrane was maintained at 10 °C above the isotropic temperature of the sample and the sample was melted on it. This arrangement was left undisturbed for 4 hours so that the membrane was filled with the sample. After which the excess on the membrane surface was removed using a filter paper. As shown in Figure 4.4 (a), in the absence of any surface treatment of the membrane pores, the 40.8 molecules exhibit an orientation parallel to the pore axis. But treatment of the membrane surface with a long chain acid, palmitic acid, makes the molecules lie in the plane of the membrane [Figure 4.4 (b)]. The untreated and palmitic acid treated cases are hereafter referred to as ANA and p-ANA, respectively.
The X-ray diffraction measurements were carried out using the PANalytical X’Pert PRO MP X-ray diffractometer with Cu Kα incident radiation (the details of the instrument and experimental set up are discussed in Chapter 2). For bulk measurements, the samples were contained in a Lindemann capillary and were cooled from the N to the SmA phase in the presence of a strong magnetic field of 1.2 T that resulted in a unidirectional orientation of the molecules. In the case of Anopore, a single membrane filled with the sample was used. The magnetic field procedure was not effective to get the orientation of the molecules in either of ANA or the p-ANA, but the intensity of the X-ray profiles suggest that the surface forces were strong enough to give good alignment.

To obtain information on the phase transition temperatures and the associated enthalpy changes, differential scanning calorimetric (DSC) measurements, were performed. A power-compensating DSC, Diamond DSC from Perkin-Elmer, was employed for this purpose. For measurements on Anopore membranes, an unfilled membrane of approximately the same size was placed in the reference cup and the Anopore with sample is kept in the sample cup. The quantity of the liquid-crystalline material inside the membrane was determined by weighing the membrane before and after filling. To obtain a better sig-

Figure 4.4: The orientation of the 4O.8 molecules inside an (a) untreated and (b) palmitic acid treated membranes.
nal/noise ratio, a stack of four pieces of the membrane filled with the sample was used. For ease of comparison, the bulk as well as the Anopore data was normalized with respect to the weight of the liquid crystal.

4.3 Results

4.3.1 Calorimetric Studies

DSC scans obtained for the bulk, ANA and p-ANA configurations for a range of heating rates, are represented in Figures 4.5, 4.6 and 4.7 respectively. It can be seen from the plots that there are several features common to all the three cases:

Figure 4.5: DSC scans obtained for the bulk sample at a series of heating rates (from top to bottom 10, 5, 3, 2, 1, and 0.5 °C/min). p indicates the normalized heat flow. The downward shift in the peak point with decreasing rate is quite clear for the N-I and CrB-SmA transitions. The SmA-N change, a weak transition, becomes hardly noticeable at the slowest rate.
Figure 4.6: DSC scans obtained for the untreated Anopore (ANA) sample at a series of heating rates (from top to bottom 10, 5, 3, 2, 1, and 0.5 °C/min). There is only a single peak below the SmA phase associated with the SmA-CrB transition. The weakening of the N-SmA transition is significant enough with slower cooling that the signature is hardly present for the slower rates.

1. The transitions show a strong dependence on the heating rate employed and become weaker with slower rates.

2. For any given rate, in terms of the peak height, the bulk has the strongest signal and the p-ANA sample, the weakest.

3. The peak temperatures shift with heating rate, a feature clearly visible for the strong transitions.

4. The shift is not the same for the different transitions.

5. The shift is dependent on whether the sample is confined or not, and also on the type of confinement.
Figure 4.7: DSC scans obtained for the palmitic acid treated membrane (p-ANA) sample at a series of heating rates (from top to bottom 10, 5, 3, 2, and 1 °C/min). The appearance of two peaks below the SmA phase clearly seen especially for the faster rates.

6. Broadening of the peaks is also observed especially in the case of the p-ANA sample.

The bulk and the ANA samples show the expected three peaks corresponding to the CrB-SmA, SmA-N and N-I transitions (see Figures 4.5 and 4.6). But, as seen in Figure 4.7, the p-ANA sample exhibits an additional peak below the SmA phase. This is the first report of an additional transition being seen whose origin can be ascribed to the confinement direction of the liquid crystal molecules. We label the lowest temperature mesophase as M2, and the phase between SmA and M2 as M1. The signatures for both the SmA-N and SmA-M1 transformations are weak, as seen in Figure 4.8, which compares the scans obtained at a fixed scanning rate (β) of 3 °C/min for the bulk and the two Anopore cases. The weak thermal natures of these two transitions make them clearly visible only in the faster heating rate scans.
Figure 4.8: DSC scans obtained at a fixed rate of 3 °C/min for bulk (green), untreated Anopore (blue), and palmitic-acid treated Anopore (red) samples. The peaks labeled 1 correspond to the N-SmA transition, 2 correspond to the SmA-CrB transition, 3 correspond to the SmA-M1, and 4 to the M1-M2 transitions. Note that the break is introduced in the scale to clearly depict the M1-M2 transition whose signature is very weak.

Rate dependence of thermal properties

(a) Transition enthalpies

The β dependence of the transition enthalpy (ΔH) values determined from integrating the strong peaks N-I, CrB-SmA (M2-M1 for p-ANA) for the different sample cases are shown in Figure 4.9. The data for both SmA-N and M1-SmA cases are not shown due to the weakness of these transitions. Also since the spread of the data is not too small especially for the CrB-SmA transition, hence no attempt is made to describe it with any quantitative relation, except to draw a linear line through the data for both the CrB-SmA and N-I cases. The equation relating the transition enthalpy (ΔH) and the rate of the transition (β) is given below. It is seen that the nonlinearity in the rate dependence of the transition enthalpy for
Figure 4.9: DSC scan rate ($\beta$) dependence of the transition enthalpy values for the bulk and the two Anopore situations. The solid lines are merely a guide to the eye.

The N-I transition increases with confinement.

$$\Delta H = \Delta H_0 + \sqrt{A_1\beta} + A_2\beta$$
$\Delta H_0$, the extrapolated zero-heating rate transition enthalpy obtained from Figure 4.9 shows a behavior that is dependent on the transition. It can be seen from Table 4.1, that the $\Delta H_0$ values for the N-I transition are comparable between the bulk and the two Anopore membrane cases. In a similar work by Iannacchione and Finotello, the specific heat of the N-I transition in the bulk was found to be intermediate between a lower value for the p-ANA and a higher value for the ANA in three cyanobiphenyls [17].

In the present studies, for the CrB-SmA transition, the ANA sample shows a 20\% lower value than the bulk sample. The M2-M1 transition in the p-ANA case also has a 9\% lower value than for the CrB-SmA case in the bulk suggesting that for the ordered transformations confinement results in reducing the enthalpy of the transitions and perhaps a lowering of ordering of the lowest temperature mesophase.

<table>
<thead>
<tr>
<th></th>
<th>Bulk</th>
<th>ANA</th>
<th>p-ANA</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-I</td>
<td>2.31±0.05</td>
<td>2.35±0.03</td>
<td>2.21±0.03</td>
</tr>
<tr>
<td>CrB-SmA</td>
<td>5.19±0.06</td>
<td>4.16±0.04</td>
<td></td>
</tr>
<tr>
<td>M2-M1</td>
<td>--</td>
<td>--</td>
<td>4.76±0.08</td>
</tr>
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</table>

Table 4.1: The extrapolated zero-heating transition enthalpy [$\Delta H_0 (J/g)$] values obtained from Figure 4.9 for the three cases bulk, ANA, and p-ANA. It is seen that the $\Delta H_0$ value is comparable for the three cases for N-I transition. Whereas for the CrB-SmA transition, the ANA shows a 20\% lower value than the bulk sample and the M2-M1 transition in the p-ANA case also has a 9\% lower value than the bulk.

(b) Transition temperature

The rate dependence ($\beta$) of the transition temperatures, taken as the peak point, $T_{\text{peak}}$, for the N-I, SmA-N and CrB-SmA (M2-M1) transformations are given in Figure 4.10. There are a few features to be noted from the diagrams. The first being that all the three sample situations show substantial dependence of the transition temperature with $\beta$, the strongest variation seen for the p-ANA case, the weakest for the bulk case and the untreated membrane having the intermediate behavior. For example, for the I-N transition when compared with the peak temperature obtained at $\beta = 0.1 \, ^\circ\text{C}/\text{min}$, the $T_{\text{peak}}$ values with $\beta = 10 \, ^\circ\text{C}/\text{min}$
Figure 4.10: DSC scan rate dependence of the transition temperatures for the bulk and the two Anopore cases. The solid lines depict fits to equation 4.1, $T_0$ stands for the zero-heating rate transition temperature.

are 0.8, 1.4, and 3.8 °C higher for the bulk, ANA and p-ANA samples respectively. It may be recalled that specific heat measurements performed on cyanobiphenyl compounds, 5CB, 7CB, 8CB and 10CB using ac calorimetric technique [17], employed the same type of Anopore membranes as in the present study and for obtaining radial alignment of the director, the membranes were treated with lecithin. These measurements showed that the specific heat is strongly dependent on the liquid crystal configuration within the pore. Further in the confined cases there was depression of transition temperature and the specific
heat peaks were rounded, broadened and suppressed as compared to the bulk samples. In our measurements, for the p-ANA case, we have two peaks corresponding to the transitions, SmA-M1 and M1-M2. Recently Sharma [18] also found that the thermal characteristics, including the transition temperature can be different between the unaligned and the aligned liquid crystal samples. In our measurements also the difference between the ANA and p-ANA cases could arise from such a reason, since the molecular alignment directions are different in the two situations and further in the p-ANA there is a randomization in the plane of the membrane.

To quantitatively describe the rate dependence of the transition temperature, several attempts have been made [19]. The simplest of these, namely, a linear dependence of $T_{\text{peak}}$ on $\beta$ is well recorded in literature [see e.g., Refs 20, 21]. Although a linear function is acceptable over a short span of $\beta$ values, it is inadequate to describe the data over a range of rates. A polynomial expression has also been used, [21], but it has no thermodynamic relevance. Illers [22] and subsequently others [23, 24] have addressed this issue by considering the thermal lag in the system. In a DSC apparatus, the thermal lag arises due to the difference between the sample temperature and the sensor temperature and/or between the sensor temperature and the furnace temperature. The thermal lags are characterized in terms of the total thermal resistance ($R$) having components from outside ($R_o$) and inside ($R_i$) the sample; the former consists of $R_i$, the contribution from the instrument, and $R_c$, the thermal contact resistance between the container and the instrument. The associated specific heat and the transition enthalpy ($\Delta H = \Delta H_o$, the zero rate value determined above) also are important in defining $T_{\text{peak}}$ for any finite heating/cooling rate. With these factors in mind, the following expression has been proposed by Neuenfeld and Schick [24],

$$T_{\text{peak}} = T_o + \sqrt{A_1 \beta} + A_2 \beta$$

(4.1)

Here $T_o$ is the true (zero rate) transition temperature, $A_1 = 2\Delta H_o R$, and $A_2 = \tau_{\text{lag}}$ is the
time constant due to the thermal lag having dependence on the specific heat and $R$. In the literature, equation 4.1 has been used without the linear term also, [25] but as is obvious from the data shown in Figure 4.10, the combination of linear and square-root terms appear to be necessary in the present case. The fitting of the data to equation 4.1 was performed by first floating all the three parameters $T_0$, $A_1$, and $A_2$. In the second step, the value of $T_0$, the zero heating rate transition temperature was held fixed and the other two parameters were allowed to vary. The latter procedure not only improved the quality of fitting (as determined by $\chi^2$ values) but also resulted in substantially lower error bars on the determined parameters, $A_1$ and $A_2$. Before discussing the results on 40.8, the data and analysis on Indium, used as a calibrant, is presented in Figure 4.11. The diagram depicting the measured data

![Diagram showing the melting temperature variation with DSC scan rate for Indium. The line depicts the fit to equation 4.1.](image)

Figure 4.11: *Diagram showing the melting temperature variation with DSC scan rate for Indium. The line depicts the fit to equation 4.1.*

and the fitting to equation 4.1, demonstrates that the magnitude of the rate-dependence is in agreement with the work of Neuenfeld and Schick [24] and also that equation 4.1 describes the data very well. The calculated $R$ and $\tau_{lag}$ values compare very well with the values
given in Ref 19. The least-squares fits obtained for the various sample situations of 40.8 are shown in Figure 4.10. The evaluated $T_0$, $A_1$, and $A_2$ values are shown in Table 4.2. Considering the ratio $A_1/A_2$, we note that the linear term strongly dominates in the case

<table>
<thead>
<tr>
<th></th>
<th>SmA-N</th>
<th>M2-M1</th>
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<tbody>
<tr>
<td>bulk</td>
<td>ANA</td>
<td>p-ANA</td>
</tr>
<tr>
<td>$T_0$</td>
<td>63.544±0.04</td>
<td>49.3±0.04</td>
</tr>
<tr>
<td>$A_1$</td>
<td>0.013±0.003</td>
<td>0.071±0.006</td>
</tr>
<tr>
<td>$A_2$</td>
<td>0.018±0.007</td>
<td>-0.028±0.006</td>
</tr>
<tr>
<td>$A_2^\dagger$</td>
<td>0.138±0.004</td>
<td>0.000±0.000</td>
</tr>
</tbody>
</table>

Table 4.2: The zero-rate transition temperature, $T_0$ (°C) and the coefficients of equation 4.1 for the different transitions and sample situations. † indicates the values obtained by not having the square root term from equation 4.1, only for the ANA case.

of ANA for both the first order transitions. To better represent this feature, we also fitted the data for ANA without the square-root term in equation 4.1. This procedure resulted in a further reduction of the error bar on the fit parameter (shown as $A_2^\dagger$, in Table 4.2), with hardly any compromise on the quality of fitting. In contrast, for the first order cases in the bulk sample, the square-root term has a higher contribution for N-SmA transition. Since the term $A_2$ is nothing but the time constant due to thermal lag, we can arrive at the following conclusions, by noting that the $A_2$ value for the bulk is small (for the first order cases) in comparison with that for the Anopore samples. As mentioned earlier, for want of better signal/noise ratio, we have used a stack of four pieces of the membrane for calori-
metric measurements, the increased lag could be due to the less effective transfer of heat to
the membranes not in direct contact with the DSC base. The coefficient $A_1$ represents the
thermal resistance $R$ involving contributions from the instrument ($R_i$), the thermal contact
resistance between the container and the instrument ($R_o$), and from the sample itself ($R_s$)
as discussed earlier. For a particular transition, $R_i$ can be taken to be the same for all the
sample situations. The part due to $R_o$ can be expected to be the least for the bulk sample for
reasons discussed above. Therefore the difference between the $A_1$ values for the Anopore
sample and that for the bulk can be taken to comprise the sum of $R_o$ and $R_s$ components.
Note that for the first order transitions, the $A_1$ values are smaller for the ANA sample than
for the bulk, and comparable or higher for the p-ANA case. Since the thermal conductivity
of the membrane used for the ANA and p-ANA is the same, it may be suggested that $R_s$
has subtractive contribution in the ANA case [thereby lowering $(R_o + R_s)$ to be below the
value for the bulk] and additive effect in the p-ANA case, perhaps dictated by the direction
of alignment of the molecules.

4.3.2 X-ray studies

Low-angle profiles

For situations where the beam traverses perpendicular to the layer normal, the low-angle X-
ray profiles give information about the thickness of the smectic layers. To get this geometry
is trivial in the bulk case. In the confined case, the p-ANA situations represent molecules
oriented perpendicular to the pore normal. In such a case the layers are contained in the
plane of the membrane. Thus the X-ray beam passing along the pore normal provides the
right geometry. However, in the ANA geometry, the molecules are oriented along the pore
axis and hence it is not possible to obtain the layer spacing reflection. Figures 4.12 and 4.13
exhibit the XRD scans obtained in the low-angle region for the bulk and p-ANA samples
in the vicinity of the SmA-CrB transition, and the temperature range over which the SmA
transforms through an induced phase (M1) to a phase labeled M2. In the case of the bulk
sample, within the two phases, SmA and CrB, there is a single resolution-limited sharp peak (Figure 4.12), which can be very well described by a single Lorentzian expression. In contrast, in the transition region the experimentally obtained profile clearly suggests the presence of two peaks, arising from contributions from the two coexisting phases, and the profile can be deconvoluted into two Lorentzians. This feature is indeed expected for a strong first order transition between two layered phases. In contrast, the p-ANA case does not show any coexistence of peaks in the transition region. More importantly, the profiles even within the phases are broadened by a factor of ~3 in comparison to that for the bulk sample. The X-ray apparatus used employs a line beam and has limited out-of-plane resolution and therefore the mosaic spread is not determined, owing to which the actual reduction in the layer correlation length is not calculated from the half widths of the profiles. However, it is to be emphasized that the p-ANA geometry forces the maximum correlation length along the layering direction to be restricted to 200 nm (the pore diameter), much smaller than typically observed for the smectic phases in unrestricted geometries.
Figure 4.13: Low-angle X-ray profiles of the p-ANA sample in the SmA, M1, and M2 phases, exhibiting a single peak in all the cases.

Layer spacing

Smectic A phase has a short-range positional order within the layer and essentially a fluid in two dimensions. On the other hand, the CrB phase has a long range positional order and long range bond orientational order. Such phases are close to being crystalline except that the molecules undergo rotational diffusion. Hence the transition from SmA to CrB is strongly first order, characterised by a jump in the layer spacing value. The temperature dependence of the layer spacing (d) for the bulk and p-ANA samples in the vicinity of the bulk CrB-SmA transition is shown in Figure 4.14. As expected, the bulk sample shows a jump in the d value at the transition and is accompanied by, as shown in Figure 4.12, coexistence of the peaks due to both the phases; both features are compatible with the fact that the transition is first order. It is seen from Figure 4.14, that for the p-ANA sample, there is a background variation in the d value, which is much stronger than for the bulk. Secondly, the absolute values are higher by about 0.3 for the anopore sample, a feature common in liquid crystals, and argued to be due to a slight stretching of the alkyl chains caused by the larger surface interaction created by the higher surface to volume ratio of the membranes [25-27]. The most important difference is that for the p-ANA sample, at the
Figure 4.14: Thermal variation of the layer spacing in the (a) bulk and (b) palmitic acid treated Anopore membrane (p-ANA) sample in the temperature range of the SmA-CrB transition. In the bulk sample, the transition is marked by a jump in the $d$ value and coexistence of peaks from both the phases as expected for a first order transformation. The behavior of the p-ANA sample is entirely different with two phases, one of them orthogonal (M1) and the other perhaps tilted (M2) either hexatic or plastic in nature, appearing below the SmA phase.

transition from the SmA phase the jump is completely absent with the $d$ value increasing smoothly (through the transformation to the M1 phase) and more surprisingly at a slightly lower temperature dropping back to nearly the same value as before the transition in the M2 phase. While the phase immediately below the SmA phase could be, CrB, just like for the bulk sample, there obviously is one more mesophase below it. The signature for the appearance of the additional phase in the sample confined in the palmitic acid coated membrane is seen in the DSC scans as discussed in the previous section.

Wide-angle Profiles

Within the layer plane, the molecules have a liquidlike arrangement in the SmA phase but exhibit a long-range positional order in the CrB phase. By sending the X-ray beam
along the layer normal direction, a wide angle ($2\theta \sim 20^\circ$) reflection is realized that directly maps out the in-plane ordering within the smectic layers, being diffuse in the SmA and condensing in the CrB phase. Such profiles obtained for the bulk and the ANA samples (in which the layer normal coincides with the pore axes) in the two phases are depicted in Figures 4.15 and 4.16, respectively. In the SmA phase, the profiles are very similar but show a drastic difference in the CrB phase, whereas the bulk sample shows a condensed peak and the ANA sample exhibits a much broader peak. Figure 4.18 shows the width (HWHM) of the reflection (inversely proportional to the correlation length of the in-plane ordering) across the transition. In the bulk sample, the transition is marked by a large jump in the value and coexistence of the peaks, as expected. In contrast, the ANA sample shows a smooth variation. More importantly, the value in the CrB phase of the confined case is much higher than in the bulk case, which actually is limited by the instrumental resolution. For comparison, we have also shown, in Figure 4.18, the HWHM values obtained [27] in the orthogonal hexatic (HexB) phase of a different material (46OBC) in the bulk and Anopore.

Figure 4.15: Wide-angle X-ray peaks in the SmA phase of bulk and ANA samples. The lines represent fits to a Lorentzian expression.
configurations. Apart from the feature, common with the present study, that confinement increases the HWHM values, these data highlight the feature that geometrical restriction results in a significant diminution in the ordering. This is also corroborated by the change in the spacing corresponding to this reflection (associated with the intermolecular distance in the layer plane) across the SmA-CrB transition, which for the confined case is 4 times smaller than for the bulk (Figure 4.17). Also the CrB phase of the ANA sample is more loosely packed (the spacing is higher by 20%) than in the bulk sample. As mentioned earlier the freezing from the SmA phase occurring in multiple steps is known in FSF systems [28, 29], but this is the first such observation in a sample confined to a porous membrane.

Figure 4.16: Wide-angle X-ray peaks in the CrB phase of bulk and ANA samples. The lines represent fits to a Lorentzian expression.
4.4 Discussion

4.4.1 Nature of the induced phase

Two salient features of the results described above are (i) confinement of the sample in the Anopore membrane leads to the induction of a new phase as described in the previous sections, and (ii) the type and extent of influence is determined by the orientation direction of an intrinsic parameter, namely, the layer normal with respect to the pore axis of the confining membrane. Before looking at the possible nature of the induced phase, let us consider the following. Drawing a parallel between the present p-ANA data and the FSF measurements reported in the literature [28], it may be suggested that the weak extra peak

Figure 4.17: Temperature dependence of the change in layer spacing ($d$) for the bulk and the ANA case. It is seen that across the SmA-CrB transition, the change in the layer spacing for the ANA is four times smaller than that for the bulk.
Figure 4.18: Temperature dependence of the half-width-at-half-maximum (HWHM) of the wide-angle reflection in the (a) bulk and (b) untreated Anopore (ANA) samples. The values being significantly higher in the CrB phase for the ANA sample (unfilled circles) when compared to bulk (filled circles) is seen in the inset of (b). The solid line in (b) is only a guide to the eye to represent a continuous variation in the width in contrast to the jump seen for the bulk sample. Panel (b) also shows, as horizontal lines labeled X and Y, the HWHM values obtained for the hexatic phase of a different sample in its bulk and confined states respectively (data taken from Ref 30). This shows that the positional order in the CrB phase of the ANA sample is stronger than that in a typical hexatic phase.

seen in the DSC scans (Figures 4.7 and 4.8) is due to the melting of the outermost layers attached to the Anopore surface (M1-SmA transition) occurring at a slightly higher temperature than the interior layers (M2-M1 transition). Such an argument would be supported by the fact that assuming a concentric layer arrangement, the volume contribution of the outermost layer would be ~ 3% of the total volume of liquid crystals within a pore, and the ΔH value for the M1-SmA change is about 1.5% of the M2-M1 transition. It should also be remembered that in this case the freezing of the layers attached to the membrane wall represents transition taking place with influences of a 3D ordered substrate (Anopore) on one side and a liquidlike “substrate” (SmA phase of the interior layers) on the other.
However, the X-ray data presented in Figure 4.14, negates this view of the additional peak in the DSC scan being due to the surface layer M1-SmA transition. The signatures of the two transitions are seen as an increase followed by a reduction in the $d$ value with temperature, and not a monotonic increase on approaching from the SmA phase. Therefore, the additional peak being caused by separate melting of the outermost layers is ruled out.

It has to be borne in mind that surface-anchoring effects can be very strong in the p-ANA case as compared to the FSF systems, where the interface of liquid crystals is with air. Further the confinement in the p-ANA membranes contains the layer normal ("1D solid" axis) as one of the directions. But in the FSF case, the containment is applicable to the two directions of the layer plane. In the present studies the pores are uniform cylindrical channels with no interconnection between them. Thus the two length scales of importance are the pore diameter (200 nm) and the smectic layer thickness ($\sim$ 3 nm). In other words, in the p-ANA geometry a pore could contain at best about 70 layers, leading to strong confinement induced effects. In this situation, the molecules are anchored perpendicular to the pore walls and in all probabilities the morphology in the smectic phase would be concentric layers, similar to that of an onion structure as shown in Figure 4.19. In such a scenario, the smectic layer normal as well as one of the layering directions will be in the plane of the membrane, and therefore the size of the membrane puts a serious limitation on the correlation length in the layering and layer normal directions. The FSF experiments on 70.7, a higher homologue of 40.8 shows a very rich phase diagram, particularly when the number of layers is reduced [31, 32]. For the 70 layer system, the bulk CrB-CrG (CrG is another plastic phase, but with molecules tilted in the layer, absent in bulk 40.8) transition is mediated by a tilted hexatic phase, SmF. In the p-ANA geometry, no X-ray reflections are seen in the wide angle ($2\theta \sim 20^\circ$) region. This could be possibly due to the reason that in this geometry only the form factor of the molecules will contribute to the intensity of the wide angle reflection. It is known that this is much weaker than the one in the case where the in-plane order can be directly seen. Owing to this feature we cannot unequivocally
establish whether the M1 and M2 phases are indeed hexatic or plastic. But in the following we provide some leading suggestions. Noting that the layer spacing is higher in the SmA phase, it can be argued that M1 is a phase with orthogonal arrangement of the molecules. On the other hand, the M2 phase has a lower \( d \) value than that in M1, perhaps suggesting tilting of the molecules. However, the \( d \) values in M2 is still higher than that in SmA, which may be due to the complete stretching of the alkyl chains in the former phase. Bearing in mind the fact that the enthalpy change is quite small across M1-SmA, and large across M1-M2, the possibility that both M1 and M2 are highly ordered plastic phases may be ruled out. Probably M1 could be a hexatic phase, while M2 is a plastic phase. It may be recalled that molecular simulations and dielectric experiments on simple fluids in narrow
slit-shaped carbon pores (as against cylindrical pores in the present case) exhibit evidence of an induced hexatic phase [2, 3]. Studies with Anopore membranes having smaller pores should enrich this phase diagram.

### 4.4.2 Influence of confinement on the transition temperature

A general trend that has been observed is that confinement decreases the transition enthalpy. Dadmun and Muthukumar [33] have attempted to give an explanation for the lowering of transition temperatures as well as transition enthalpies on the basis of surface anchoring and finite size effects. According to this argument small finite clusters undergo the transition at a temperature lower than that in the bulk owing to the fact that clusters (or domains) could be poorly correlated. Melting in pores does not differ fundamentally from melting of free particles in a strongly disperse state and in both cases the process can be regarded as the size effect [34]. The presence of curved pore surface may only facilitate breakdown of the long-range positional order and in the limiting case of a monolayer it can result in complete absence of such order.

The formation of small crystals was first theoretically described by Gibbs [35]. The related theory for the effect of curvature on the vapour pressure of liquid droplets was derived by Thomson [36]. The actual expression used to estimate $\Delta T_m$, the depression in the melting point of substances in confined geometries, often called the Gibbs-Thomson equation, is given by

$$\Delta T_m = T_m - T_m^R = \frac{2T_m \sigma_{sl}}{\Delta H_m \rho R}$$

Here $T_m$ and $T_m^R$ stand for the melting point of the sample in bulk and confined states, respectively, $\sigma_{sl}$ is the average interfacial tension between the solid and liquid phases, $\Delta H_m$ is the bulk enthalpy of melting, which in the present case represents the orientational melting N-I as well as the 2D positional melting CrB-SmA transformations, $\rho$ is the mass density of the sample, and $R$ is the radius of the pore. In the case of the N-I transition, this expres-
Table 4.3: Calculated interfacial tension $\sigma_{sl}$ and the Thomson length $L$ for the two anopore cases.

<table>
<thead>
<tr>
<th></th>
<th>ANA</th>
<th>p-ANA</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma_{sl}$ (N/m)</td>
<td>$L$ (nm)</td>
</tr>
<tr>
<td>N-I</td>
<td>$1.0 \times 10^{-3}$</td>
<td>0.87</td>
</tr>
<tr>
<td>CrB-SmA</td>
<td>$2.0 \times 10^{-3}$</td>
<td>0.77</td>
</tr>
<tr>
<td>M2-M1</td>
<td></td>
<td>$10.9 \times 10^{-3}$</td>
</tr>
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Table 4.3 lists $L$ and the interface energy $\sigma_{sl}$ for the N-I and CrB-SmA (M2-M1 for p-ANA) transitions. Both, $\sigma_{sl}$ and $L$ are seen to depend on the confinement condition having lower values for the ANA case. These $L$ values are much higher compared to the Thomson length for the melting transition of non-liquid crystalline materials, especially water for which $L = 0.15$ nm [39], suggesting that the size of the nuclei formed is much larger than in the case of crystallization of water. The value of $\sigma_{sl}$ for the N-I transition for the ANA case is in the same range as that for 5CB [34]. More importantly, both the parameters being higher in the case of p-ANA suggest that the in-plane alignment of the molecules perhaps increases the effect of the surface much more than in the untreated case.

Finally, a caveat concerning the difference in the thermal behavior between the ANA and p-ANA cases. Unlike in the standard practice, allowing $\Delta H_m$ to have different values for the two confined cases and considering the quantity $\Delta T_m \Delta H_m / T_m$ to be constant...
(for the same transition the other parameters in equation 4.1 should have been identical for ANA and p-ANA), the confinement influence in the ANA and p-ANA situations cannot be explained. But the point to be borne in mind is that while the nematic order is locally enhanced by confinement, especially in the p-ANA case, the directors in different pores can become decoupled. Therefore, the effects should have been stronger for the N-I transition, unlike what our experiments suggest. The only other variable in equation 4.2 that can be different between the two cases is $\sigma_{sf}$, whose value is perhaps dependent on whether the liquid crystal interface is with alumina (ANA case) or with palmitic acid (p-ANA).

### 4.5 Conclusions

The results presented in this chapter demonstrate that confinement in cylindrical pores can have a strong influence on the transition from the plastic to the liquid crystalline phase and that the direction of confinement can bring about drastic changes, even to the extent of inducing a new phase in one case, and lowering the positional ordering in the other. On the basis of these observations, it may be speculated that experiments performed with a membrane of reduced pore size, would perhaps transform the CrB phase of the bulk to the HexB phase in the confined situation. Further experiments by tuning the pore diameter is expected to shed more light on these features.
References


