

X-ray and dielectric measurements of the smectic-*A*–hexatic-*B* transition in bulk and confined geometries

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We report x-ray and dielectric measurements on a liquid crystal exhibiting a smectic-*A*–hexatic-*B* (Sm-*A*–Hex-*B*) transition in bulk and confined geometries. The confined geometry experiments have been performed by filling the compound, *n*-butyl 4′-*n*-hexyloxybiphenyl-4-carboxylate, into Anopore membranes with 20 nm pore size. The surprising result seen in the x-ray studies on both the bulk and the Anopore samples is the presence of unusually strong second harmonic reflection arising from the smectic layers in both the Sm-*A* and Hex-*B* phases. In fact, the third harmonic reflection is also observed in the entire temperature range of the Hex-*B* phase and close to the transition in the Sm-*A* phase of the bulk sample, with the ratio of I_{2q_0}/I_{q_0} , and I_{3q_0}/I_{q_0} being $\sim 1/40$ and $1/470$, respectively (here I_{q_0} , I_{2q_0} , and I_{3q_0} correspond to the peak intensities of the first, second, and third harmonic reflections). These features point to the fact that the layering is much better defined in this system, unlike the usual description of pure sinusoidal mass density wave with a typical value of 10^{-4} for I_{2q_0}/I_{q_0} . Another notable feature observed is that whereas the extent of positional correlations of the molecules within the smectic layer, is comparable in the Sm-*A* phase of the bulk and Anopore samples, the correlations are reduced in the Hex-*B* phase. In the bulk as well as the Anopore case, the critical behavior of the positional correlations is found to be well described by a power-law expression with the exponent α being slightly larger for the Anopore sample. It is also seen that the weak first order nature of the transition seen in the bulk, gets weakened further, perhaps becoming second order. Despite such significant differences between the bulk and Anopore samples, the dynamics associated with the director fluctuations is only slightly influenced by confinement.

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INTRODUCTION

The smectic-*A* (Sm-*A*) phase of liquid crystals is a layered system, whose structure is characterized by a one-dimensional mass density wave quantified by a two-component order parameter [1]. The fluidlike nature of the layers and the associated influence on the fluctuations of the layer planes has an important implication, *viz.*, the Sm-*A* phase does not possess true long-range translational order. The mass density wave will therefore not be a square wave in nature but a sinusoidal function. Consequently in the x-ray diffraction pattern the higher order diffraction maxima are either absent, or when present will be extremely weak. In fact, experiments have shown that the intensity of even the second harmonic peak is about 10^4 times smaller when compared with that of the principal peak [2–4]. It should however be noted that the molecules studied are strongly polar in nature having a polar terminal group resulting in the formation of a partially bilayer phase. On the other hand, it may be noted that the formation of the smectic phase is aided by microphase separation of the rigid core and paraffinic tail portions of the molecules. Thus a deviation from the pure sinusoidal density modulation and consequent improvement in the intensity of the higher harmonic peaks can be expected for systems with paraffinic chains at both ends of the molecule. But a high resolution study [5] showed that again in this case the intensity of the harmonic peaks is very small, being comparable to that observed for polar compounds.

Generalization of the concepts of dislocation-mediated melting in two dimensions and its application to liquid crys-

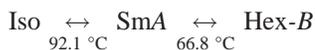
tals led to the prediction [6] and subsequent observation [7] of the three-dimensional-stacked hexatic liquid crystalline phase (Hex-*B*). This phase has again a layered structure and exhibits short-range positional order within the layer just as in the Sm-*A* phase. However, it possesses a bond-orientational order defined as the orientational ordering of the geometric bonds connecting the neighboring molecules in the plane of the layers. Although observed quite recently [7], the Hex-*B* phase and its tilted versions have been well studied in order to understand the phenomenon of dislocation-mediated melting.

Investigations wherein geometrical restrictions have been imposed on the liquid crystalline sample have yielded a wealth of information [8]. Apart from the obvious method of reducing the cell gap, various porous materials have been used for the purpose of confinement. These include polymer matrices (polymer dispersed liquid crystals), porous glasses, silica gels and aerosils, and porous filters like Millipore, Nucleopore, and Anopore membranes. Of these, Anopore membranes are attractive as they have highly parallel cylindrical pores with narrow size distributions and smoother cavity surface. The influence of confined geometry has been reported in systems with transitions involving the nematic (*N*) [9–13], Sm-*A* [14,15], chiral smectic-*C* (Sm-*C*^{*}) [16–19], and crystal-*B* [20,21] phases. A common feature observed in these studies is that confinement can alter (generally diminish) the transition temperature. It can also change the nature of the transition. For example, in the case of both isotropic-*N* and Sm-*A*–Sm-*C*^{*} transitions, a weakening of the first order character has been observed. Some of the effects observed in

these studies have also been attributed to the enhanced influence of surfaces and suppression of thermal fluctuations in the nematic order parameter [8]. Despite such concerted effort to understand the effect of confinement on different phases, its influence on the hexatic phase has not been studied so far. Here we report the first investigation of the influence of confinement on the Sm-A–Hex-B transition.

EXPERIMENTAL

Measurements have been carried out on *n*-butyl 4'-*n*-hexyloxybiphenyl-4-carboxylate (46OBC for short), having the following phase sequence in bulk [22]



The Anopore membranes used in these studies were purchased from Whatman, USA and are made from aluminum oxide and have parallel cylindrical pores penetrating the 60 μm thickness normally, with a nominal pore size of 20 nm. Before the usage the membranes were thoroughly degassed for extended periods of time. The procedure adapted to fill the sample into the pores of the Anopore membrane is described elsewhere [19,21]. Calorimetry experiments were done using a Perkin Elmer DSC7 calorimeter. For measurements on a bulk sample, an empty cup was used as a reference; for measurements on Anopore membranes an unfilled membrane of approximately the same size was placed in the reference cup. X-ray experiments were done with the help of an image plate setup (Mac Science DIP1030), details of which are given in an earlier paper [19]. It is known that if untreated membranes are used, the liquid crystalline molecules tend to align along the pore axis. This is the required configuration to study the in-plane correlations and such measurements were carried out with membranes as received. The measurements of the layering and the associated harmonic peaks require the layer to be normal to the x-ray beam direction and thus the molecules have to be orthogonal to the membrane pore axis. To obtain such an alignment the membranes were treated with a long chain acid (palmitic acid), a procedure known to result in the molecules being aligned in the plane of the membrane [8]. The studies on the bulk sample were carried out by having the sample in a 1 mm diameter Lindemann capillary. To carry out the dielectric experiments on the bulk sample, ITO coated plates with a pretreatment of silane were used. A combination of this coating, which is known to promote the alignment of the molecules such that the long axes are perpendicular to the substrate, and a 2.4 Tesla magnetic field were used to obtain homeotropically aligned mesophases by slowly cooling the sample from the isotropic phase. For the measurements on the Anopore sample, untreated membranes, which as already mentioned, induce homeotropic alignment (molecules oriented along the pore axis). The Anopore membrane was sandwiched between two ITO coated glass plates serving as electrodes. A wide-frequency range impedance analyzer (Solatron model 1260) along with a broadband dielectric

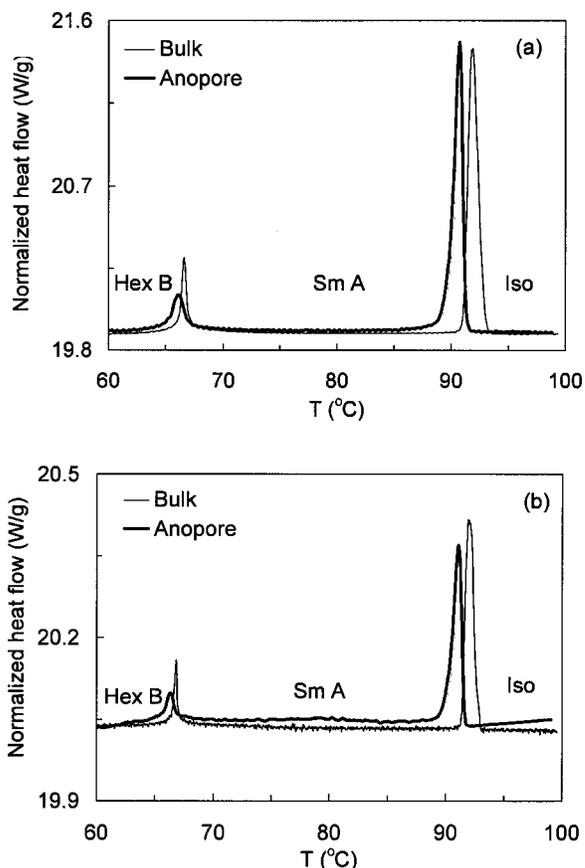


FIG. 1. Differential scanning calorimetric scan in the heating mode for the bulk and the Anopore sample obtained with a heating rate of (a) 5 °C/min and (b) 1 °C/min. It should be noted that for the Sm-A–Hex-B transition the peak width is more and the peak height is lower for the Anopore sample than for the bulk sample. Notice that the data in (b) is on an enlarged scale.

converter (BDC-N, Novocontrol) and controlled by WinData software (Novocontrol) were employed.

RESULTS AND DISCUSSION

DSC measurements

Figure 1(a) shows DSC scans obtained with the bulk and Anopore samples while heating the sample in the temperature range above the melting point at a rate of 5 °C/min. It must be mentioned here that for the measurements on the Anopore sample, the quantity of the liquid-crystalline material inside the membrane was determined by weighing the membrane before and after filling. For ease of comparison, the bulk as well as the Anopore data has been normalized with respect to the weight of the liquid crystal. The two peaks seen for the bulk sample correspond to the Hex-B–Sm-A and Sm-A–Iso transitions. This phase sequence and the associated transition temperatures are in very good agreement with the data reported in the literature [22]. The scan for the Anopore sample looks qualitatively similar and therefore we presume that it has the same phase sequence as that of the bulk sample. X-ray studies, to be discussed later, corroborate this argument. The confinement of the sample in the

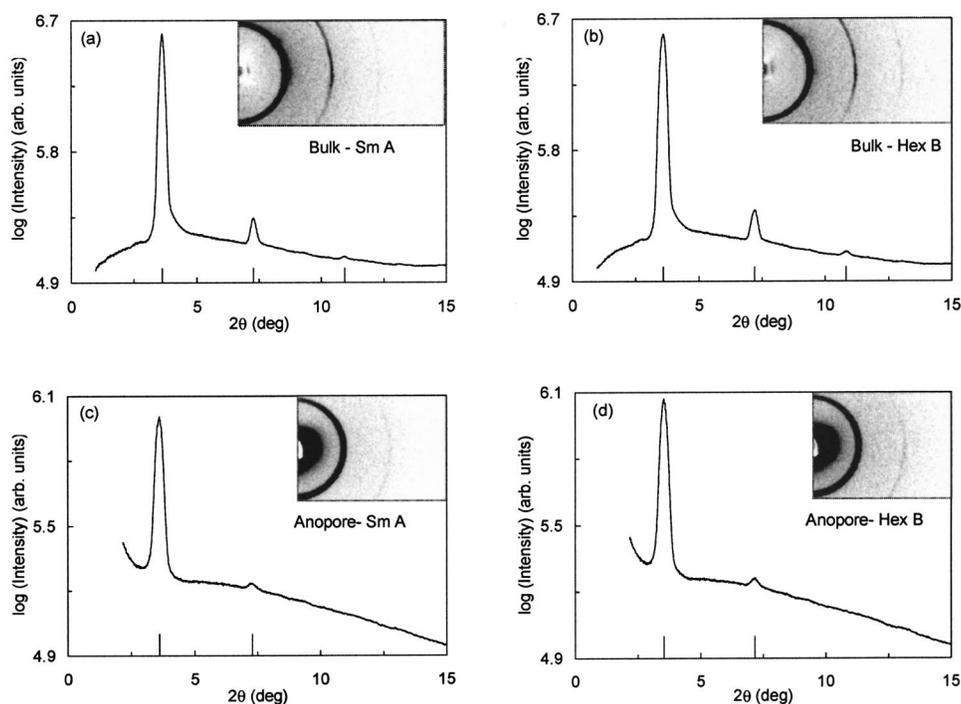


FIG. 2. Diffraction patterns (insets) and the one-dimensional intensity vs 2θ profiles in the low-angle region of the Sm-A phase (a,c) and Hex-B phase (b,d) of the bulk and Anopore samples. The feature to be noted particularly is the presence of higher harmonic reflections.

membrane however introduces some differences. Firstly, it broadens both the Iso-Sm-A and Sm-A-Hex-B transitions, although to different degrees: the width for Iso-Sm-A increases from 1.5 to 1.9 °C, but the width for Sm-A-Hex-B gets doubled increasing from 0.8 to 1.8 °C. Secondly, the peak height is essentially the same for the Iso-Sm-A transition, whereas for the Sm-A-Hex-B transition it reduces by a factor of 2. We also observe a small (~ 1 °C) confinement-induced shift in the transition temperatures. It may be recalled that transition shifts, peak height suppression, and broadening of the transition upon confinement in narrow pores has been well documented in the literature [8]. There is a substantial contribution of the specific heat to the DSC signals as can be seen from the drastic reduction in the signal level when the heating rate is reduced to 1 °C/min [Fig. 1(b)].

X-RAY MEASUREMENTS

Low-angle diffraction

The insets of Figs. 2(a)–2(d) show the diffraction patterns obtained in the Sm-A and Hex-B phases of the bulk and Anopore samples at low angles (the Anopore membranes used for these studies were coated with palmitic acid to facilitate the orientation of the molecules in the plane perpendicular to the membrane normal). The intensity versus diffraction angle (2θ) profiles extracted from these x-ray diffraction patterns are also shown in the same diagrams. The most significant feature to be noticed is the presence of multiple reflections in both the phases. The peak 2θ values determined by fitting the raw data to a Lorentzian

expression are such that the values for the higher angle reflections are exact integer (within 1% over the entire temperature range studied) multiples of the lowest angle peak, indicating that they are the higher-order harmonic reflections of the fundamental. The observation of the second- and third-harmonic peaks is rather surprising, since it is well known that smectic layering can be described by a pure sinusoidal wave and therefore the higher-order harmonic reflections from the layering, even if present, should be extremely weak. Indeed, as mentioned in the introduction, experiments on polar as well as nonpolar compounds have clearly demonstrated that the intensity of the second harmonic reflection is about 10^4 times weaker compared to that for the fundamental [2–5]. Thus, in the present case the second harmonic is 200 times stronger than the commonly observed. Even the third harmonic is an order of magnitude stronger than the second harmonic seen for other materials. These features imply that the layering is much better defined in 46OBC. Confining the material in the Anopore membrane results in only a slight diminution in the relative strength of the second harmonic. However, due to the strong background scattering arising from the Anopore matrix itself, we were not able to separate out the third-harmonic reflection.

The temperature dependence of I_{100} , the intensity of the fundamental reflection as well as I_{200}/I_{100} , the ratio of the intensities of the second harmonic to the fundamental, for both the bulk and the Anopore samples are shown in Figs. 3(a)–3(d). For both the samples, the transition point is clearly marked by a substantial increase in I_{100} , although the increase appears more gradual for the Anopore sample. The harmonic intensity ratios also show about a 30% increase when the material transforms from the Sm-A to the Hex-B

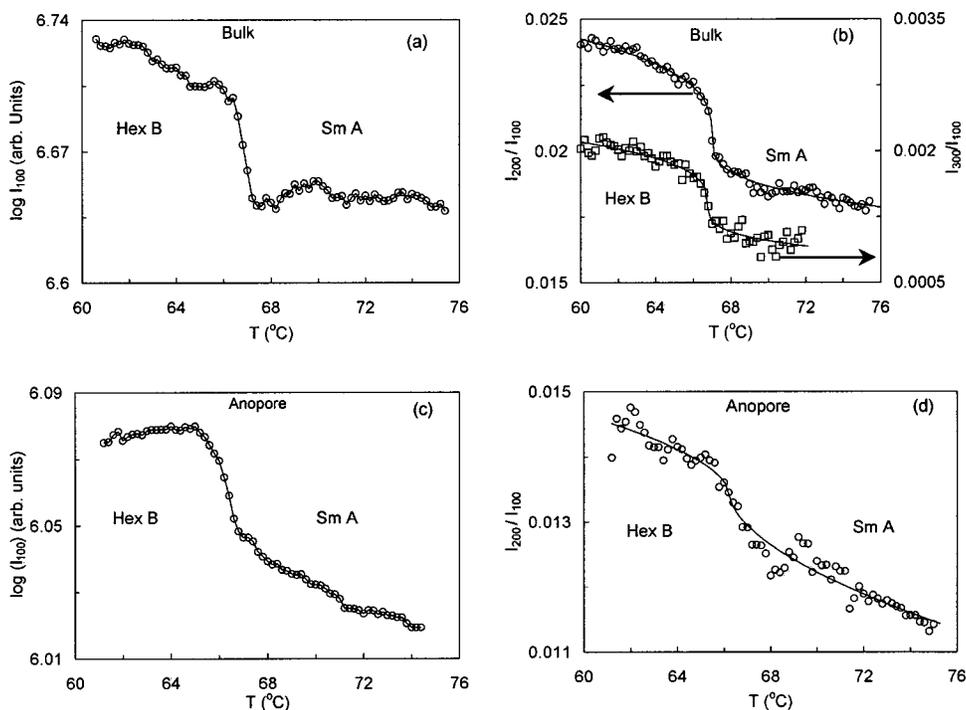


FIG. 3. Temperature dependence of I_{100} , the peak intensity of the fundamental reflection (a,c), and the ratio of the intensities of the higher harmonic to the fundamental reflection (b,d) of the bulk and Anopore samples. In both the samples the onset of the transition to the Hex- B phase is marked by an increase in the intensity of the fundamental reflection as well as the ratio.

phase. We have also observed that for the bulk sample, the third-harmonic peak is observed in both the Sm- A and Hex- B phases. The absolute values of the ratio are lower for the Anopore sample, possibly caused by the finite size effect due to the small pore size of the Anopore. As mentioned earlier, due to the palmitic acid coating, the molecules lie perpendicular to the walls of the pores. Since the layer spacing is about 25 \AA (see discussion below) and the pore diameter is 200 \AA , only about 8 layers can be accommodated inside a pore. Such a limitation may cause the magnitude of the layering to be altered and consequently diminishes the intensity of the I_{200} reflection in comparison to that of I_{100} .

The temperature dependence of the layer spacing d_{100} for the bulk and Anopore samples is presented in Figs. 4(a) and 4(b). The qualitative behavior, *viz.*, the value increases as the temperature is decreased with a steeper increase at the transition, remains the same even for the confined samples. However, the absolute values as well as the overall increase are slightly larger for the Anopore sample, perhaps 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. The slope d_{100}/dT is comparable in the Sm- A phase (-0.017 and $-0.019 \text{ \AA}/^{\circ}\text{C}$ for the bulk and Anopore samples, respectively), but significantly different in the Hex- B phase (-0.004 and $-0.029 \text{ \AA}/^{\circ}\text{C}$, respectively). It is also noticed that the increase in d_{100} at the transition is less steep for the Anopore sample than for the bulk, in agreement with the feature seen in the DSC scans, namely, that the transition is weaker for the Anopore sample.

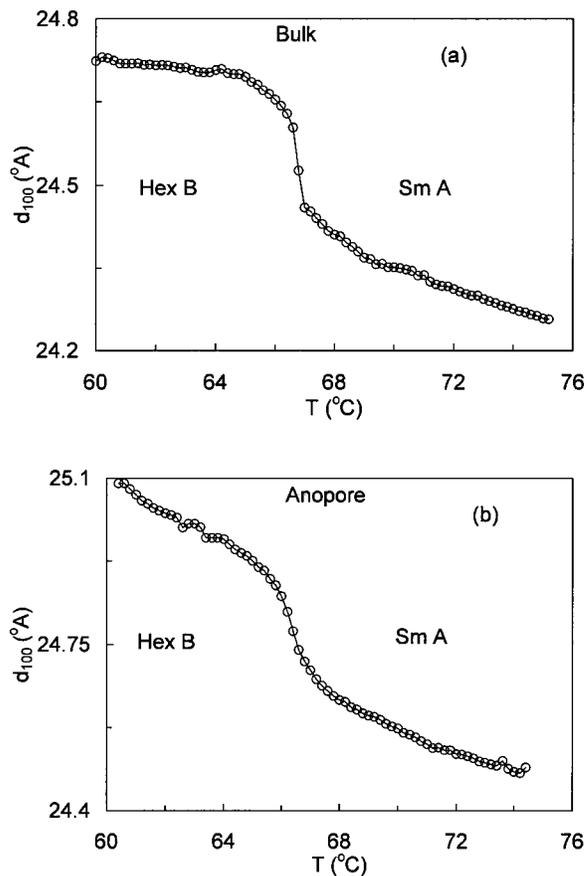


FIG. 4. Thermal variation of the layer spacing for the (a) bulk and (b) Anopore samples. The solid line is only a guide to the eye.

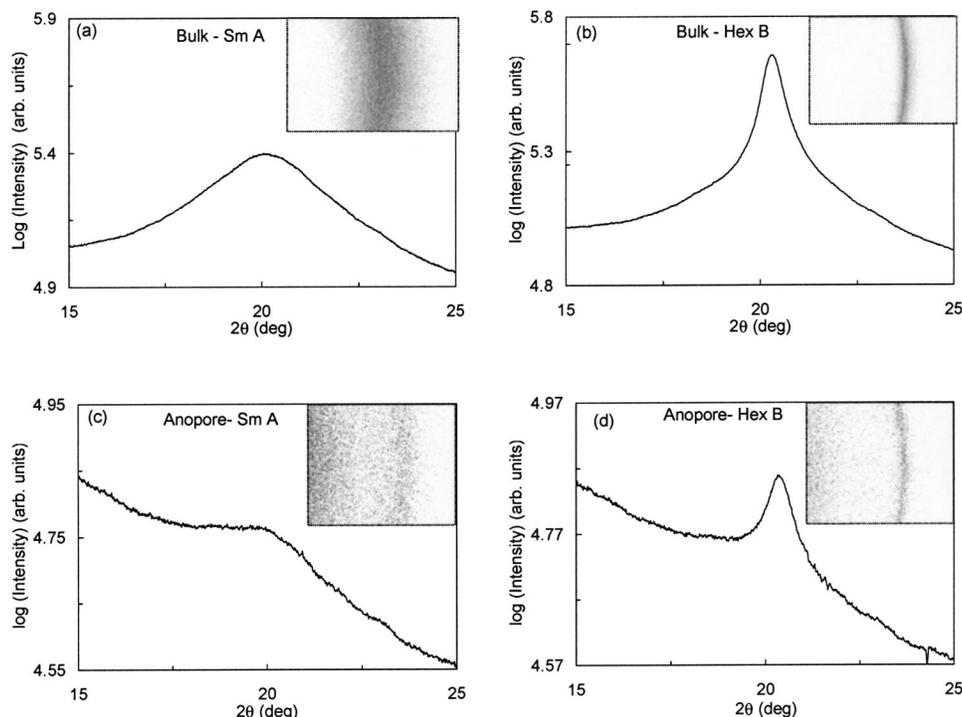


FIG. 5. Diffraction patterns (insets) and the one-dimensional intensity vs. 2θ profiles in the wide-angle region of the Sm-A phase (a,c) and Hex-B phase (b,d) of the bulk and Anopore samples. Although liquidlike in both the phases, the profiles are much sharper in the Hex-B phase.

Wide-angle diffraction

In addition to the low-angle reflections a peak is seen at wide angles, centered at $2\theta \sim 20^\circ$, arising from correlations between molecules within individual layers. The diffractograms obtained in this region for the bulk and Anopore samples are shown in Figs. 5(a)–5(d). To directly map out the in-plane ordering within the smectic layers, untreated membranes were used so that the molecules would be oriented along the pore axis and thus along the x-ray beam direction. The in-plane positional ordering within the layer is liquidlike in both the Sm-A and Hex-B phases, although the extent of correlations should be more for the Hex-B phase. The resulting diffraction peak is thus broad and diffuse, as shown in Fig. 5. On a qualitative level, the patterns obtained for the bulk and Anopore samples seem to be comparable, thus showing that the phase sequence in the bulk is unaltered upon confinement.

To extract quantitative information from the profiles, the data were fitted to a Lorentzian expression (over the entire temperature range of measurement the quality of fitting was excellent). Aeppli and Bruinsma [23] proposed a theoretical model taking into account the coupling of hexatic to density fluctuations. This theory calculates that unless the temperature is well above the Sm-A–Hex-B transition, a square-root Lorentzian (SRL) should describe the structure factor of the system. Experiments carried out on thin and thick free-standing films have shown this to indeed be true [24]. With this in mind we fitted the data shown in Fig. 5 to SRL form, and find that both in the Sm-A and Hex-B phases there is only a slight improvement in the quality of fitting as com-

pared to that of the Lorentzian form. Since the Lorentzian form provides a good fit to the data over the entire temperature range, we use data extracted using this form and show the temperature variation of Q_o , the wave vector of the peak position and κ , and the associated half width in Figs. 6 and 7, respectively. It is clear that the onset of the Hex-B phase causes a marked increase in the in-plane density (seen as an increase in Q_o) and the in-plane positional correlations which are proportional to κ^{-1} .

The theory of Aeppli and Bruinsma [23], mentioned above, shows that the critical behavior of Q_o and κ is determined by the mean square value of the hexatic order parameter $\langle |\Psi|^2 \rangle$, whose temperature derivative is the specific heat. Hence, at temperatures close to the transition there will be singular contributions to Q_o and κ . Since the singularity of the specific heat can be expressed in terms of a power-law behavior with α as the exponent, we can write

$$Q_o(t) = Q_c [1 \mp A^\pm t^{1-\alpha}] \quad (1)$$

and a similar expression for the temperature dependence of κ . Here Q_c is a constant, $t = [(T - T_c)/T_c]$, T_c being the Sm-A–Hex-B transition temperature] is the reduced temperature, α is the exponent, and A^+/A^- , the amplitude ratio characterizing the specific heat. The solid lines in Figs. 6(a) and 6(b) show the fit obtained for the bulk and Anopore samples by floating all the variables, *viz.*, Q_c , T_c , A^\pm , and α . The best fit values of $T_c = 66.83^\circ\text{C}$, $A^+/A^- = 1.89 \pm 0.08$, and $\alpha = 0.47 \pm 0.01$ obtained for the bulk sample are in close agreement with those reported from x-ray measurements on free-standing films [24] as well as the specific heat studies [25] on

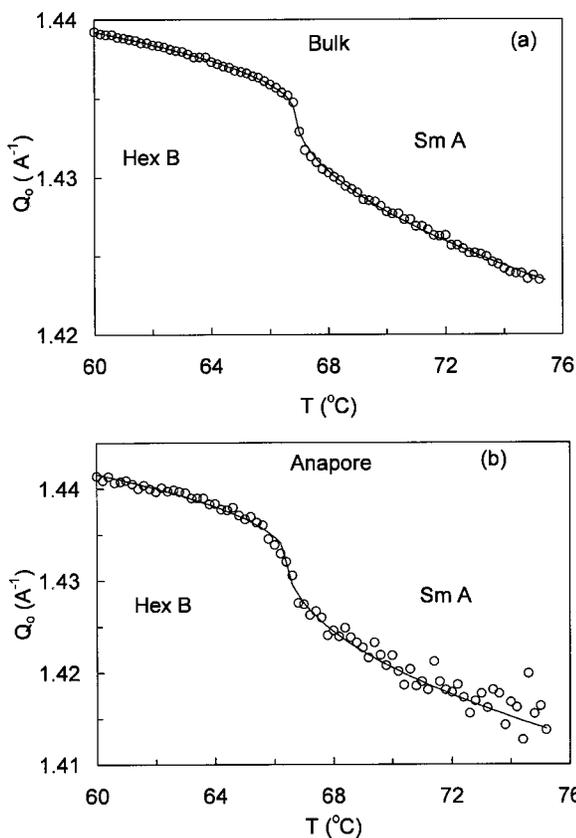


FIG. 6. Variation of the wave vector Q_o of the wide-angle reflection in the (a) bulk and (b) Anopore samples. The solid line is a fit done to equation (1); the best fit value of the exponent $\alpha = 0.47 \pm 0.01$ for the bulk and $\alpha = 0.50 \pm 0.01$.

the bulk sample. The critical behavior of the Anopore sample does not seem to be very different, although there is a slight increase in the value of $\alpha (= 0.50 \pm 0.01)$ and a small decrease in the ratio $A^+/A^- (= 1.73 \pm 0.13)$. The temperature dependence of the half width κ in both the bulk and Anopore samples are shown in Figs. 7(a) and 7(b). Just as for Q_o we see that the onset of the transition leads to a drastic change in the value of κ . The kind of temperature variation of κ shown in Figs. 7(a) and 7(b) makes it tempting to attempt a fit to the expression predicted by the theory [23]. However, since we have not deconvoluted the data with respect to the intrinsic instrumental resolution nor corrected for the sample mosaic, we have not performed such a fitting. Even from the measured half-width data shown in these figures it may be noted that in the Sm-A phase the values obtained for the bulk and the Anopore are quite similar, but the limiting value of κ in the Hex-B is about 30% higher for the Anopore sample. This suggests that confinement of the sample into the porous matrix reduces the in-plane positional correlation, a feature that is not surprising for the following reason. In the geometry used for these experiments, the molecules are along the normal to the plane of the membrane or in other words the layer plane coincides with the plane of the membrane. Therefore the dimension of the layer would be limited by the diameter of the pore ($\sim 200 \text{ \AA}$). Hence, in the Sm-A phase where the correlation

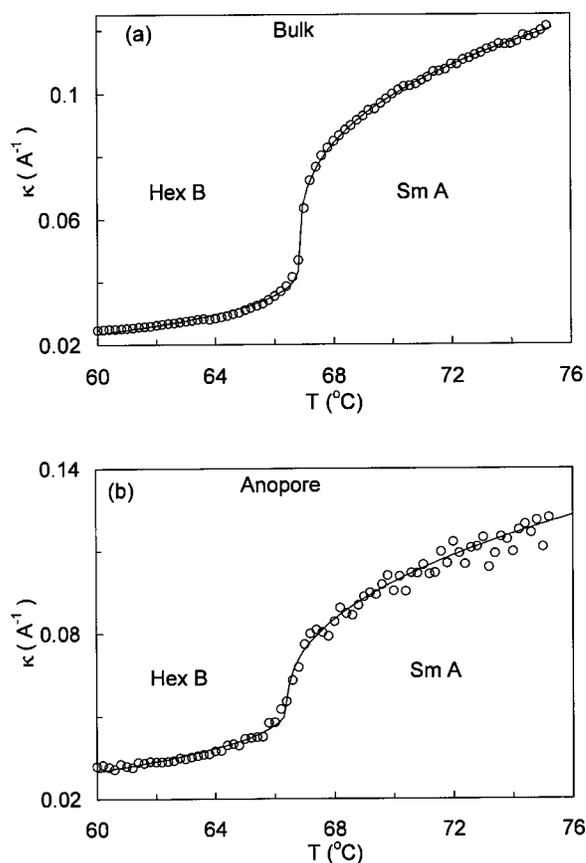


FIG. 7. Temperature dependence of the half width of the wide-angle reflection in (a) bulk and (b) Anopore samples. The reciprocal of κ is directly proportional to the correlation length of the in-plane positional order. The solid line in both sets of data is only a guide to the eye. It may be mentioned that the wide angle peak in the crystal-B phase of the compound 4O.8 has a width of $\kappa = 0.01 \text{ \AA}^{-1}$ and thus can be considered to be the instrumental resolution of the setup used.

length of the positional correlations is quite small ($\sim 20 \text{ \AA}$), the Anopore matrix does not influence the values much. On the other hand in the Hex-B phase the correlation becomes large and comparable to the pore diameter ($\sim 160 \text{ \AA}$) and therefore finite size effects can dominate.

Dielectric measurements

The temperature variation of the measured capacitance [26] of the bulk sample at a fixed frequency is shown in Fig. 8(a). On cooling from the isotropic phase the capacitance value decreases across the Iso-Sm-A transition and continues to have a value lower than in the isotropic phase till crystallization, establishing the fact that the material has a negative dielectric anisotropy. The Sm-A-Hex-B transition is also marked by a clear decrease in the capacitance. These features are in very good agreement with those reported earlier [22]. Figure 8(b) shows such data for the Anopore sample. Again we see clear changes across the transitions as well as the feature that values in the mesophases are lower than that in the isotropic phase. This, in fact, is proof of the good homeo-

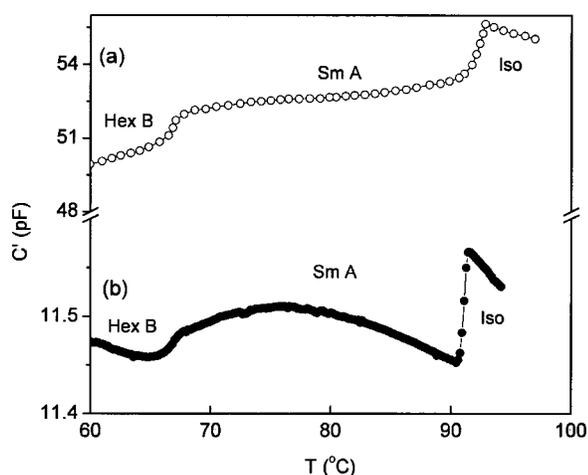


FIG. 8. Temperature dependence of the sample capacitance in the (a) bulk and (b) confined geometries. The transitions are clearly seen in both the samples.

tropic alignment of the sample in the membrane.

To extract the value of the relaxation frequency (f_R) the raw C'' ($=C'D$, where C' is the capacitance and D the loss factor) vs f , the measuring frequency data were fit to the Havriliak-Negami equation [27]. Throughout the entire range of measurement of both the bulk and Anopore samples, only a single relaxation was seen and the profiles could be very well described by a Debye relaxation. The temperature variation of f_R in the bulk and Anopore samples are shown in Fig. 9. (The data have been presented as a function of reduced temperature $T-T_c$, to facilitate better comparison.) Confinement has only a small effect on the absolute value of the relaxation frequency in both the phases. In fact, the Anopore sample has a slightly higher f_R value than the bulk sample. For example at $|T-T_c|=5$ °C, the values in the Sm-A phase are 97 and 139 kHz and in the Hex-B phase, 3 and 3.8 kHz for the bulk and Anopore samples, respectively. Such a behavior is in agreement with that seen for the N -Iso transition [28], but is at variance with that observed in systems involving a transition to crystal- B phase. For example, in the case of the compound 4O.8 showing a Sm-A-Cr- B transition the f_R value decreases by nearly 2 orders of magnitude when the material is confined in 20 nm diameter Anopore membranes [21]. For a polar compound confined in macroporous sodium borosilicate glass with a pore diameter of 86 nm, there was a slight reduction in the f_R value upon confinement [20]. Thus it appears that the nature of the low temperature phase determines the influence of the confinement on magnitude of the relaxation frequency. In the present case confinement makes the director fluctuations slightly faster. To extract the associ-

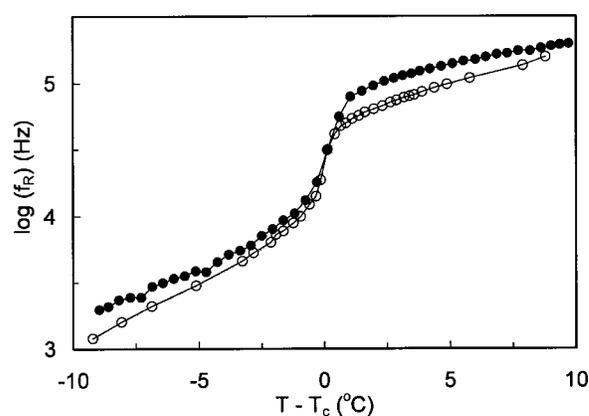


FIG. 9. Plot showing the thermal variation of the relaxation frequency f_R for the (o) bulk and (•) Anopore samples. The value of f_R decreases by about an order of magnitude across the transition in both the cases. Notice that the absolute value of f_R is slightly higher for the Anopore sample.

ated activation energy (W_A) values the data obtained for both the bulk and the Anopore samples was fit to an Arrhenius expression by considering the data away from the transition in the two phases separately. The calculated W_A values for the bulk and Anopore samples are 108 and 84 kJ/mol in the Sm-A phase and 231 and 172 kJ/mol in the Hex-B phase, respectively. This again corroborated the slight reduction in the positional correlation in the Hex- B phase of the Anopore sample, as seen by x-ray measurements.

In summary we have reported the comparative behavior of a compound exhibiting a smectic- A -hexatic- B transition in bulk as well as in confined geometry. The main result is the observation of strong higher harmonic peaks in both the Hex- B and Sm- A phases, although the magnitude of the intensity increases in the Hex- B phase. As is the case for other liquid crystalline transitions, the strength of the already weak first order Sm- A -Hex- B transition is further weakened upon confinement. For both the samples the temperature dependence of the in-plane positional correlation can be described by power-law behavior with the exponent being higher for the Anopore case. The actual magnitude of the correlations is diminished in the case of the Anopore sample. In contrast, the frequency associated with the director fluctuations is slightly higher for the Anopore sample.

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- [1] See, e.g., S. Chandrasekhar, *Liquid Crystals*, 2nd ed. (Cambridge University Press, Cambridge, 1992).
 [2] P. E. Cladis, R. K. Bogardus, W. B. Daniels, and G. N. Taylor, *Phys. Rev. Lett.* **39**, 720 (1977).
 [3] A. J. Leadbetter, J. C. Frost, J. P. Gaughan, G. W. Gray, and A.

Mosley, *J. Phys. (Paris)* **40**, 375 (1979).

- [4] P. E. Cladis, J. Stamatoff, D. Guillon, M. C. Cross, T. Bilash, and P. Finn, in *Advances in Liquid Crystal Research and Applications*, edited by L. Bata, (Pergamon, Oxford, 1981).
 [5] B. M. Ocko, A. R. Kortan, R. J. Birgeneau, and J. W. Goodby,

- J. Phys. (Paris) **45**, 113 (1984).
- [6] R. J. Birgeneau and J. D. Litster, J. Phys. (France) Lett. **39**, 399 (1978).
- [7] R. Pindak, D. E. Moncton, S. C. Davey, and J. W. Goodby, Phys. Rev. Lett. **46**, 1135 (1981).
- [8] For an excellent collection of review articles in this field, see *Liquid Crystals in Complex Geometries*, edited by G. P. Crawford and S. Zumer (Taylor Francis, London, 1996).
- [9] M. Kuzma and M. M. Labes, Mol. Cryst. Liq. Cryst. **100**, 103 (1983).
- [10] G. P. Crawford, R. Stannarius, and J. W. Doane, Phys. Rev. A **44**, 2558 (1991).
- [11] G. S. Iannacchione and D. Finotello, Phys. Rev. Lett. **69**, 2094 (1992).
- [12] M. D. Dadmun and M. Muthukumar, J. Chem. Phys. **98**, 4850 (1993).
- [13] G. P. Sinha and F. M. Aliev, Phys. Rev. E **58**, 2001 (1998).
- [14] G. S. Iannacchione, J. T. Mang, S. Kumar, and D. Finotello, Phys. Rev. Lett. **73**, 2708 (1994).
- [15] T. Bellini, N. A. Clark, and D. W. Schaefer, Phys. Rev. Lett. **74**, 2740 (1995).
- [16] F. M. Aliev, in *Liquid Crystals in Complex Geometries*, edited by G. P. Crawford and S. Zumer (Taylor Francis, London, 1996), p. 345.
- [17] M. Skarabot, S. Kralj, R. Blinc, and I. Musevic, Liq. Cryst. **26**, 723 (1999).
- [18] S. A. Rozanski, R. Strannarius, F. Kremer, and S. Diele, Liq. Cryst. **28**, 1071 (2001).
- [19] K. L. Sandhya, S. Krishna Prasad, D. S. Shankar Rao, and Ch. Bahr, Phys. Rev. E **66**, 031710 (2002).
- [20] J. Werner, K. Otto, D. Enke, G. Pelzl, F. Janowski, and H. Kresse, Liq. Cryst. **27**, 1295 (2000).
- [21] K. L. Sandhya, Geetha G. Nair, S. Krishna Prasad, and Anjali Khandelwal, Liq. Cryst. **28**, 1847 (2001).
- [22] See, e.g., C. Nagabhushan, Geetha G. Nair, B. R. Ratna, R. Shashidhar, and J. W. Goodby, Liq. Cryst. **3**, 175 (1988).
- [23] G. Aeppli and R. Bruinsma, Phys. Rev. Lett. **53**, 2133 (1984).
- [24] S. C. Davey, J. Budai, J. W. Goodby, R. Pindak, and D. E. Moncton, Phys. Rev. Lett. **53**, 2129 (1984).
- [25] T. Pitchford, G. Nounesis, S. Dumrongrattana, J. M. Viner, C. C. Huang, and J. W. Goodby, Phys. Rev. A **32**, 1938 (1985).
- [26] Since the calculation of the empty cell capacitance is not trivial in Anopore membranes, we present here data in terms of the measured capacitance rather than calculating the dielectric constant.
- [27] S. Havriliak and S. Negami, J. Polym. Sci., Part C: Polym. Symp. **C14**, 99 (1966).
- [28] S. A. Rozanski, R. Strannarius, H. Groothues, and F. Kremer, Liq. Cryst. **20**, 59 (1996).