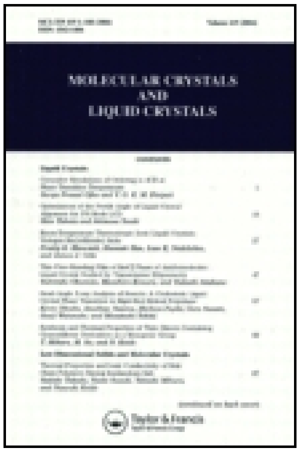

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SMECTIC LAYER ORIENTATION IN CONFINED GEOMETRIES

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Abstract The orientation of the smectic-A and -C* layers, inside 25 μm pores of glass capillary arrays, has been studied by high-resolution x-ray diffraction. The pores were coated with lecithin in order to ensure perpendicular anchoring of molecules at the surface. A chevron-like layer structure was seen in the smectic-A phase of 8CB, while a uniform structure was found in the smectic-C* phase of, both, ZLI-3041 and CBC.

INTRODUCTION

It has been known for some time that liquid crystals behave differently in confined geometries[1,2] than they do in the bulk. For example, transition temperatures are suppressed and the heat capacity due to critical fluctuations, near a phase transition, is diminished. The observed changes at the second order nematic to smectic-A (NA) transition[3] are remarkably similar to those observed in confined[4] He at the λ-point.

Attempts to facilitate a quantitative comparison with He are currently underway at the Kent State University. Recent NMR[5], optical[6], and heat capacity[3,7] studies have revealed that the magnitude of these changes depends on the alignment of the molecules in microscopic, cylindrical pores of Anotec filters. These effects have been explained in terms of the relative magnitudes of the correlation length and the confining dimension.

Since x-rays directly probe the orientation of smectic layers and the correlation lengths associated with smectic fluctuations near the NA transition, we are applying high resolution x-ray diffraction to study the effects of confinement. Here, we report preliminary results of our study of smectic layer orientation in cylindrical pores of glass capillary arrays(GCA).

EXPERIMENTAL DETAILS

Three different materials, each with different mesomorphology, have been investigated. The first material studied, 8CB, was chosen because it had previously been studied, by several techniques, under confinement. 8CB has both a nematic and smectic-A (Sm-A) phase. The other materials, ZLI-3041 (E. Merck) and CBC (Ajinomoto), were chosen for their ferroelectric smectic-C* (Sm-C*) phase. In addition to the ferroelectric phase, each has a Sm–A phase. ZLI-3041 also has a 5 K wide cholesteric phase above the Sm-A phase. The sample ZLI-3041 is a commercial mixture of several components while the other two are one component systems.

Several different media were used for the purpose of confining the liquid crystal material. Each of them consisted of a substrate perforated with cylindrical pores. The pore size for the different filters ranged from 0.6 to 25 μm. Anotec and Nucleopore filters were used initially. However, neither of these provided an adequate scattering volume because of low (coverage) density of pores and small pore lengths. A third medium used for confinement was glass capillary arrays (GCA). The commercially available GCA provided a large scattering volume which was easily adjusted since the GCA can be ground to the desired thickness.

All of the results presented in this paper were obtained from experiments performed with liquid crystals confined in GCA. The GCA used had a pore size of 25 μm in diameter and approximately 0.5 mm in length. Because of the scattering geometry, it was necessary to have the liquid crystals anchored perpendicularly to the walls of the cylinders. This perpendicular anchoring was ensured by first coating the walls of the GCA pores with lecithin, a surfactant known to provide perpendicular alignment[8]. The lecithin was first mixed with hexane in a 1:50 (lecithin:hexane) ratio. The GCA were then dipped in this mixture and thoroughly wetted. Upon removal of the GCA from the mixture, the hexane was allowed to evaporate, leaving behind a layer of lecithin. The thickness of the lecithin layer was determined to be small in comparison with the pore size. The coated GCA were then heated to a temperature which corresponded to the isotropic phase of the particular liquid crystal. The liquid crystal was then placed on the heated GCA and melted, thus filling the pores by capillary action. The filled GCA was then slowly cooled and any excess liquid crystal material removed from the outer surface of the GCA.

X-ray scattering experiments were performed on a four-circle Huber goniometer with an 18 KW Rigaku rotating anode generator as the source. A pair of Ge crystals were used as monochromator and analyzer to obtain high resolution. A Na(Tl)I scintillation detector was used to detect the scattered x-rays. Three different types of scans were performed in order to determine the smectic layer structure inside the cylindrical pores. First, $2\theta/\theta$- (or $q_{||}$-) scans were performed to measure the smectic layer spacing, d. Then θ- and χ-scans were performed to determine the in-plane and out-of-plane mosaicity, respectively. The angular resolution was 0.00025° for the 2θ and θ angles and 0.0025° for the χ-scans. The sample temperature was controlled to within 10 mK with a resistance-bridge based temperature controller.

RESULTS AND DISCUSSION

Layer spacing and orientation for the three liquid crystal samples were studied as a function of temperature. Typically, once mounted in the goniometer, the sample was heated into the isotropic phase and then cooled into its different smectic phases. Within each phase, scans were taken at several different temperatures.

The results of scans performed with 8CB in the Sm-A phase are shown in figures 1-3. In this case, a scan was performed before heating to the isotropic phase. The asymmetry of the diffraction peak (fig 1), obtained from 2θ/θ-scans, indicates that the smectic layers are distorted. This layer distortion results in a continuous variation of the layer spacing, d. Throughout the entire range of temperatures encompassed by the Sm-A phase, the 2θ-peak position was relatively stable, indicating that d is independent of temperature.

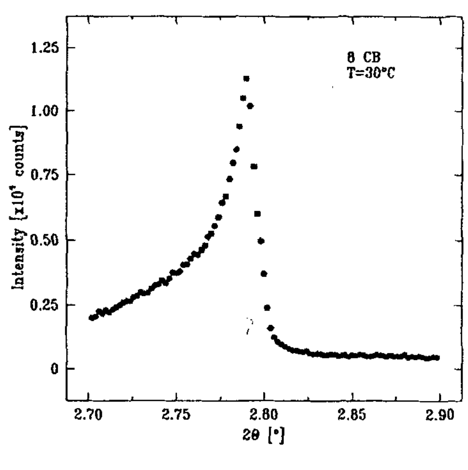


FIGURE 1. Asymmetric Bragg peak from 8CB in the Sm-A phase.

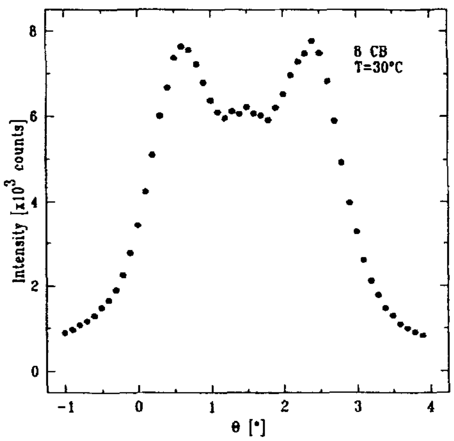


FIGURE 2. In-plane mosaic scan of freshly filled GCA.

The appearance of several peaks in the θ-scans (Fig. 2) shows that the smectic layers form different domains within the GCA pores. In the freshly filled cell, three such domains are seen, in Fig. 2, at approximately 0.65, 1.5, and 2.4 degrees. Upon heating to the isotropic phase and then cooling, only two of these domains, at 0.65 and 2.4 degrees, remain (Fig. 3). This arrangement suggests a ~ 178^0 chevron structure of smectic layers. Chevron structure in the Sm-A phase is unusual, however this type of structure has been previously reported[9] for 8CB between parallel glass plates which had been coated with polyvinyl alcohol and then rubbed. In that case, small pretilt (normally found in such cells) may have been responsible for the formation of chevrons. In the present case, observation of chevron structure in the Sm-A phase in lecithin coated pores is very surprising.

Results of 2θ/θ-scans for ZLI-3041 (Fig. 4) are similar to 8CB scans in the asymmetry of the scattering peak, suggesting that the smectic layers are under strain. In the Sm-A phase, the peak position is independent of temperature, while, as expected from the temperature dependance of the molecular tilt angle in the Sm-C phase, the peak position in the Sm-C* phase changes with temperature, giving rise to a temperature dependent layer spacing.

In contrast to 8CB, the θ–scans for ZLI-3041 (Fig. 5) revealed only one domain within the pores of the GCA. This result suggests a bookshelf geometry (uniform layers) which is

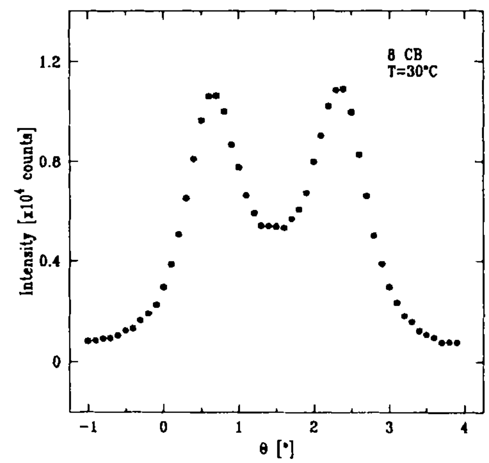


FIGURE 3. θ-scan after heating to isotropic phase.

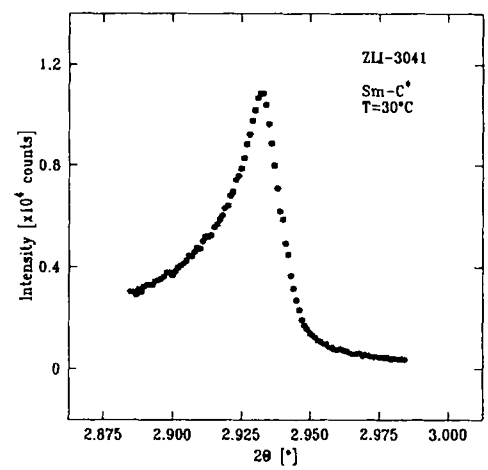


FIGURE 4. Scattering peak from ZLI-3041; asymmetry indicates layers under strain.

highly desirable for display applications. This arrangement can be attributed to strong anchoring and perpendicular alignment of liquid crystal molecules at the surface of the pores.

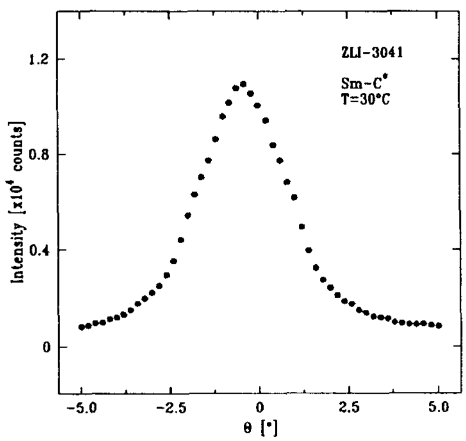


FIGURE 5. Single θ-scan peak, revealing that one domain was formed.

The χ–scan for ZLI-3041 (Fig. 6) shows two scattering peaks, approximately 60° apart. The difference in intensity of the two peaks is due to a misalignment of the scattering apparatus.The origin of the two scattering peaks appears to be the hexagonal cross section of the GCApores. Smectic layers can form parallel to each side of the hexagon. Our results can not distinguish between (a) smectic domains separated by 60° present in each pore, and (b) smectic layers parallel only to one side of the hexagon in each pore but parallel to different sides in different pores. We plan to perform careful χ–scans over a wider angle to determine if smectic layers orient parallel to each side with equal probability.

The smectic layer spacing in the Sm-A phase of ZLI-3041, shown in figure 7, is nearly temperature independent. In Sm-C* phase, it changes rapidly with the temperature dependent molecular tilt.

The results for CBC, shown in figures 8 and 9, are much like those of ZLI-3041. An asymmetric scattering peak, caused by strained smectic layers, is seen in 2θ/θ-scans. The single peak seen in θ–scans implies that there is no chevron structure. However, the peak is not very sharp and well defined like that of ZLI-3041. This suggests that the molecular

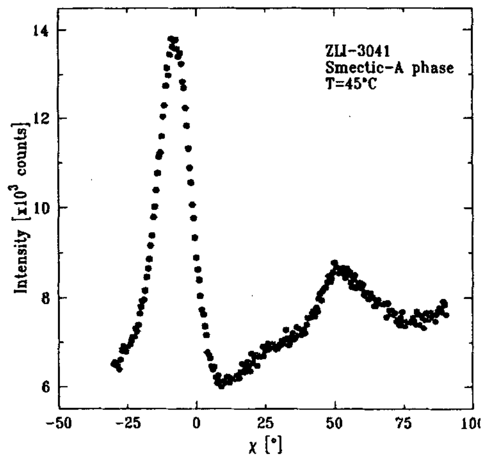


FIGURE 6. χ–scan for ZLI-3041; two peaks at -10° and 50° due to hexagonal pores.

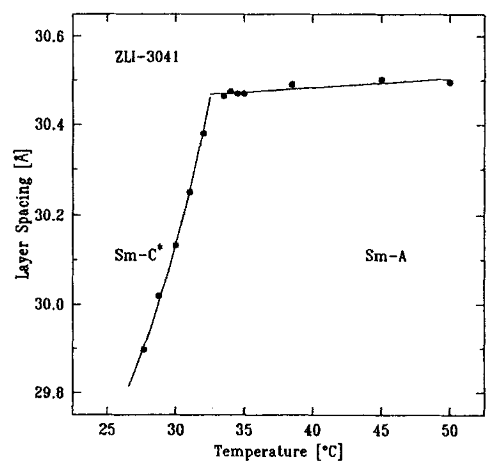
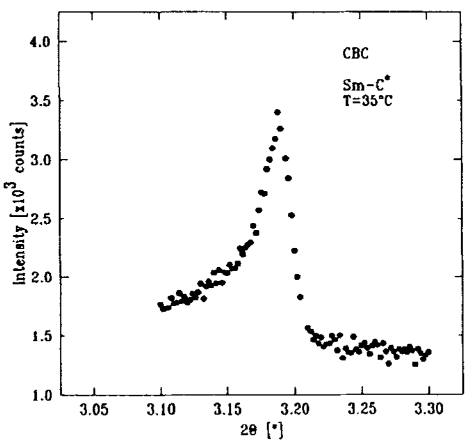


FIGURE 7. Layer spacing for ZLI-3041 in the Sm-A and Sm-C* phases.



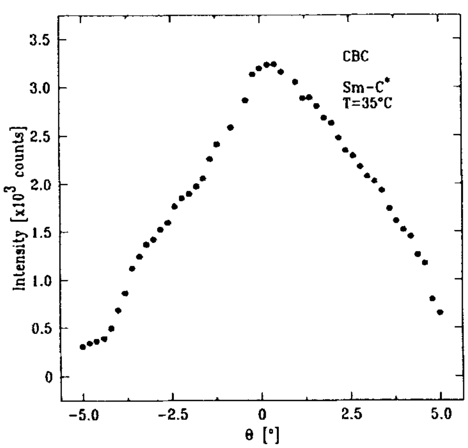


FIGURE 8. 2θ- and θ-scans for CBC.

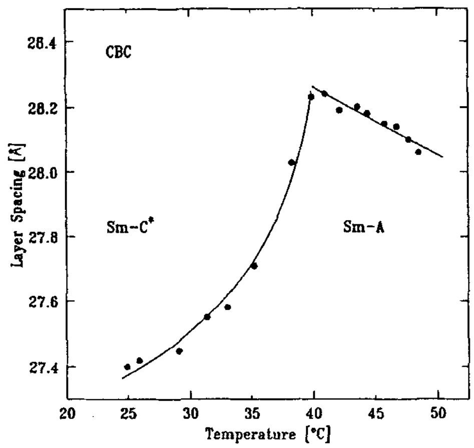


FIGURE 9. Layer spacing for CBC in Sm-A and Sm-C* phases.

alignment was not very good. Again, the layer spacing in the Sm-C* phase was found to be strongly dependent upon temperature (Fig. 9), as expected. The difference in the temperature dependence of *d* in the Sm-A phases of CBC and ZLI-3041 was caused by modification (to different extents) of the nematic order parameter, S. CBC has a direct Sm-A to isotropic transition phase requiring significant changes in S in the Sm-A phase. In contrast, most of the changes in S occur in the cholesteric phase of ZLI-3041. As a result, *d* in this case is not as strongly dependent on temeparture as for CBC.

The major difference in the structures, formed in the GCA by the three materials, is the evidence of chevron structure in 8CB. Chevrons, although expected for the two ferroelectric samples ZLI-3041 and CBC, were not observed. This result can be explained in light of the optical[1,6] and recent NMR studies[5]. These studies have shown the existence of several different nematic director configurations inside the cylindrical pores. In one configuration, the molecules were aligned perpendicularly to the surface of the pores and formed a defect line along its axis. The other configuration showed that as the center of the cylinder was approached, the molecules tended to relax out of the plane and lie parallel to the axis of the cylinder, forming what is called an "escaped radial" configuration. This type of configuration is consistent with the double peak seen in theta scans of 8CB. The θ-scans showing a single peak suggest the defect line configuration.

SUMMARY

The results of our study of smectic layer orientation in cylindrical pores show that, for ZLI-3041 and CBC, the smectic layers are formed parallel to the axis of the pores. A chevron-like structure was found for 8CB. In all three samples, the layer spacing showed the expected temperature dependences in the Sm-A and Sm-C* phases.

Future studies will involve a variety of materials and a systematic decrease in the pore size. We will look for crossover effects expected when the pore size becomes comparable to the smectic correlation length near the NA transition. The use of smaller pore sizes will reduce the scattering volume of the sample making it necessary to use synchrotron radiation. We will also study anchoring properties of different surfactants.

ACKNOWLEDGEMENT

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