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Optical observations of layer ordering in helical smectic A* liquid crystals

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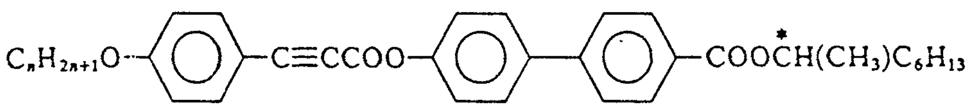
We report the first optical microscopic observation of characteristic textures and the associated layer ordering in a recently discovered, helical smectic A* phase on a multiple domain substrate. The experimental results are quite unusual but consistent with a mean-field model of the twisted grain boundary phase.

Recently, a novel liquid crystalline phase that exhibits smectic as well as cholesteric characteristics has been reported in a certain homologous series of ferroelectric liquid crystals (LCs), the (*R*)- and (*S*)-1-methylheptyl 4′-[(4″-*n*-alkoxyphenyl)propioloyl-oxy] biphenyl-4-carboxylates [1]. This novel helical smectic A_A^* (S_A^*) phase is a liquid crystal analogue of the Abrikosov phase of type II superconductors [2,3], in which blocks of smectic layers have an infinite extent in a direction transverse to the axis of the cholesteric pitch. The materials showing this S_A^* phase are generally highly chiral, and their racemic versions exhibit only the ordinary smectic A (S_A) phase.

While the layered structure is evident by X-ray diffraction [4], the structure revealed by optical studies in the range of the visible wavelength shares common features with cholesteric (Ch) LCs. Because of this dichotomous behaviour of the S_A^* phase, it is of interest to investigate the nature of its surface ordering and the resultant structure on various treated surfaces. In this Communication we report the first optical microscopic observation of the characteristic textures and the associated layer ordering of this phase on a treated substrate with multiple boundary conditions. The experimental results are quite unusual but consistent with a proposed model [2] for the twisted grain boundary (TGB) phase.

It is well-known that LCs can be oriented on a chemically and/or physically treated surface because of the anisotropy in the surface forces [4]. The substrate used in our study has several regions treated differently so that layer ordering in the S_A^* and other phases can be easily distinguished. The material studied was (*S*)-1-methylheptyl 4′-[(4″-*n*-tetradecyloxyphenyl) propioloyl-oxy]biphenyl-4-carboxylate ($C_{14}1\ M_7$), which has the general chemical formula:



The phase sequence of this material on cooling is [1]; $I \rightarrow S_A^* \rightarrow S_C^* \rightarrow S_3 \rightarrow S_4$. The transition temperatures for the I–S_A^* and S_A^*–S_C^* transitions are 93·8°C and 89·7°C, respectively. The shorter homologues of the series possess a typical S_A to S_C^* phase

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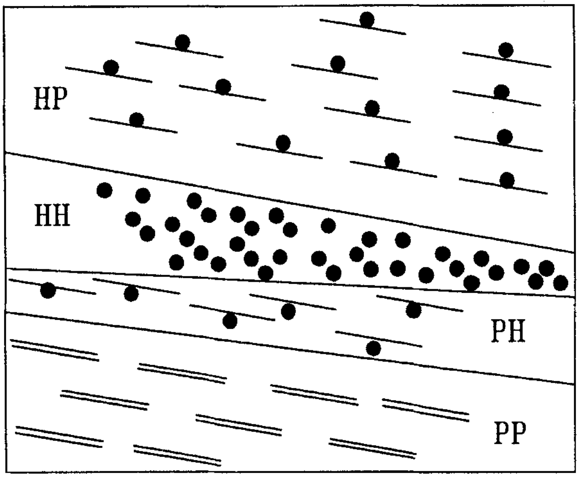

Figure 1. The patterns of a multiple domain substrate; from the top to the bottom of the substrate, homeotropic and homogeneous layers present (HP), both homeotropic layers present (HH), homogeneous and homeotropic layers present (PH), and both homogeneous layers present (pp). The easy axis of molecular orientation, created by unidirectional rubbing, is represented by the straight lines.

transition. The homogeneous surface was produced by coating a glass substrate with poly(1,4-butylene terephthalate) polymer, followed by unidirectional rubbing. The homeotropic surface was prepared by spin-coating a 5 per cent solution of octadecyltrimethoxy silane in ethanol, and then drying the substrate at 120°C for about an hour. The surface was cleaned with a jet of ethanol after baking it to remove any residue prior to cell assembly. The cell spacing was maintained with 8 μm thick spacers.

The patterns of a multiple treated substrate are shown in figure 1. Typical textures of an aligned S_A^* samples of $C_{14}1M_7$ on different regions of the substrate are shown in figures 2(*a*)–(*d*). The photographs were taken between crossed polarizers at various temperatures. The temperature was controlled by a Mettler FP 82 microfurnace in conjunction with a FP 5 control unit. Figure 2(*a*) is a photograph taken at 94·0°C during cooling the sample from the isotropic to the S_A^* state. The growth of a helical S_A^* structure from the isotropic liquid results in iridescent textures, similar to the cholesteric texture developed in a homeotropic geometry (HH). On subsequent cooling the sample close to the S_C^* phase, the textures characteristic of the S_A^* phase were fully developed at 91·0°C, as shown in figure 2(*b*). In a planar geometry (PP), the S_A^* phase exhibits multiple connected platelets, related to integral multiples of the helical pitch of the phase. On further cooling, the focal conic domains are developed from the S_A^* phase at 87·0°C in the S_C^* state, as shown in figure 2(*c*). Figure 2(*d*) is a photograph of the S_A^* texture that reappeared at 90·0°C after heating the S_C^* state. One of the most interesting features is the texture with filaments, shown in figure 2(*d*), which grow in the homeotropic region (HH) when the sample was heated from the S_C^* into the S_A^* state. Furthermore, the filaments can be aligned in a direction parallel to an external electric field [5].

We first examine the difference in molecular alignment between a typical S_A phase and the helical S_A^* phase. For a racemic version of this material, its layered structure was qualitatively the same as an ordinary S_A structure grown on a similar substrate. In a PP geometry, for example, the molecules arrange themselves along the rubbing axis (b) in

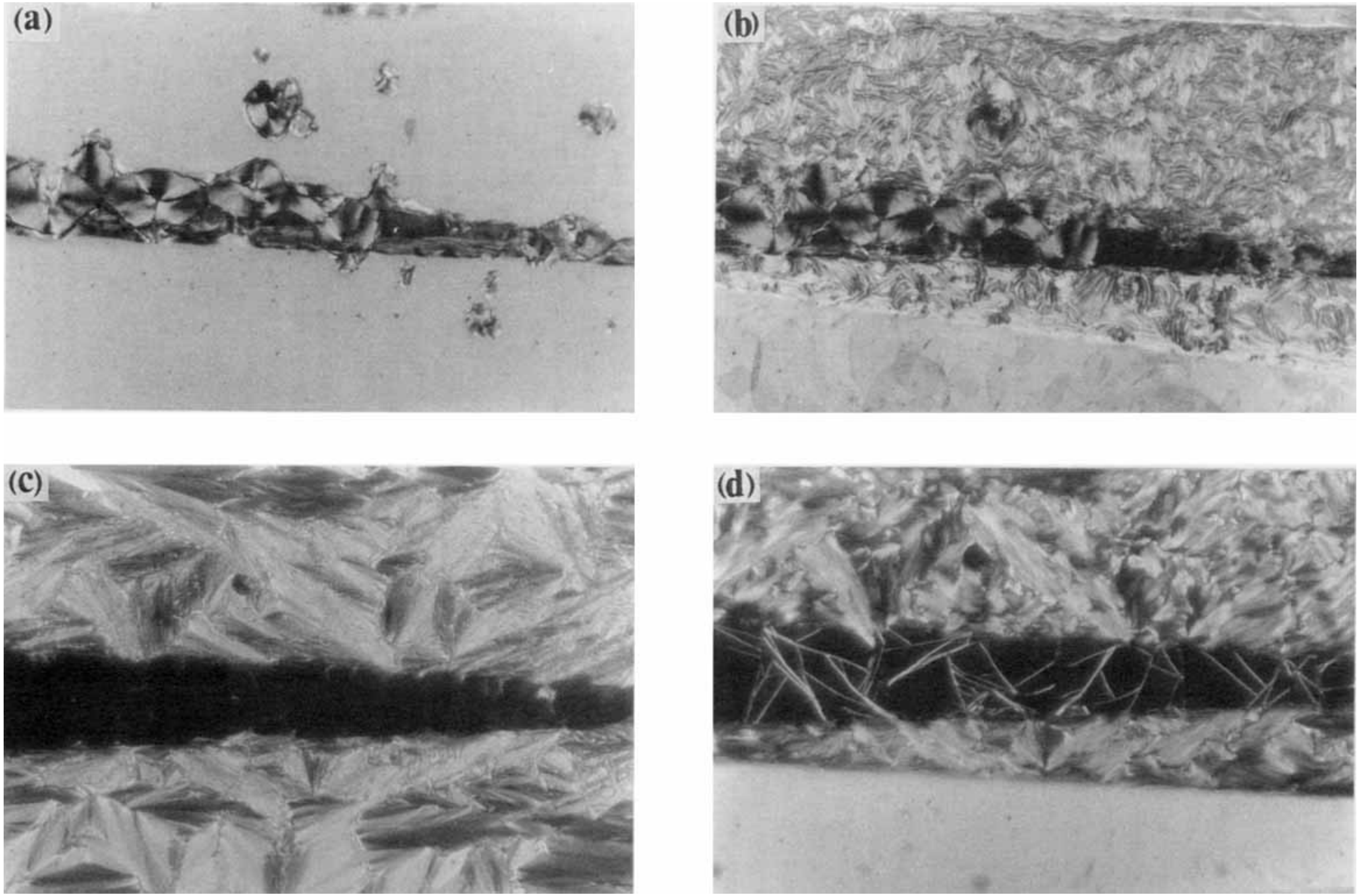

Figure 2. An aligned sample of the smectic A* phase (all × 65 magnification); (*a*), (*b*), (*c*), and (*d*) are photographs taken between crossed polarizers at 94·0°C, 91·0°C, 87·0°C and 90·0°C, respectively. The isotropic phase cooled into the S_A^* phase in (*a*) and then into the S_C^* phase in (*b*). The texture deep in the S_C^* phase is shown in (*c*), and (*d*) is when the S_C^* phase was heated into the S_A^* phase. Different regions of the treated substrate are shown in figure 1.

the plane of the substrate, and the smectic layers developed in a direction perpendicular to the substrate. This structure resembles optically a slab of uniaxial material, and therefore when one of the crossed polarizers coincides with its optic axis, a complete extinction is observed. However, the results of a chiral modification of certain homologues are quite different.

In the PP geometry, the molecules of the chiral versions are arranged along the rubbing axis at the surfaces, but their axes tend to rotate with respect to b into the bulk. Consequently, a small amount of light can pass through the sample even under the crossed polarizers, and thus the extinction is not perfect. Furthermore, the transmitted light intensity is almost independent of the angle between the polarizer (or analyser) and b. This behaviour is very similar to that of a tight pitch cholesteric material, viewed between crossed polarizers with a light of wavelength λ provided $\lambda \ll p\Delta n$. Here p and Δn are the cholesteric pitch and the birefringence of the material, respectively. This suggests that unlike the racemic version, for chiral versions the molecular orientation rotates away from b in the bulk while maintaining the integrity of layer ordering in a plane parallel to the surface.

The pitch of the chiral material studied here was found [6] to be in the range from $0\cdot5\,\mu$m to $1\,\mu$m close to the S_A^*–S_C^* phase, which is in the range of the wavelength of visible light. The molecular chirality is thought to play a critical role in the twist of the smectic layers in one of two ways. In one case, the smectic layers remain fairly well defined over a certain distance beyond which the the effective twist occurs. The twist is then incorporated into the system by successive blocks of well-defined smectic layers with respect to the layer plane, separated by defect regions. Clearly, in this model the twist is confined within the defect region which is referred to as TGB. In another model, the smectic layers are still constrained parallel to each other as before, but the twist continuously develops within each smectic block as if the system possesses a sort of cholesteric phase with layer ordering. Accordingly, this structure would not be optically the same as the TGB phase, but would be similar to the cholesteric phase with enhanced orientational order. Our optical studies are quite consistent with the model of the TGB phase for the S_A^* phase.

We now discuss the characteristics of two S_C^* structures derived from the chiral S_A and helical S_A^* phases. When a well-aligned S_A phase is cooled into the S_C^* state, two domains develop, which correspond to the two possible orientations of the molecular axis at the surface while preserving the smectic layer structure. Although the smectic layers appear in a direction perpendicular to the surface, they are normally arranged in a chevron geometry as is the case for other materials [7, 8]. For the S_A^* case, however, randomly oriented, and thus quite iridescent S_C^* structures are expected to be obtained. This is very similar to the textures of the S_C^* phase developed directly from a tight pitch cholesteric phase. The formation of this type of texture comes from the nucleation of the helical structure in different areas of the sample.

It was observed that this random texture can be converted into a well-oriented single domain by utilizing an interdigitized electrode method [5]. The magnitude of an applied electric field should be at least the critical field strength for unwinding the helix of the S_C^* state at a given frequency. The results for this field treatment are very similar to those for aligning the S_C^* material, reported previously [9]. However, there are some distinctions such as the alignment angle between the smectic layers and the rubbing axis b. For the S_C^* phase derived from the S_A^* phase, this angle quickly approaches 25° in the vicinity of the S_A^*–S_C^* transition. On the other hand, for the S_C^* phase grown from the cholesteric phase, it slowly saturates to about 45° with decreasing temperature to the

Ch–S_C^* transition [10]. Finally, it may be noted that a treated substrate with multiple boundary conditions is very useful for characterizing various textures associated with surface ordering of LC phases of high molecular chirality.

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References

[1] Goodby, J. W., Waugh, M. A., Stein, S. M., Chin, E., Pindak, R., and Patel, J. S., 1989, *Nature, Lond.*, **337**, 449; 1989, *J. Am. chem. Soc.*, **111**, 8119.

[2] Renn, S. R., and Lubensky, T. C., 1988, *Phys. Rev.* A, **38**, 2132.

[3] Lubensky, T. C., and Renn, S. R., 1990, *Phys. Rev.* A, **41**, 4392.

[4] For a comprehensive discussion, see Cognard, J., 1982, *Alignment of Nematic Liquid Crystals and Their Mixtures* (Gordon & Breach).

[5] Patel, J. S., Lee, S.-D., and Goodby, J. W. (unpublished).

[6] Srajer, G., Pindak, R., Waugh, M. A., Goodby, J. W., and Patel, J. S., 1990, *Phys. Rev. Lett.*, **64**, 1545.

[7] Ouchi, Y., Lee, J., Takezoe, H., Fukada, A., Kondo, K., Kitamura, T., and Mukoh, A., 1988, *Jap. J. appl. Phys.*, **27**, L-725.

[8] Rieker, T. P., Clark, N. A., Smith, G. S., Parmar, D. S., Sirota, E. B., and Safinya, C. R., 1987, *Phys. Rev. Lett.*, **59**, 2658. Clark, N. A., and Rieker, T. P., 1988, *Phys. Rev.* A, **37**, 1053.

[9] Patel, J. S., Lee, S.-D., and Goodby, J. W., 1989, *Phys. Rev.* A, **40**, 2854.

[10] Patel, J. S., and Goodby, J. W., 1986, *J. appl. Phys.*, **59**, 2355.