Journal of Optoelectronics and Advanced Materials Vol. 7, No. 1, February 2005, p. 265 - 268

SURFACE ORIENTATION OF SMECTICS *C* AND NEMATIC WITH SHORT RANGE SMECTIC *C* ORDER USING A HOLOGRAPHIC DIFFRACTION GRATING

B. Katranchev*, M. Petrov

Laboratory "Optics and Spectroscopy", Institute of Solid State Physics,
Bulgarian Academy of Sciences, 72, Tzarigradsko Chaussee Blvd, 1784 Sofia, Bulgaria

Using as orienting solid surfaces a holographic diffraction grating (etched into a glass substrate with period Λ = 450nm and a sinusoidal profile) we have studied the growth of nematic (N) and smectic C (S_C) liquid crystal textures of 4,n-otyloxybenzoic acid (n-OBA). A smectic A (S_A) state does not existing in the bulk phase diagram of n-OBA, and rotation of the single local monocrystals (SML) was observed on imposing a bulk twist on the LC system. We compare both the erasure activation energy of the S_C textures, memorized in the nematic temperature range, and the azimuthal surface energy Q and δQ, provided by holographic diffraction grating topography. We propose a model for the SML rotation and smectic A induction.

(Received December 9, 2004; accepted January 26, 2005)

Keywords: Liquid crystals, Holographic diffraction gratings, Bulk twist, Smectic C

1. Introduction

The nematic (N) liquid crystal phase, preceding upon cooling the smectic C (S_C) liquid crystal state, was named [1] nematic with short range smectic C order. The surface orientation of these liquid crystal phases is rather complicated, due to their complex structures. A typical peculiarity of the S_C is the restriction of the director **n** to rotate (or reorient) around a cone with apex 2ω inside the smectic layer (s). Here, ω is the tilt angle between **n (**the nematic director**)** and the smectic layer's normal **N**. Until now, two types of smectic C phase are known [1]. The first type, denoted as C_1, is characterized by a tilt angle which is temperature independent. This type of smectic C_1 is displayed by the materials investigated here: 4,n-alkyloxybenzoic acids, n,OBA, (n-homologue number) with $n \geq 7$. Here we present the results for 4-n-octyloxybenzoic acids (8,OBA), which show mesomorphic behaviour because of the presence of a sufficiently high concentration of dimers, formed via hydrogen bonds. The dimers can be closed (with two hydrogen bonds) or open (with just one hydrogen bond).

The specific character of smectic C, initiates the specific character of the nematic with short range smectic C order and in turn a unique surface orientation. Thus, **n** is forced to rotate simultaneously on both a cone coaxial with the surface normal (s) and a cone coaxial with the smectic layer's normal N. As a result, the director at the surfaces can be switched between stable surface orientation states by external forces.

The formation of large single local monocrystals in smectic C phases is a major problem, since the orientation, in a uniform manner, over the entire area of the active liquid crystal depends strongly on the coordination of the layer and the director orientations. We present large and well oriented SLM, convenient for study of the effect of the surface memorization (SME). Understanding the SME mechanism has become very important in recent years, when it was found that the SME

*Corresponding author: boykopk@issp.bas.bg

dominates the usual weak elastic anchoring in the "flow alignment effect". Therefore, surface memorization could be studied from two aspects: (i) memorization of an oriented smectic texture in the nematic phase region, and (ii) "flow alignment". We discuss only the first aspect in the present paper.

As indicated in [2], a quantitative study of surface memorization could be realized if one can control the two fundamental processes - recording and erasure, characterizing by the recording (t_{rec}) and erasure (t_{er}) times. Until now, such control has been achieved by thermal excitation over the memorized texture, including a counteracting torque proportional to the thermal activation k_BT, where k_B is the Boltzmann constant. The most important parameter driving SME is the erasure activation energy Q, calculated from the relationship $t_{er} = t_o \exp(Q/k_BT)$, where t_o is an extrapolation parameter. The main role in the memorization is played by the thermal energy of the physical adsorption, which is about 80 kJ mol^{-1} (0.8 eV). We have found that the SME erasure activation energy Q for 8,OBA oriented by a set of surface coatings (mainly conducting) [3] - is three to four times higher than the physical adsorption energy $Q_{ads,}$ which is usually about 1 eV. In order to detect the difference $Q–Q_{ads}$, we investigated SME, applying a sequence of erasure external effects, and represented the total activation energy Q as a sum of different components: $Q = Q_{ads} + Q_{el} + Q_{mech} + \delta Q$ The components are the adsorption (Q_{ads}), electric (Q_{el}), and mechanical ($Q_{mech}+\delta Q$) energies, with δQ representing the mechanical energy connected only with the surface topography.

We used a regular holographic grating for a more exact calculation of δQ in the present paper. Furthermore, by varying the properties of the basic grating element, like amplitude and period (A and Λ), one can induce both very weak and strong surface energies. The SLM growth and their rotation upon varying both the holographic grating parameters and the external bulk twist in the process of SME is also examined in the present paper. Smectic A (S_A) induction will be considered in the context of the imposed bulk twist.

2. Experimental results

Using the bulk twists as the external influences against the SME, we separated the bulk from the two substrate surfaces, allowing the surface conditions to be studied. The twist action was applied before growth of the S_C phase, thus preventing memorization.

Our choice of the regular surface topography required the surface profile to be smooth, with a large wavelength compared to the N correlation length ξ, and without important roughness at a ξ-scale i.e. holographic gratings with a sinusoidal profile. The surface undulation of the uni-dimensional sinusoidal grating, observed by AFM, is shown in Fig. 1. The wavelength Λ and amplitude A of the surface undulation are 450nm and 50nm, respectively. Thus, for our one dimensional grating: $z = A_x \sin(2\pi x/\Lambda)$. We calculated the azimuthal anchoring energy, W_φ, using the Berreman [4] model, by the dependence $W_\varphi = 1/2W_{\varphi o}\sin^2(\varphi_s–\varphi_o)$. Here, $W_{\varphi o} = 1/2KA_x^2(2\pi/\Lambda)^3$, K is the effective elastic constant and $L = K/W_{\varphi o}$ is the extrapolation length [1]. L is a measure of the azimuthal energy. Using various twisted cells with Ω between 0 and $\pi/2$ we looked for the evolution of recording and erasure of the smectic C texture in the N temperature range for 8,OBA.

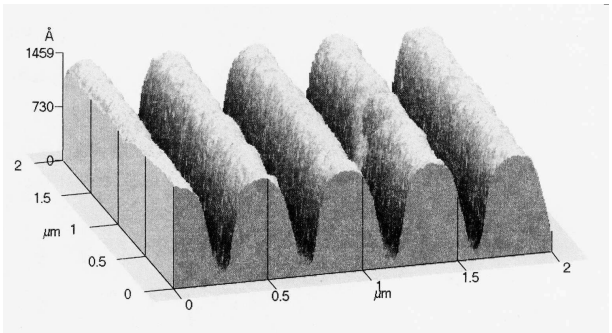

Fig. 1. Holographic gratings with a sinusoidal profile of amplitude A = 50 nm and surface undulation Λ = 450 nm.

By the applied bulk twist, we have revealed two interesting phenomena: the sharp rotation at Ω_c=39° of the SLC long axis relative to the initially created "easy" axis and induction of the S_A state, which does not exist in the bulk phase diagram of 8,OBA. Figs.2 and 3 show the rotation of the long SLM axis l at Ω_c. There is hysteresis at the beginning of the rotation. The difference of the Ω_c values with increasing and decreasing bulk twist (keeping the other experimental parameters constant) is ≈ 4°.

Fig. 2. Smectic C phase of 8,OBA at twist Ω = 36°.

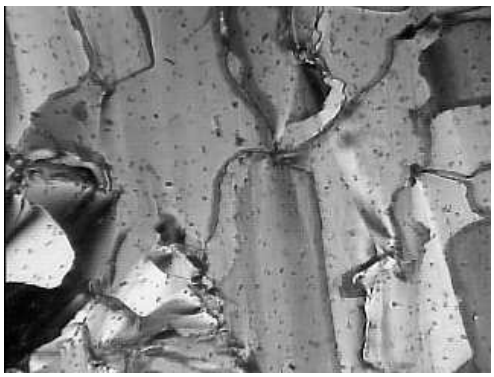

Fig. 3. Smectic C phase of 8,OBA at twist Ω = 90°.

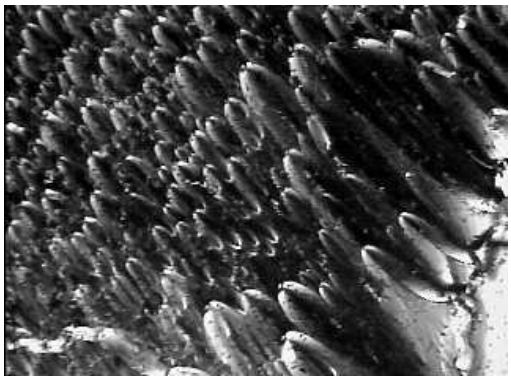

Fig. 4. Smectic A phase of 8,OBA at T = 101 °C.

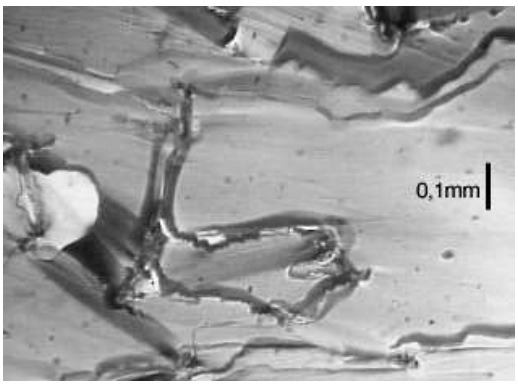

Fig. 5. Smectic C phase of 8,OBA at T = 103 °C.

The induced S_A state, expressed with the simple confocals typical for this phase is shown in Fig. 4. Furthermore we observed for the first time unusually large (≈ 0.6 mm^2) and well oriented SLM (see Fig. 5).

3. Discussion and concluding remarks

The evolution of the S_C texture with increasing twist deformation Ω demonstrates that at Ω > 39°, the orientation of the long axes of the SLM is perpendicular (Fig. 3) or parallel (Fig. 5) to the $\mathbf{n_0}$ direction. This implies that starting with Ω = 39°, the bulk dominates over the surface and the texture (expressing the possible co-ordination of **n** with the layer orientations **s**) is independent of the surface anchoring. On the contrary, for 0 ≤ Ω < 39°, the magnitude of the bulk twist is not enough and the surface dominates. Due to the observed hysteresis and the sharp twist value changing the surface state, we assign this effect as a first order surface phase transition phenomenon, deserving special study. Furthermore, by creating weak anchoring one can rotate the S_C SLM easily. Combined with SME, the phenomenon could be interesting in LC display applications.

Let us analyze the phenomenon on the basis of the surface anisotropy and the corresponding balance of the surface and bulk forces. Due to anisotropic interaction at the LC-solid surface (van der Vaals anisotropic adsorption forces), a nano-sized monolayer grows. As a result of monolayer grows. As a result of the highly anisotropic 8-OBA molecules, containing a few interactive centers (benzene and dimer rings respectively) an alignment on a substrate, meaning some kind of local anisotropy, is created in the vicinity of the LC - solid substrate interface. The anisotropic topographical structure also ensures surface elastic adaptation. When both kinds of anisotropy act simultaneously, the actual "easy" axis must be determined by the compromise reached between them.

We consider the SLM rotation at Ω_c as a surface "anchoring" breaking (change of the $\mathbf{n_o}$ azimuth from $\varphi = 0$ to $\varphi \neq 0$ (φ_s), leading to the SLM long axis **l** rotation. Taking into account the two kinds of anisotropy indicated above, and the fact that in our case (grooved gratings) the more sensitive factor to the bulk twist in the balance of these anisotropies is the azimuthal anchoring, the resultant surface energy is now that of Rapini-Papoular [5]: $f_s = -(1/2)K_{22}/L\cos^2\varphi$.

The total free energy [1], per unit area is $f = f_s + f_{b,}$ where $f_b = (K_{22}/2d)(\varphi_t)^2$ - the bulk elastic energy. φ_t is the actual twist angle, which deviates from the angle Ω imposed by us. The deviation can be expressed as $\varphi = \Omega - \varphi_t$ or $\varphi_t = \Omega - \varphi$. Thus f is $(K_{22}/2d)(\Omega-\varphi)^2$ - $(1/2)(K_{22}/L)\cos^2\varphi$. From $\delta f/\delta\varphi = 0$, the torque balance is $(2K_{22}/d)(\Omega-\varphi) - (K_{22}/L)\sin2\varphi=0$, and $W_{el} = K_{22}/L = 2K_{22}(\Omega-\varphi)(d\sin2\varphi)$ or $1/L=2(\Omega-\varphi)(d\sin2\varphi)$. It follows that when φ approaches Ω, W_{el} tends to zero and L tends to infinity. In contrast, when φ tends to zero (diminution of the twist), L expresses surface "anchoring" breaking or surface instability observed as SLM rotation.

Using the dependences $t_{er} = t_o\exp(Q/k_BT)$ and $W_{\varphi o} = 1/2KA_x^2(2\pi/\Lambda)^3$ and the method of the static SME erasure (keeping N for a certain interval t_{er} at a fixed and sufficiently high temperature T_{er}, (see Section 1) we have estimated Q = 1.8 eV and δQ = 0.5 eV. Since Q contains both components Q_{ads} and δQ (note that δQ is expressed by $W_{\varphi o}$), we found that by variation of the grating parameters A and Λ, the difference $Q- Q_{ads}$ can be controlled. Such control is the basis for understanding the SME mechanism, where the mechanical part of the erasure activation energy δQ was not estimated until now.

The observed accompanying effect (induction of a S_A phase), confirms [6] the prediction that an intermediate state is possible under some conditions: i. a weak phase transition N-S energy h ($h< k_BT$), as is the case of 8, OBA and ii. an imposed twist deformation on the LC system, such that $k=\lambda/\xi$ (λ is the depth of the distortion penetration) is bigger than $2^{-1/2}$. Moreover, the imposed deformation relaxes in regular system of dislocations or simple confocals. On the other hand (see [6]), when χ (a measure of the imposed distortion amplitude) is $\approx 2\pi/d$ (d is the cell thickness) and $\mathrm{curl}\delta n \neq 0$, then the N - S transition temperature decrease, creating an intermediate S_A state. By imposing the twist angle Ω, we create the change of k (by λ) and χ, which ensures the N - S transition temperature decrease and in turn N and the surface smectic layering coexistence accompanied by K_{22} divergence [1]. In such a way, we induce the smectic A structure.

A theoretical analysis of the smectic A induction in LCC, as well as the SLM long axis rotation, will be presented in a future paper.

Acknowledgement

This study was supported by Grant No. 1307 from the Ministry of Education and Science of Bulgaria.

References

[1] P. G. de Gennes, J. Prost, The Physics of Liquid Crystals, Oxford: Clarendon Press (1993).
[2] M. Petrov, L. Tsonev, Liq. Cryst. **21**, 543 (1996).
[3] L. Tsonev, M. Petrov, G. Barbero, Liq. Cryst. **24**, 853 (1998).
[4] D.W. Berreman, Phys. Rev. Lett. **28**, 1683 (1972).
[5] A. Rapini, M. Papoular, J. Phys. (Paris) **30**, C4-54, (1969).
[6] P. G. de Gennes, Sol. St. Commun. **10**, 753 (1972).