Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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Online publication date: 29 June 2010

To cite this Article Demikhov, E. I. , John, M. and Krohn, K.(1997) 'Preliminary communication Anomalous behaviour of photoactive free-standing smectic films under illumination', Liquid Crystals, 23: 3, 443 — 445
To link to this Article: DOI: 10.1080/026782997208361
URL: http://dx.doi.org/10.1080/026782997208361

LIQUID CRYSTALS, 1997, VOL. 23, NO. 3, 443–445

Preliminary communication
Anomalous behaviour of photoactive free-standing smectic films under illumination

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(*Received 31 October 1996; in final form 10 February 1997; accepted 13 February 1997*)

Illumination of free-standing smectic films doped with azo dyes produces bubbles in the SmA phase; these cannot be observed in bulk samples. The bubbles appear in the films with some time delay after the beginning of illumination. This time delay depends linearly on $(T_{IA} - T)$, where T_{IA} is the smectic A–isotropic transition temperature. This dependence shows that illumination induces in the interior of the films a smectic A–isotropic phase transition. The SmC* in-plane director field configuration depends on the orientation of the polarization plane of the incident light. In the SmC* phase no bubbles are observed even on continuous illumination.

Recently, free-standing smectic films have become of great interest [1–3] because they provide a suitable means to study dimensional cross-over and surface ordering effects. In spite of valuable progress in understanding the behaviour of free-standing films, the properties of photoactive free-standing films have not been studied until now. There are several reasons to expect unusual properties in photoactive free-standing films. In the field of Langmuir films there has been considerable activity on photoinduced optical anisotropy (POA) in films of azo dyes [4–6]. Illumination with polarized light induces an optical axis perpendicular to the polarization plane. At present there are two competing qualitative models of this effect. In refs [5, 6] the POA effect is considered as a result of recrystallization: the light absorbtion induces *trans–cis*-configurational changes. The relaxation of the *cis*-configuration to the ground state (*trans*) occurs in the anisotropic molecular field of non-excited molecules, with an average orientation perpendicular to the polarization plane. This elastic field leads to an orientation of the relaxed molecules in the direction perpendicular to the polarization plane. According to this model, from the mechanical point of view, the orientation effect occurs due to the interaction of the molecules with the substrate. The other model [7] is based on a simple thermal activation mechanism. The absorbed light dissipates in the system and causes a local temperature increase. This local heating activates molecules which can occupy new orientational states.

Free-standing films (FSF) have two free air–liquid crystal boundaries and no substrate. This can qualitatively change the anchoring of molecules and the behaviour of the system on illumination. The massive substrate has two functions in liquid crystal cells: it determines the boundary conditions for the director field and it works as a thermostat in the case of photoactive processes. Therefore measurements of photoactive processes for free-standing films can help to elucidate the mechanism of photoinduced optical anisotropy.

In this paper we report the first study of photoactive free-standing films. We found that the illumination induces bubbles of isotropic liquid. This phenomenon is qualitatively new with respect to the behaviour of the SmA phase in cells. It is interesting that the bubbles were not observed in SmC* films, even on long-term illumination. In the SmC* phase, the illumination induces reorientations of the director field.

We studied a 9 weight% mixture of the dye azo-4: [4-(4-ethylphenylazo)phenyl]nonylamine) [8], and the smectic liquid crystal C7: 4-[(2*S*,3*S*)-2-chloro-3-methylpentanoyloxy]-4-heptyloxybiphenyl. The mixture has the following transition temperatures (°C): I (62) SmA (53) SmC*. The transition temperatures of this mixture were slightly lower with respect to pure C7. Azo-4 has an analogous chemical structure to materials which were studied in Langmuir films in refs [4–6] and absorbs light in the range 400–500 nm. The transition temperature determinations were carried out by optical microscopy using a green filter to avoid heating of the films.

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0267–8292/97 $12·00

Free-standing films with dimensions of $0{\cdot}8 \times 1\,mm^2$ were drawn in a frame consisting of two brass rails and two movable brass blades [3]. Films of a homogeneous thickness were produced in the smectic A phase. Free-standing film properties were studied for a broad range of numbers of layers (from 5 to 1000). The experimental set-up was based on the inverted Olympus-PMG-3 microscope, which enabled simultaneous visual observations (using different optical filters) and reflectivity measurements over the visible region of wavelengths. A 50 W halogen lamp was used for illumination and the films were protected from heating by the green IF550 filter of the microscope. The number of smectic layers was determined by optical diffraction measurements on the smectic A phase as described in [1, 9]. This method allows the exact determination of the number of layers for a wide range of film thicknesses [9]. To study photoactive processes in films we again used the common 50 W halogen lamp of the microscope.

Figure 1 shows the results of illumination of a 100 layer C7 film doped with 9 weight% of azo-4. The illumination induces amorphous bubbles in the SmA phase, which appear with some delay time τ after commencing the illumination. The bubbles disappeared when we reduced the intensity of the illumination below the threshold value I_0 or when we introduced the green filter into the microscope.

Figure 2 shows the linear dependence of τ on $(T_{IA} - T)$. The delay time varied between 2 and 20 seconds over the temperature interval of the SmA phase. On continuous illumination, the bubbles grow and finally lead to the rupture of the film. Therefore it was impossible to study the properties of the bubbles in thin films.

Figures 3 (*a*) and 3 (*b*) show the change of the director field configuration after rotation of the polarizer in the case of the SmC* phase of the mixture studied. These images were recorded with only one polarizer. As was

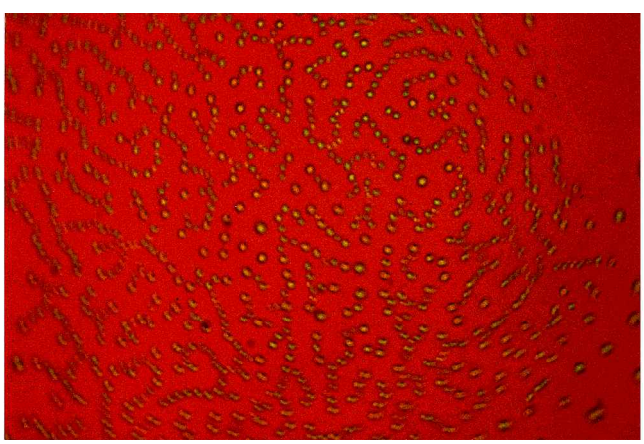


Figure 1. Induction of bubbles in a 100 layer film after 4 s of illumination.

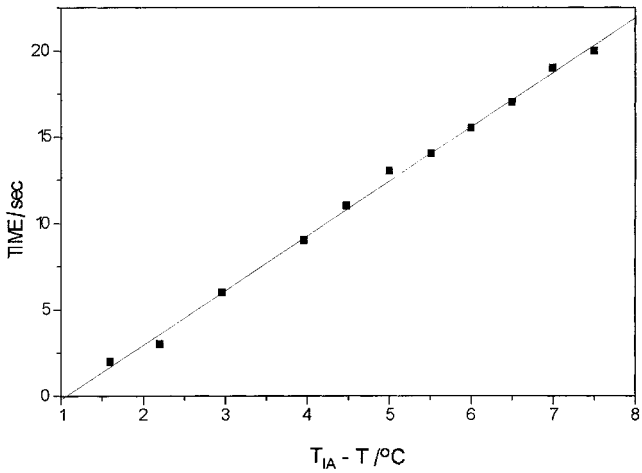
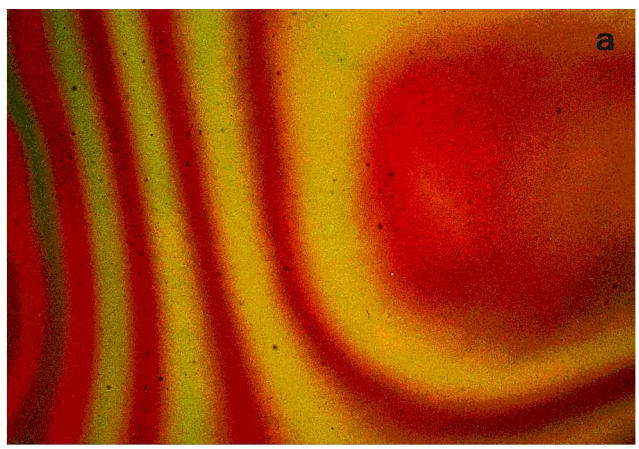


Figure 2. The dependence of the illumination time necessary to induce bubbles on $(T_{IA} - T)$.



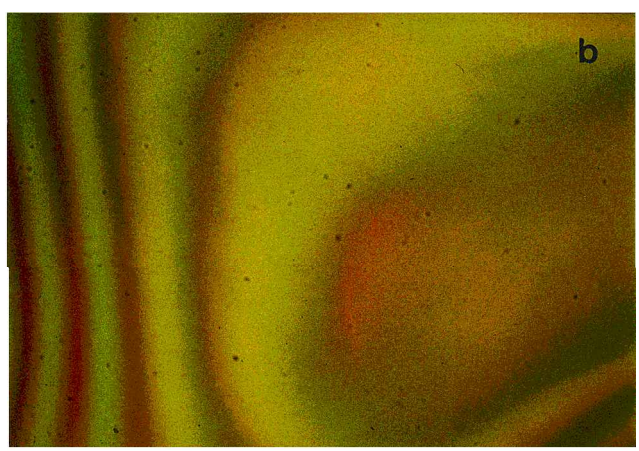


Figure 3. (*a*) The striped state in a 400 layer film after 20 min of illumination; (*b*) the same striped state after rotation of the polarizer by 90 degrees and sealing the sample for 20 min.

shown in [10], the SmC* phase reveals the stripe texture in materials with high enough spontaneous polarization. This texture maps the two-dimensional field of the director projections onto the smectic planes, and conveniently registers the changes in the film structure on illumination. The SmC* phase of the mixture studied shows a striped texture similar to that of pure C7, and figure 3 (*a*) shows the initial state of the 400 layer film texture after 20 minutes of illumination for some fixed direction of the polarizer. After that the polarizer was rotated by 90 degrees and the sample held there for 20 minutes again. The final texture is shown in figure 3 (*b*). The changes of the texture are relatively small, but observable. It is interesting that the bubbles were not induced in the smectic C* phase even in the case of very long illumination. Figures 4 (*a*) and 4 (*b*) show corresponding models of the director field.

The linear dependence shown in figure 2 shows clearly that illumination induces a local melting in the films. Because of the linearity of the curve we assume that the material in the bubbles is in the isotropic state. The light absorption induces *trans–cis*-transitions. The excited molecules relax back to the *trans*-form and the energy difference between the two energetic states dissipates in the system in the form of heat. This experiment demonstrates that the evolved heat is sufficient to induce the SmA–isotropic transition. If the illumination is prologed, the bubbles continue to grow and finally the film will break. The mechanical stability of the films is guaranteed by the better ordered boundary layers. This feature is to some extent similar to the effect of layer thinning of smectic films above SmA–nematic and SmA–isotropic transitions [11, 12], where the interior melting occurs on heating above these transition temperatures.

Figure 5 shows the film cross-section with bubbles inside. The melting of the interior of the films can be explained in two ways: (i) the dye molecules are in some way distributed inhomogeneously across the films; (ii) if the dye molecules are distributed homogeneously across the film, the experiment shows that the boundary layers are really *colder* than the film's interior and need longer illumination times for melting to occur.

In conclusion, we would like to emphasize that the behaviour of dyes in free-standing films is qualitatively different with respect to bulk samples confined between two glass slides. The linear dependence in figure 2 can be explained by a melting of the film's interior, but an alternative explanation is that the illumination of the same film at different temperatures results in different proportions of photochromic molecules being in the excited state and therefore disrupting the smectic order

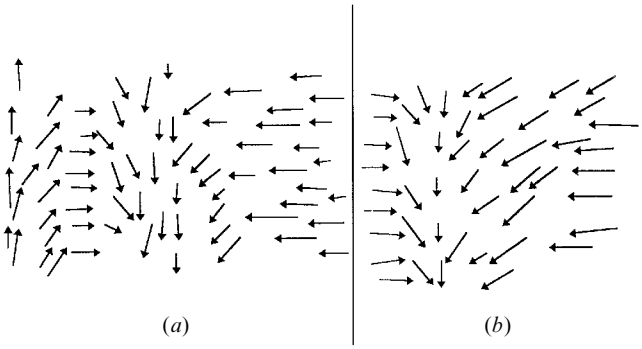


Figure 4. (*a*) and (*b*) present models of the **c** director field corresponding to figures 3 (*a*) and 3 (*b*), respectively.

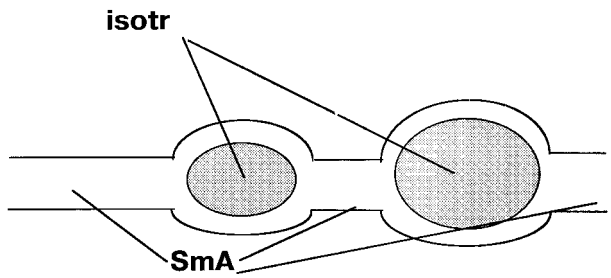


Figure 5. Diagram of the SmA film cross-section.

to varying degrees at different temperatures. More detailed investigation of the mechanism of the bubble formation will be a basis for future work, and it is a surprizing effect that no bubbles could be observed in the smectic C* films. The results of this work clearly show however that the thermal activation mechanism [7] is more plausible.

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