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

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First published on: 21 May 2009

To cite this Article Zhang, Ke , Liu, Na , Twieg, Robert J. and Bos, Philip J.(2009) 'Tuning the sensitivity of a liquid crystal-based chemical/biological sensor using a novel double layer alignment film', Liquid Crystals, 36: 10, 1031 — 1035, First published on: 21 May 2009 (iFirst)
To link to this Article: DOI: 10.1080/02678290902761018
URL: http://dx.doi.org/10.1080/02678290902761018

Liquid Crystals,
Vol. 36, Nos. 10–11, October–November 2009, 1031–1035

Taylor & Francis
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INVITED ARTICLE

Tuning the sensitivity of a liquid crystal-based chemical/biological sensor using a novel double layer alignment film

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(Received 18 December 2008; final form 19 January 2008)

Liquid crystal-based detectors of bio/chemical molecules based on a surface alignment transition of the liquid crystal director have been demonstrated. This type of detector could be made more sensitive if the alignment transition was more abrupt and tunable to be at a 'trigger' point for the desired level of concentration of the target molecule. In this study, we investigate the use of 'double layer alignment films' to cause a more abrupt change in the bulk surface alignment of a liquid crystal-based sensor of lecithin. We show that the detection level of the percentage of lecithin dissolved in the liquid crystal host can be controlled from greater than 4% for a conventional single layer alignment film, to less than 0.1% using the double layer alignment film method. This result verifies an earlier theory, which predicted that a double layer alignment film should provide an abrupt surface alignment transition. The utility of this controllable surface alignment transition as a sensor lies in the anisotropy of liquid crystal materials and the amplification of a detectable signal arising from this anisotropy that results from the alignment of the bulk liquid crystal material in contact with it. For example, the surface alignment change would be expected to cause a large change in capacitance (×2) of a micro-capacitor on an integrated circuit. This work provides a direction for enhancement of liquid crystal-based sensors of other biomolecules, drugs and chemicals.

Keywords: chemical sensor; biosensor; liquid crystal; alignment film; sensitivity; detection limit; fluoropolymer; polyimide; anchoring transition; pretilt; lecithin

1. Introduction

Liquid crystals are easily orientable and anisotropic materials (*1*). The combination of these characteristics makes liquid crystals (LCs) ideal material for sensor applications (*2–8, 12–14*). Many chemical/biological species can induce detectable responses in LCs either by themselves (*12–14*), or more commonly, paired with specially tailored substrates and thin alignment layer films (*2–4, 6–8, 15–18*). This technique has many attractive advantages, such as simple, compact design and label-free detection.

The sensitivity of most LC sensors involves a number of factors, including the interaction between the LC and the surface. When the interaction between the LC and the initial surface (i.e. the surface before exposure to a target species) is very strong, it may be difficult (requiring a high concentration of target molecules) to trigger the orientation change. Therefore, in order to increase the sensitivity, it is crucial to tune the interactions between the LC and the initial surface just above the threshold required for the orientation change. Also, it is desirable for a sensor to have an abrupt change in the orientation of the LC material when the target species is present as shown in Figure 1.

In this paper, we propose and demonstrate a novel double layer alignment film (DLAF) (*19*) to address the issue of sensitivity. We have chosen a surfactant compound, lecithin (*20*), as a target molecule to demonstrate the capability of tuning the sensitivity of the sensor system. Lecithin is the most widespread phospholipid in nature and a major constituent in living cell membranes. There is increasing demand for fast, accurate and inexpensive detection of lecithin due to its relationship with Graves' disease, anaemia, sugar diabetes, nephropathy and hepatocirrhosis. Although we focus here specifically on lecithin detection, our concept can also be applied to other cases where an immobilised receptor is involved.

2. de Gennes' 'local Frederickes Transition' theory

Our approach was to follow the work of de Gennes who showed that DLAFs can be expected to yield an abrupt alignment transition (*9, 10*). In his work, the bottom layer affects LC alignment through a long-range van der Waals force and the top coating layer influences the first molecular layer of LC molecules by short-range (electrostatic and/or steric) interactions.

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ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678290902761018
http://www.informaworld.com

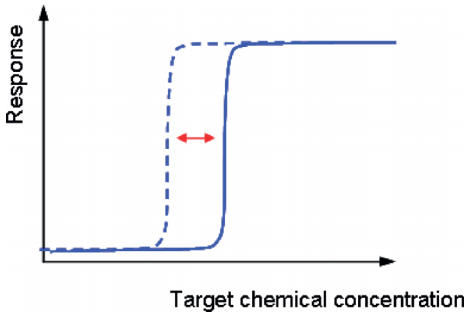

Figure 1. An ideal response of a chemical sensor. A sharp step transition is desired for unambiguous positive/negative detection. The ability to tune the transition point (threshold concentration) is crucial to adjust the sensitivity of the sensor.

The final orientation of LC molecules in the bulk results from a balance between the long-range van der Waals force reaching from the bottom layer and the elastic force due to the surface anchoring of the first molecular layer in contact with the top alignment film. According to the de Gennes 'local Frederiks transition theory' (*9, 10*), the energy of the interface (J m^{-1}) can be written as:

$$F = -\frac{1}{2}A\sin^2\theta_0 + \int_d^\infty \left[\frac{1}{2}U(z)\sin^2\theta + \frac{1}{2}K\left(\frac{d\theta}{dz}\right)^2\right]dz. \quad (1)$$

Here, de Gennes was considering the case where the top layer promotes planar alignment ($\theta_0 = \pi/2$ in his notation), and the bottom layer promotes homeotropic alignment ($\theta_0 = 0$). In Equation (1), A describes the short range anchoring and $\theta_0 = \theta(d)$ is the orientation angle at the interface; $U(z)$ is the van der Waals torque and $U(z) \sim z^{-3}$ when the alignment is uniaxial (*21, 22*). Here, z is the distance between the LC molecules and the bottom layer, d is the top layer thickness, K is an average elastic constant for the particular LC. Either planar or perpendicular anchoring was considered and it is assumed that there is no deformation ($\theta_0 = \theta$) of the LC director orientation to eliminate the elastic energy. Therefore, the formula is simplified to:

$$F = -\frac{1}{2}A\sin^2\theta + \frac{1}{2}\sin^2\theta\int_d^\infty U(z)dz. \quad (2)$$

As can be seen, as θ increases, the first term decreases the energy of the system and the alignment becomes more nearly planar, while the second term increases the energy of the system. Therefore, the first term tends to drive the LC orientation to a planar state, while the second term tends to drive the LC orientation to a homeotropic state. As the second term is dependent on d, we can adjust its value by changing d. When $A \approx \int_d^\infty U(z)dz$, an anchoring transition can occur.

In other words, the thickness of the top layer influences the strength of the van der Waals force at the interface between the alignment film and the LC. Therefore, by adjusting d, the LC alignment states can be changed between planar or homeotropic in a double layer system. de Gennes showed that for these types of alignment layer systems, an abrupt alignment angle transition is expected as d is changed.

3. Experimental

In order to realise de Gennes' theory, we designed a novel DLAF, which consists of two polyimide layers. For the first layer, we selected a common commercial polyimide, Pyralin 2555, which is a copolymer made from benzophenone tetracarboxylic dianhydride (BTDA) and a mixture of the two diamines, 4,4'-oxydianiline (ODA) and m-phenylenediamine (MPD) (see Figure 2 for chemical structures). It is well known that a rubbed 2555 thin film induces

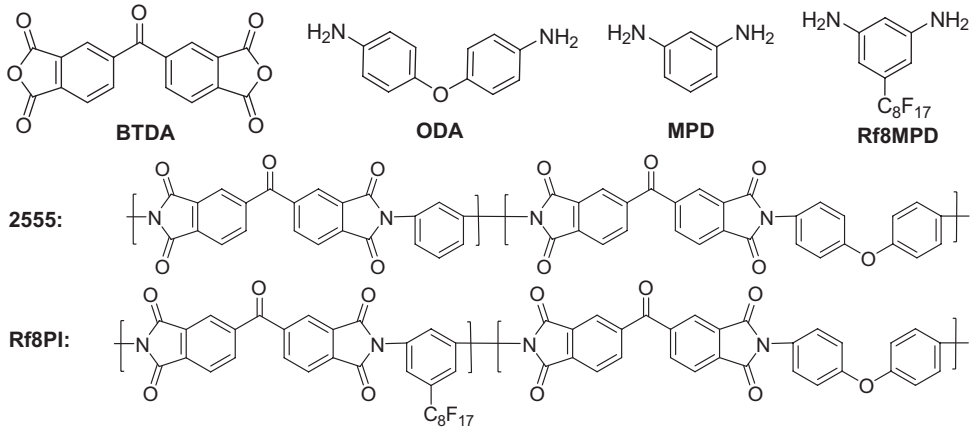

Figure 2. The chemical structures of the 2555, FPI polyimides and their monomeric components.

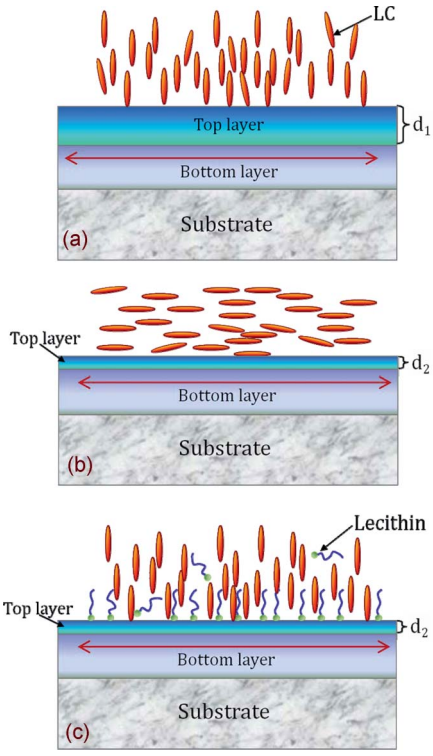

Figure 3. Schematic drawings of various liquid crystal orientations on a double layer alignment film. When the top layer is thick (a), any long-range Van de Waals force from the bottom layer is shielded by the top layer. The result is that the short-range interaction wins and the LC aligns homeotropically. When the top layer is thin (b) any long-range Van de Waals force may overcome the short-range interaction from the top layer, and the LC aligns homogeneously. In (c), the mixture of lecithin (or other chemical species), in low concentrations with the LC may enhance the short-range interaction and again produce a homeotropic trigger anchoring transition if the additive tends to localise at the interface.

strong planar alignment for LCs. We also introduced a second layer, which favours homeotropic alignment of LCs on the top of the 2555 layer. The concept here is to adjust carefully the top layer thickness in order to control the threshold of the final alignment of the LC on the DLAF as illustrated in Figure 3.

As mentioned above, we chose a fluorinated polyimide (FPI) as the top layer material (see Figure 2). The heavily fluorinated side chains of the FPI are expected to reside preferentially on the surface owing to their low polarisabilty, and serve as a source of low surface tension, which favours homeotropic alignment of LC molecules. The backbone structure for this polyimide is similar to that found in 2555 so as to promote wetting and the formation of a uniform double layer structure. Both the homeotropic alignment and the uniform double layer structures have been demonstrated previously in separate experiments (*19*).

We expect planar alignment (the same alignment obtained as for a 2555 single layer alone) when the top layer is not present (created by use of a spin-coating solution where the solids concentration is around 0), and homeotropic alignment when the top layer is continuous and thick enough to shield any influence from the bottom layer, and essentially be treated as a single layer alignment film. Further, we expect the orientation of the LC material will exhibit an abrupt transition as a function of the thickness of the top layer.

To check the above hypothesis, we coated glass substrates with DLAFs, which consist of FPI of different thicknesses on top of the rubbed 2555 layer. The DLAF-coated substrates were assembled into 16 μm-thick sandwich cells with anti-parallel rubbing directions between the top and bottom plates. The LC ZLI 2293 was capillary filled into the cells and the LC alignment was examined between crossed polarisers. We obtained an abrupt anchoring transition from planar to homeotropic alignment as a function of the FPI thickness (proportional to the solids concentration) (*19*). This abrupt transition agrees well with the de Gennes theory and has been observed by others in different systems (*23, 24*).

4. Results and discussion

We tested the response to lecithin of a series of DLAFs of different top layer thickness. We mixed lecithin with ZLI 2293 at several concentrations and filled empty cells coated with a range of different DLAFs. Figure 4 shows the typical LC orientation profile on four DLAF samples, which differ in the solids content of

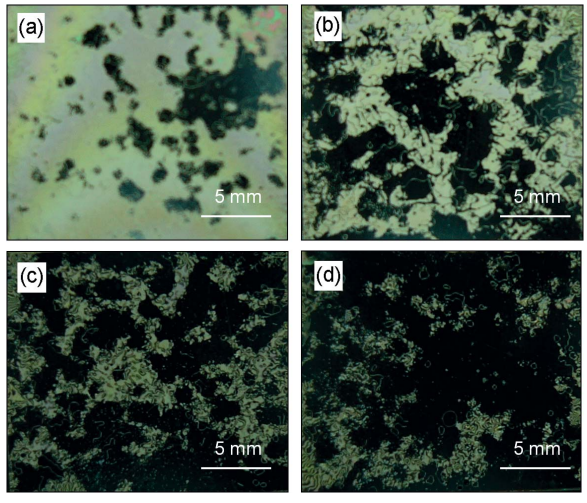

Figure 4. Cell images between crossed polarisers at a fixed lecithin concentration (0.26% in ZLI 2293) while varying the solids content of the coating solution used to create the top layer of the double layer alignment film. (a) to (d) top layer coating concentrations are 0.1%, 0.3%, 0.5% and 0.68%, respectively.

the coating solution and using a single lecithin concentration. When the top layer is thin (e.g. low solids content at 0.10%), most areas of the cell appear bright due to planar alignment. As the top layer gets thicker (increasing solids content: 0.30%, 0.50%, 0.68%), more black regions (i.e. homeotropic alignment) appear. Note that the pictures show a mixture of regions that are aligned homogeneously or homeotropically, rather than showing a uniform area of intermediate pretilt. This demonstrates the abruptness of the alignment transition as predicted by DeGennes. To quantify the effect of the thickness of the top alignment layer, we processed the cell images with a computer program to measure the area ratio between the homeotropic regions to the total area. The relationship between this ratio to lecithin concentration for the different DLAF compositions is plotted in Figure 5.

A cell prepared with a single layer of only 2555 shows no response to the addition of lecithin up to 4% (which exceeds the saturated concentration of lecithin in ZLI 2293). On the other hand, DLAFs with thick top layers (e.g. resulting from 0.68% solids concentration) behave like single layer FPI and show mostly homeotropic alignment at all lecithin concentrations examined. At medium top layer thickness, one can see the orientation transition from planar to homeotropic as lecithin concentration increases. More importantly, as the top layer thickness increases, the critical lecithin concentration for inducing the orientation transition decreases. If we define a

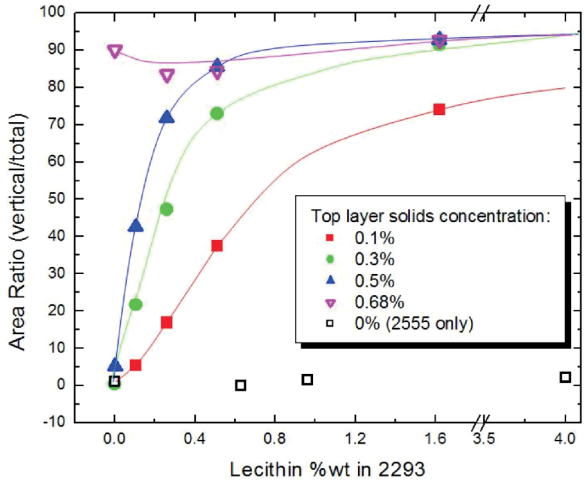

Figure 5. The area ratio of cell images, at top layer solids concentration levels (thickness of the top layer), as a function of dissolved lecithin in the liquid crystal host. The area ratio is defined as the homeotropic area (vertical aligned area) divided by the entire area. The lines in the graph are manually added to connect groups of data points for visual assistance.

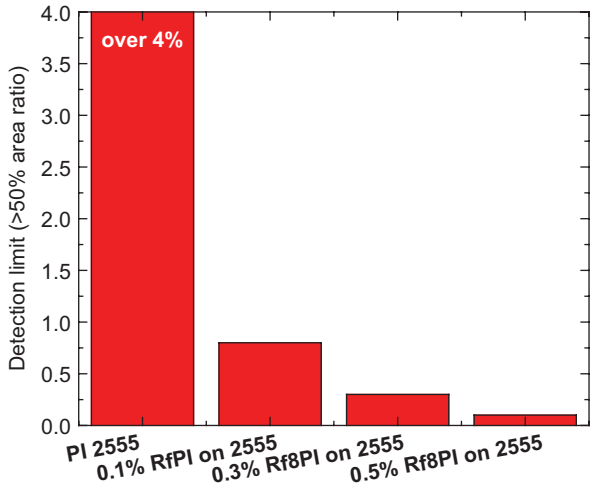

Figure 6. The detection limit of lecithin using different double layer alignment films.

'positive' detection of lecithin as 50% cell area conversion to homeotropic, it is clear this detection limit is reduced dramatically as the DLAF's top layer thickness increases, as shown in Figure 6. For 0.5% DLAF, which is at the boundary for the pretilt transition of pure LC (Figure 1), about 0.1% wt lecithin concentration can be positively detected.

5. Conclusions

In conclusion, we have devised a DLAF to tune the orientation of LCs in sensor applications. The DLAF consists of a thin fluorinated polyimide layer on the top of a rubbed non-fluorinated, polyimide layer (PI 2555). The DLAF has a continuous two-layer structure, where the top layer thickness can be changed (e.g. by adjusting the solids concentration of solutions used for spin-coating). When they act independently, each alignment film produces a distinctive orientation of LC. In DLAF, as the top layer thickness increases, the interaction between the bottom layer and the LC is reduced and as a result, an orientation change occurs. Chemical/bio species can affect this orientation switch by directly interacting with the alignment film, or potentially through specific receptor anchors built into the alignment film in advance. More importantly, we have demonstrated that the sensitivity of the detection can be tuned by adjusting the top layer thickness of the DLAF.

Acknowledgements

This work was supported by DuPont. The authors would like to thank Brian Auman at DuPont for discussions on fluorinated polyimide synthesis.

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