

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Photopolymerization induced orientation transition in a nematic liquid crystal cell

Zili Li^a

^a Science Center, Rockwell International Corporation, Thousand Oaks, California, U.S.A.

To cite this Article Li, Zili(1995) 'Photopolymerization induced orientation transition in a nematic liquid crystal cell', *Liquid Crystals*, 19: 3, 307 – 311

To link to this Article: DOI: 10.1080/02678299508031984

URL: <http://dx.doi.org/10.1080/02678299508031984>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Photopolymerization induced orientation transition in a nematic liquid crystal cell

by ZILI LI†

Science Center, Rockwell International Corporation, Thousand Oaks,
California 91360, U.S.A.

(Received 30 November 1994; accepted 14 February 1995)

We report the observation of a liquid crystal tilt transition from homeotropic to planar orientation induced by photopolymerization of the alignment layer in the absence of liquid crystal. The alignment agent is a unique, polymerizable lecithin (DC₂₃PC), which induces homeotropic alignment before UV exposure. After non-polarized UV exposure, a tilted orientation is obtained. Moreover, further buffing of the UV treated substrate yields a homogeneous alignment. We believe that the conformation change in the lecithin array caused by solid state polymerization is primarily responsible for the transition. These results help to explain the mechanism of liquid crystal alignment and will lead to several potential applications.

1. Introduction

Liquid crystal alignment is important to both fundamental and applied liquid crystal research. Recently, activity in this area has substantially increased because of its relevance to basic interfacial physics and its importance to liquid crystal displays [1, 2]. The alignment is typically achieved by coating the substrates with alignment agents so the liquid crystal interacts directly with the alignment agents. The anisotropic nature of both the alignment agent and the liquid crystal results in a number of potential liquid crystal orientations, the most common being the homeotropic and homogeneous alignments. In the former, the substrates are often coated with surfactant molecules or others of similar nature, such as lecithin. This usually results in an orientation of liquid crystal perpendicular to the substrate. For the latter, the common alignment method is to coat the substrate with a type of polymer (typically polyimide) which tends to yield an orientation in which the liquid crystal molecules lie down on the substrate (planar orientation). Subsequent rubbing of this surface results in a monodomain alignment: namely, the liquid crystals align along the rubbing direction (homogeneous alignment). Even though the mechanism of the liquid crystal alignment has been widely studied, it is not yet completely understood. For some applications, a reliable and simple method to generate a large pretilt angle is highly desirable.

To date, the most common method for producing high pretilt (above 10° from the substrate) used a rubbed polyimide (PI) film or obliquely deposited SiO [3]. The SiO method is costly. The rubbed PI approach involves

attaching side groups on the PI backbone and buffing with low rubbing strength (RS) [4]. Thus far, this approach, which has basically evolved from using rubbed low-pretilt PI, has not been highly reproducible. The fundamental problem is that, like any molecular system with high aspect ratio such as PI, these molecules tend to lie down in the plane of the underlying substrates. The high surface tension of PI, in turn, favours planar orientation of the liquid crystal. These properties of PI are inevitably exploited to produce a planar orientation.

Homeotropic alignment is typically obtained by using alignment agents that have polar head groups and long alkyl chains, such as various surfactants and lecithins. As a result, these molecules orient perpendicular to the substrate with the polar head groups attached to the substrate. The surface tension of the surfactant is usually smaller than that of the liquid crystals, which favours a homeotropic liquid crystal alignment. If we can somehow make a conformational change in the alignment array structure, a high pretilt alignment might be produced from the original homeotropic alignment. This is the main motivation of this study.

Recently, the alignment induced by polarized UV radiation of alignment layers has attracted considerable attention due to the possibility of developing a rubbing free liquid crystal alignment process [5, 6]. For example, Sun and his co-workers at Hercules have achieved photoalignment by incorporating dye into either the liquid crystal or alignment layer [7]. The focus has been mainly on the planar orientation and the orientation change is limited to the alignment in the substrate plane. Ichimura *et al.* have observed that UV radiation of 365 nm induces a tilt transition from homeotropic to planar orientation [8]. In

† Electronic mail: zli@scimail.remnet.rockwell.com

their case, the *trans*-*cis* isomerization induced by the ultraviolet radiation causes the transition, and the transition can be reversed by visible wavelength radiation. This leads to the conclusion that the system is only orientationally bistable and potentially unstable in ambient light.

In this paper we report that the tilt transition from homeotropic to planar orientation can be induced by photopolymerizing the lecithin alignment layer in absence of liquid crystal. Moreover, subsequent buffing of the UV treated lecithin layer induces homogeneous liquid crystal alignment. Conversely, buffing of a non-UV-exposed lecithin layer does not affect its original homeotropic alignment characteristics. We believe that the conformation change in the lecithin array caused by solid state polymerization is primarily responsible for the transition. These results help to explain the mechanism of liquid crystal alignment and indicate that the steric interaction between liquid crystal and the aligning agent plays a major role in the alignment mechanism. By changing the experimental parameters, such as intensity of the UV radiation and rubbing strength, control of the tilt angle is possible.

2. Results

In our study, 1,2-bis(10,12-tricosadiynol)-*sn*-glycerol-3-phosphocholine (DC₂₃PC or DC_{8,9}PC) was used as the alignment agent. This phospholipid, which was first synthesized at the Naval Research Laboratory about 10 years ago, is known for its formation of a tubular structure [9] and possesses unique structural properties. The main difference between this and other lecithins is that in the middle of both alkyl chains are diacetylene groups (see figure 1). When exposed to short wavelength UV or more energetic radiation, the diacetylene groups will undergo a 1,4-addition polymerization. In this study we investigated the effect on liquid crystal alignment due to the polymerization of this lecithin.

Our main experimental results came from comparing the liquid crystal alignment on two types of substrates: first, substrates treated with this lecithin (DC₂₃PC) only; and second, substrates exposed to the unpolarized UV radiation after coating with DC₂₃PC. Furthermore, to see the effect of rubbing, we designed a two-region or split liquid crystal cell consisting of substrates having two regions on the same slide, one region with rubbing and the other without rubbing (see figure 2). This type of cells allowed evaluation of both UV exposed and unexposed cells under conditions with rubbing and without rubbing.

The DC₂₃PC material used in our experiment was directly purchased from the vendor (Avanti Polar Lipids, Inc.) and used as is without further purification. 15 mg DC₂₃PC was dissolved in 30 ml reagent grade chloroform. The indium-tin oxide (ITO) coated glass slide was

cleaned thoroughly by a process which included detergent + sonication and acetone + sonication. An alignment layer was formed by dipping the substrate (2 cm × 2 cm in size) in the solution several times. Visual inspection after coating revealed quite uniform coating on the slide. However, we did not observe the characteristic colour change associated with this polymerization, which indicates that the film coating is quite thin [9]. After coating, the substrates were put inside an N₂ chamber for at least a 1 h purge. To avoid unnecessary UV exposure,

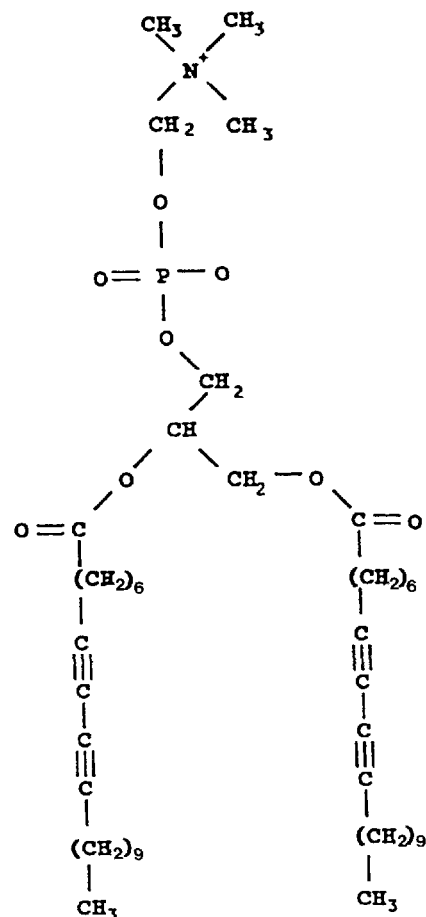


Figure 1. Molecular structure of DC₂₃PC molecules. Polymerizable diacetylene groups occur on both branches of the alkyl chains.

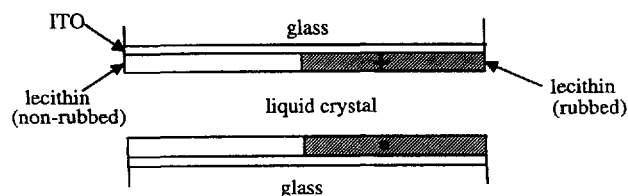


Figure 2. Schematic of the cross section of the two-domain liquid crystal cell. The rubbing direction is indicated by the cross (inward) and the dot (outward).

the whole experiment was performed under yellow illumination.

One set of substrates was further irradiated with unpolarized UV radiation. Two types of UV sources were used: a single band source of 365 nm and a broad band source from an Oriel 100 W mercury lamp. The light from the broad band source was collected by a condenser lens and the intensity at 254 nm on the substrate was measured using a calibrated UV power meter to be 15 mW cm^{-2} . The different exposure times were tested and results in this paper are limited to total exposures exceeding 15 J cm^{-2} . On both types of substrates (UV exposed and non-exposed), one half of the surface was subsequently hand rubbed unidirectionally using a clean room paper without touching the other half of the surface (see figure 2).

Finally, the cells were assembled with the rubbing directions antiparallel. The cell spacing in these experiment was set at approximately $7.5 \mu\text{m}$ by a pair of mylar spacers. The cells were filled with eutectic mixture liquid crystal E7 or single compound liquid crystal CCN-47, both purchased from E. Merck. The filled cells were never exposed to UV radiation to avoid possible photochemical reaction in the contained liquid crystals. The alignment and the tilt angle were determined by both polarizing microscopy and crystal rotation measurement.

Perfect homeotropic alignment was achieved in both rubbed and non-rubbed regions of the cells that were not exposed to UV radiation. Under the polarized microscope, no difference was observed between the rubbed and the non-rubbed regions of the same cell (see figures 3 (a) and 3 (b)). This observation agrees with our previous experimental results using cells consisting of substrates coated with regular, non polymerizable lecithin ($\text{L-}\alpha\text{-lecithin}$, type X-E purchased from Sigma). Buffing of the substrates coated with various concentrations of this lecithin had no effect on the alignment. Homeotropic orientation was always obtained.

The liquid crystal alignment for UV irradiated cells was changed totally (see figure 3 (c)). A tilted multidomain structure resulted on the non-rubbed region of the cell (left-hand region in the photo). Polarizing microscopy indicates a planar orientation. Very good homogeneous alignment was achieved in the rubbed part of the cell (right-hand region of the photo), with the nematic director aligned in the rubbing direction. To precisely determine the pretilt angle, the standard crystal rotation measurements were performed with the laser beam focusing on the rubbed part of the cell. The results are shown in figure 4 and the measured tilt angle is $(0 \pm 0.5)^\circ$. These results seem to be independent of dipping times for this concentration of solution.

The polymerization of diacetylene has long been known to be wavelength dependent, and this dependence is

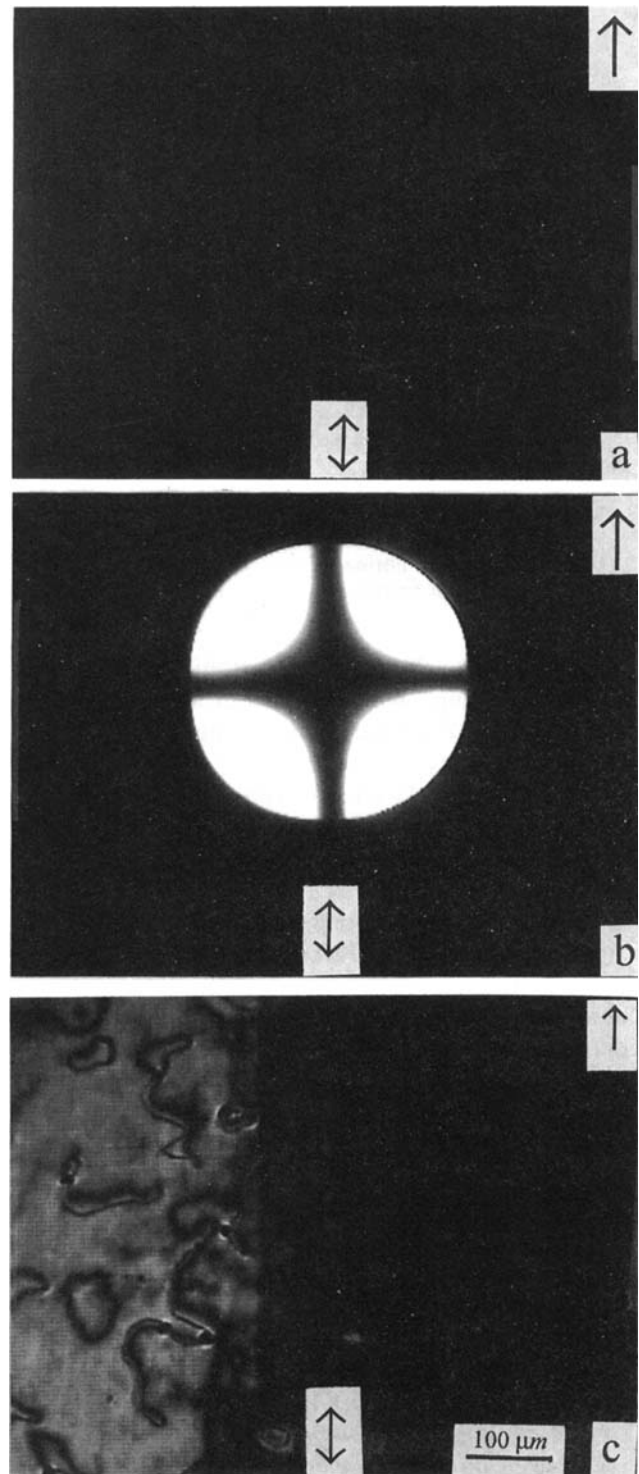


Figure 3. Microscopic photographs of the observed transition. All three photos are taken at the boundary line (double arrow in the photos) between the rubbed region (single arrow indicating the rubbing direction) and non-rubbed region (left side in the photo) of the cell (see figure 2). (a) The non-UV exposed substrates; (b) the conoscopic figure of figure 3 (a); (c) the UV exposed substrate. The polarizer direction is parallel to the boundary line.

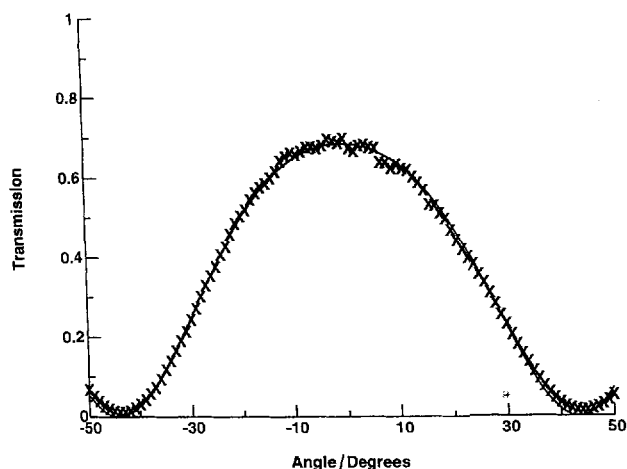


Figure 4. Pretilt angle measurement result on UV exposed and subsequently rubbed cell. The plot is normalized transmitted intensity versus incident angle between laser beam and substrate normal. Cross: experimental data; solid line: best fit with pretilt angle being zero.

related not only to the diacetylene itself but also to the attached side groups, with the onset of absorption being near 300 nm [10]. For this compound long wavelength UV will not cause polymerization [9, 10]. To test that we indeed are observing the effect of a polymerization process rather than some other spurious effect, such as heating, a long wavelength UV source of 365 nm was used to radiate the substrate at an intensity of 19 mW cm^{-2} for more than 30 min. There was no orientational change of the liquid crystal in these cells. Also, for this lecithin, there is a chain melting temperature, T_m , above which the photopolymerization will not occur [9]. The T_m for this is 40°C . Our experiment was performed at room temperature to assure that we did not exceed T_m .

The discussion turns now to the mechanism of this observed transition. Without a molecular level microscopic probe, the detail of the final conformation of the lecithin array is difficult to pinpoint, but some mechanisms can definitely be ruled out. Lecithin has low surface tension, which tends to favour homeotropic alignment. Given that the process here is solid state polymerization and that the alkyl chain is flexible, the surface tension is unlikely to undergo much change. E7 is noted for its high polarity, but lecithin induces homeotropic alignment for all types of liquid crystals, polar or non-polar alike [11, 12], so the dipolar interaction is not the cause. Another possibility is that after UV radiation there is an increase in ionic concentration which could in turn change the electric double layer, which is responsible for some observed tilt transitions [13, 14]. This is also unlikely. To further illustrate this argument, we used the second material CCN-47, which has a very large negative dielectric anisotropy, $\Delta\epsilon \approx -8.5$ at 40°C . Not surpris-

ingly, the same results were obtained. By comparing all the possible scenarios which could occur with the range of test parameters we conclude that the electric double layer that may result from ionic impurities is not critical to the observed alignment transition. Moreover, neither is the nature of this polymerization likely to cause any significant change in the ionic concentration.

The above discussions leave us with the conformation change in the array of the lecithin after polymerization as the most plausible explanation of the observed transition. The reduction of the alkyl chain length and the tilting of the array or the combination of both effects will contribute to this transition. The structure of this lecithin suggests the following scenarios. The polymerizable groups are located in the middle of alkyl chains. After the polymerization, the chain length is effectively reduced by half and as the length is reduced, the aligning power is also reduced. The commercial lecithins used for homeotropic alignment have more than 15 carbons on each chain [11, 12]. This suggests that there is a threshold carbon length for homeotropic alignment, which is likely to be larger than 10. This 'magic number' seems to be also applicable to other homeotropic alignment agents [11]. The tilt of the array is another possibility. Solid state polymerization will involve the bond rotation as illustrated in [10]. Conceivably the resulting array will be reoriented following the polymerization and this will in turn induce non-homeotropic alignment. Recently, Lando *et al.*, [15], studied Langmuir–Blodgett films formed by these molecules and found that the chains orient at an angle of $\approx 30^\circ$ from the layer normal. Unfortunately, no such experiment, to the best of our knowledge, has been done on polymerized films of this material [16].

A comparison of the alignment of liquid crystals using the oblique deposition of SiO and the polymerizable lecithin as in our experiment is interesting. The alignment of liquid crystals using obliquely deposited SiO substrate has been shown to be due to the formation of the tilted SiO columns through self-shadowing [17]. The alignment depends on 'lattice constants' of the columns. Given the similar ratio of a/d (a : width of the column, d : the period of the array) for our case and the SiO, the minimum column length for the SiO is at about 50 \AA . Below this threshold the homeotropic alignment will not occur [18]. For our case, the length changes from about 40 \AA before, to about 20 \AA after polymerization. Moreover, the SiO inherently aligns liquid crystals in a planar fashion. Our results agree very well with this picture. Again, the dominant role is the steric interaction or geometric factor.

3. Conclusions

In conclusion, we observed a polymerization induced tilt transition from homeotropic to planar orientation. The mechanism for this transition is the conformation change

in the alignment array caused by the photopolymerization. Both shortening and tilting of the array could induce this transition. Microscopic probes such as STM, or AFM can verify this condition. We also expect that the anchoring strength will change due to the conformational change, which we intend to investigate. This will help us to further understand the origin of the transition. Other areas for further investigation include the dependence of the tilt angle on the polarization and intensity of UV, the rubbing strength. Furthermore, the modification of the structure of the monomer will definitely impact this photopolymerization induced alignment. This potential new way to control liquid crystal tilt angle can be of considerable importance to some applications.

The author benefited greatly from the fruitful discussions with Bruce Winker, Gene Koch, Bill Gunning, Jero Lando and C. Rosenblatt. Don Rizzi and Leonard Hale helped with the tilt measurement and Dave Bernard provided the UV power meter. Their assistance is greatly appreciated. This work was supported by Rockwell Independent Research and Development Funds.

References

- [1] JEROME, B., 1991, *Rep. Prog. Phys.*, **54**, 391.
 [2] UCHIDA, T., and SEKI, H., 1990, *Surface Alignment of Liquid Crystals in Liquid Crystals: Application and Uses*, edited by B. Bahadur (World Scientific, Singapore).
 [3] JANNING, J. L., 1972, *Appl. Phys. Lett.*, **21**, 173.
 [4] ISOGAI, H., 1993, *Display and Imaging* (in Japanese), **1**, 211.
 [5] SCHADT, M., SCHMITT, K., KOZINKOV, V., and CHIGRINOV, V., 1992, *Jap. J. appl. Phys.*, **31**, 2155.
 [6] MARUSII, T. YA., and RENIKOV, YU. A., 1993, *Molec. Mater.*, **3**, 161.
 [7] GIBBONS, W. M., SHANNON, P. J., SHAO-TANG SUN, and SWETLIN, B. J., 1991, *Nature*, **351**, 49; SHAO-TANG SUN, GIBBONS, W. M., and SHANNON, P. J., 1992, *Liq. Crystals*, **12**, 869; CLARK, M., 1991, *Physics World*, p. 21.
 [8] ICHIMURA, K., SUZUKI, Y., SEKI, T., HOSOKI, A., and AOKI, K., 1988, *Langmuir*, **4**, 1214.
 [9] YAGER, P., and SCHOEN, P. E., 1984, *Molec. Crystals liq. Crystals*, **106**, 371.
 [10] WEGNER, G., 1977, *Pure appl. Chem.*, **49**, 443.
 [11] COGNARD, J., 1982, *Molec. Crystals liq. Crystals, Suppl.*, **1**, 1.
 [12] HILTROP, K., HASSE, J., and STEGEMEYER, H., 1994, *Ber. Bunsenges. phys. Chem.*, **98**, 209.
 [13] BARBERO, G., and DURAND, G., 1990, *J. appl. Phys.*, **67**, 2678.
 [14] NAZARENKO, V., and LAVRETOVICH, O., 1994, *Phys. Rev. E*, **49**, R990.
 [15] LANDO, J. B., and SIDIWALA, R. V., 1990, *Chem. Mater.*, **2**, 594.
 [16] LANDO, J. B., 1994, private communication.
 [17] GOODMAN, L., MCGINN, J. T., ANDERSON, C., and DIGERONIMO, F., 1977, *IEEE Trans. Electr. Dev.*, **24**, 795.
 [18] HIROSHIMA, K., and MOCHIZUKI, M., 1980, *Jap. J. appl. Phys.*, **19**, 567.