Liquid Crystals

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

Atomic force microscopy characterization and liquid crystal aligning effect of polymerizable diacetylene Langmuir Blodgett films

Dong-Feng Gu[a][b]; Charles Rosenblatt[a]; Zili Li[c]

[a] Department of Physics, Case Western Reserve University, Cleveland, Ohio, U.S.A. [b] Science Center, Rockwell International Corporation, [c] Science Center, Rockwell International Corporation, Thousand Oaks, California, U.S.A.

To cite this Article Gu, Dong-Feng , Rosenblatt, Charles and Li, Zili(1995) 'Atomic force microscopy characterization and liquid crystal aligning effect of polymerizable diacetylene Langmuir Blodgett films', Liquid Crystals, 19: 4, 489 — 496

To link to this Article: DOI: 10.1080/02678299508032010

URL: http://dx.doi.org/10.1080/02678299508032010

LIQUID CRYSTALS, 1995, VOL. 19, NO. 4, 489–496

Atomic force microscopy characterization and liquid crystal aligning effect of polymerizable diacetylene Langmuir Blodgett films

by DONG-FENG GU† and CHARLES ROSENBLATT*‡
Department of Physics, Case Western Reserve University, Cleveland,
Ohio 44106, U.S.A.

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

(*Received 16 December 1994*)

The surface topology of polymerizable diacetylenic lecithin Langmuir Blodgett (LB) films deposited on indium–tin oxide (ITO) coated glass substrates has been investigated using atomic force microscopic (AFM) techniques. The liquid crystal alignment effect of the LB films was compared to that of the random film formed by dipping the ITO glass into chloroform–lecithin solution. The orientation of a nematic monodomain based on these substrates was changed from homeotropic to tilted upon ultraviolet (UV) irradiation, and a planar alignment was achieved if the substrates were UV treated and buffed. AFM pictures reveal that the substrate surface corrugation is decreased by both random coating and LB film coating before photopolymerization. After UV irradiation, some unique star-like features were found on the monolayer LB film. These features provide evidence that the conformation of the diacetylene chains has been changed due to the photopolymerization, thus causing the liquid crystal orientation to undergo a transition from homeotropic to tilted alignment.

1. Introduction

The nature of the substrate surface is the dominating factor in liquid crystal alignment. With the ubiquitous applications of liquid crystal displays, much effort has been made toward a complete understanding of the mechanism of alignment at the molecular level. In practice, rubbed polyimide-coated substrates are usually used to provide an orientation in which the liquid crystal molecules are parallel to the surface (planar). For the homeotropic alignment, the substrates are often coated with a layer of surfactant, resulting in a perpendicular orientation of the liquid crystal director with respect to the cell surface. Nevertheless, it is quite difficult to control the interface at the molecular level using rubbing or random film coating methods.

Recently, the orientation induced by depositing on the substrate a polymeric monolayer or polymeric LB film has attracted considerable interest [1–9]. In LB film deposition, the amphiphile molecules are introduced on to surfaces in a molecularly controlled manner, facilitating a high quality and rub-free liquid crystal alignment. Most of these works, however, have focused on LB application of a polyimide film as the aligning surface. The mechanisms of the alignment of these films have been investigated using scanning electron microscopy (SEM) [10, 11], Fourier transform infrared spectroscopy (FTIR) [12], transmission electron microscopy (TEM) [12], scanning tunnelling microscopy (STM) [11], and atomic force microscopy (AFM) [13] techniques, revealing that the molecular arrangement in LB films is responsible for the liquid crystal alignment. Like any molecular system with high aspect ratio, polyimide molecules tend to lie down in the plane of the underlying substrate and are oriented by the dipping process. Therefore, the alignment direction tends to be along the dipping direction. Manipulation of the LB film properties at the molecular level provides opportunities to alter the tilt angle. Besides dipping, polarized UV radiation of the LB film also can be used to induce alignment parallel to the substrate [14, 15]. Ichimura *et al.* [2], observed that UV irradiation of a LB monolayer of an azobenzene side-chain amphiphilic polymer at wavelength $\lambda = 365$ nm induces a tilt transition from homeotropic to planar orientation. Moreover, the transition can be reversed by further irradiation at visible wavelengths [2]. The mechanism of the transition was

---

* Author for correspondence.

† Current address: Science Center, Rockwell International Corporation.

‡ e-mail address: cxr@po.cwru.edu.

found to be the *trans-cis* isomerization induced by the photoexcitation. The magnitude of the change in the tilt angle depends on the azobenzene packing density. Such a photofunctional surface provides a new way of tailoring at molecular level the liquid crystal aligning behaviour of the substrate surface, and has been named by Ichimura *et al.* [2], as 'command surface'.

It is well known that diacetylene monomers can undergo topochemical polymerization in the solid state initiated by radiation (UV or γ-ray), heat, or stress [16–18]. For example, 1,2-bis(10,12-tricosadinol)-sin-glycerol-3-phosphocholine ($DC_{23}PC$ or $DC_{8,9}PC$) is a diacetylene with a hydrophilic head and two hydrophobic alkyl tails, both of which have diacetylene groups in the middle. This material was first synthesized at the Naval Research Laboratory and is well-known for its formation of a tubule structure in water [19]. When this phospholipid is deposited at an air–water interface at sufficiently high packing density, the molecules will be oriented vertically, with head groups at the interface and the tails pointing away from the interface. In the dipping procedure, a layer of LB film is deposited on to the substrate during the drawing action, so that the diacetylene heads attach to the substrate and the tails maintain the same conformation as on the water surface. The vertically aligned tails point outward from the substrate, thereby forming 'molecular brushes', a good candidate to align liquid crystal molecules homeotropically. Upon UV irradiation, the diacetylene groups undergo a 1–4 addition polymerization. As a result of this process, the alkyl tails—which have now become side-chains—have a tilt of about 30° with respect to the normal to the plane of the film [20]. This change in the molecular conformation induced by the photopolymerization presumably will alter the surface aligning character, and will be discussed in more detail below. A large tilt of the liquid crystal molecules away from the original homeotropic state is thus expected. Li [21] recently reported that a transition from homeotropic to planar alignment was induced on substrates coated with random film of $DC_{23}PC$ upon short-wavelength UV irradiation.

Due to its subnanometer resolution and non-invasive character, atomic force microscopy (AFM) has been used to image the LB films [13, 22–24], including those formed by unpolymerized diacetylenes [25]. In this paper, we report on investigations of the effect of the topological characteristics of the polymerizable phospholipid monolayer using AFM technique, and study its alignment effects on liquid crystals both with and without photopolymerization. We have three concerns: (i) the difference between polymerized and unpolymerized surfaces; (ii) the mechanism of the liquid crystal alignment transition induced by the photopolymerization; and (iii) the influence of processing conditions such as dipping speed.

2. Experimental

The $DC_{23}PC$ material used in our study was purchased from Avanti Polar Lipid Inc. and used as is without further purification. This $DC_{23}PC$ was dissolved into reagent grade chloroform to form a 0·5 mg ml^{-1} solution. Before and after the dissolution, the sample was refrigerated in a dark environment. The ITO coated glass slides (2 cm × 3 cm in size) were cleaned sequentially with a detergent, acetone, and ethanol in a sonificator. The ITO substrates were then dried in a vacuum chamber for a duration > 10 h.

Preparation of the diacetylene LB film was carried out in a Class 100 clean room facility with Class 10 work stations. A Lauda film balance was used to deposit the $DC_{23}PC$ molecules on to substrates to form LB films. The trough was cleaned with acetone and rinsed with Milli-Q water, and then completely filled with Millipore water (18 mΩ cm^{-1}). The $DC_{23}PC$ solution was gently applied to the water surface, facilitating formation of a Langmuir film. 5 min elapsed before compression of the diacetylene film to allow the chloroform to fully evaporate. The water temperature was maintained at 20°C. A floating Teflon barrier attached to a linear variation differential transducer was computer controlled to perform the compression of the film, and to keep the film at a constant surface pressure of 30 dyne cm^{-2} during the dipping process. The area compression rate was 30 cm^2 min^{-1}. The isotherm (pressure/density curve) was quite typical, with the surface pressure starting to increase sharply at a surface molecular density of 45 Å^2/molecule and collapsing at 30 Å^2/molecule [26]. Several dipping speeds were used. The transfer ratios of these dippings were determined by measuring the area of the substrates and the reduction in the area of the free-standing diacetylene monolayer on the water surface. The influence of dipping speed on the liquid crystal alignment will be discussed later. We found that the diacetylene molecules are *only* deposited on to the ITO substrate upon withdrawal of the substrate from the water (a Z-type fashion), similar to the case of using a bare clean glass slide. Considering the fact that the transfer ratio we measured ranges from 0·95 to 1·15, one monolayer was added to the substrate in each withdrawal action. When the number of layers increased beyond four, some $DC_{23}PC$ deadsorbed upon reimmersion, such that the layers took on a patchy appearance under the microscope. The drying time between consecutive dippings was 10 min. For studying *random* films, the ITO substrate was simply dipped into diacetylene/chloroform solution and withdrawn from it four times.

A narrow band UV lamp of intensity 1500 μW cm^{-2} at wavelength = 254 nm was used in the photopolymerization. The substrate and the lamp were placed in a box which was continuously purged with dry nitrogen gas, and the UV illumination time was approximately 10 min.

During UV exposure, care was taken to prevent overheating of the sample, since the chain melting temperature of $DC_{23}PC$ is about 42°C. The substrates were spaced with 10 μm diameter glass beads, and were glued together with 5 min epoxy. The nematic liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl (5CB) was introduced into the sample cells by capillary action in the isotropic phase, at approximately 36°C.

Alignment of the liquid crystal was observed using an Olympus polarizing optical microscope. The absorption spectra in the visible wavelength range of the LB film were measured using a Varian visible spectrometer (model Cary-1). AFM experiments were performed with a Nanoscope III microscope from Digital Instruments. The scan head had a maximum range of 15 μm × 15 μm. All AFM images presented in this paper were obtained using the constant-deflection mode and with the substrates in air at room temperature. A 100 μm triangular wide-leg cantilever of spring constant $0{\cdot}58\,\mathrm{N\,m^{-1}}$ was used, and typical contact forces were about 10 nN. Some grooved topological features in our experiments occurred if the force was higher than 15 nN, indicating that the surface structure was disturbed by the probing tip. Each image was completed within 8 min, at scan rates ranging from 1 to 4 Hz, depending on the scan size.

3. Results and discussions

The substrates used in this study were ITO coated glass slides. To examine the topological features of the LB film, we first scanned the bare ITO substrates. The surface of the bare ITO coated glass is rougher than we expected. As shown in figure 1, in an area about 0·8 μm × 0·8 μm, there are typically about 10–12 ‘hills’ with heights of 10–15 nm. Note that the length scale in the z direction in AFM images is different from those in the x and y directions. Nevertheless, the roughness can provide a reference for information about the packing of the diacetylene molecules on ITO surface. After a layer of $DC_{23}PC$ was deposited on to the ITO substrate, the surface became much smoother. In figure 2, a typical AFM image of the diacetylene LB monolayer before polymerization is shown. As with figure 1, such a landscape is characteristic of the entire film. The dipping was along the vertical direction as indicated by the arrow, and the dipping speed was $5\,\mathrm{mm\,min^{-1}}$. As evidenced in figure 2, the characteristic ‘hills’ seen in figure 1 either disappear or diffuse into the background. We suspect that the diacetylene molecules may be packed vertically on those relatively flat areas; and, on those areas where ‘hills’ appear the diacetylene molecules do not readily ‘stand up’ because of the tilted surface with respect to the plane of the substrate. Therefore, the homogeneity of the packing of diacetylene degrades on those hilly areas of the bare ITO substrate, rendering the overall surface flatter. This decrease in the surface corrugation caused by coating of the LB film is consistent with other results reported in the literature [7, 25].

The UV polymerized monolayer LB film on ITO surfaces shows several unique features. Figure 3 exhibits the image of a monolayer LB film on ITO, where figure 3 (*a*) shows the unrubbed and figure 3 (*b*) shows the rubbed film. The dipping direction and the dipping speed are the same as specified for figure 2. In figure 3 (*a*), the presence of the star-like features is quite evident, and is clearly a result of the photopolymerization of the diacetylene LB film. As described earlier, the UV induced polymerization takes place via a 1–4 addition process. This heterogeneous topological reaction requires that the distance between reacting neighbour diacetylene molecules is less than approximately 4 Å [26, 27]. Therefore, the degree of packing greatly influences the conversion of the diacetylene monomer into polymer. Packing may be influenced, for example, by the already polymerized part which has a monoclinic symmetry and a tilt of the side-chain axes. This tilting will induce stress within the film and disrupt the uniformity of the packing of the unpolymerized part. The thermal fluctuation and mechanical vibration in the dipping process may also create some defects in the LB film. Moreover, as the process of polymerization leads to a molecular tilt, the tilting is likely to be co-operative in nature and a given region will take on a tilt in some arbitrary direction [20], provided that the substrate is ideally flat and the packing is perfect. Based on electron diffraction results and modelling, Lando and Sudiwala [26] proposed that the probable propagation of polymerization was along the diagonal direction of the unit cell. However, our substrate is ‘bumpy’ and the packing is not perfect, and thus the polymerization will be similar to recrystallization process with the presence of many nuclei: the polymerization happens at some nucleation sites first and then propagates along directions determined by surface topological characters. As a result, polycrystalline domains will be formed, with a different molecular tilting direction in each domain. The appearance of the star-like topological features seems to support the above reasoning. Also, as evidenced by electron [28] and optical microscopy pictures [29], two-dimensional domain structures may form during spreading and compression of the diacetylene monolayer and remain unchanged during dipping and polymerization unless an excessive dipping rate is used [30]. However, our AFM investigation of the $DC_{23}PC$ LB film did not indicate any formation of the star-like domain structure prior to the polymerization.

Under the influence of an adequate friction force, the orientation of these domains is likely to be biased along one direction. This was indeed observed on the substrate coated with polymerized LB film and then hand-rubbed

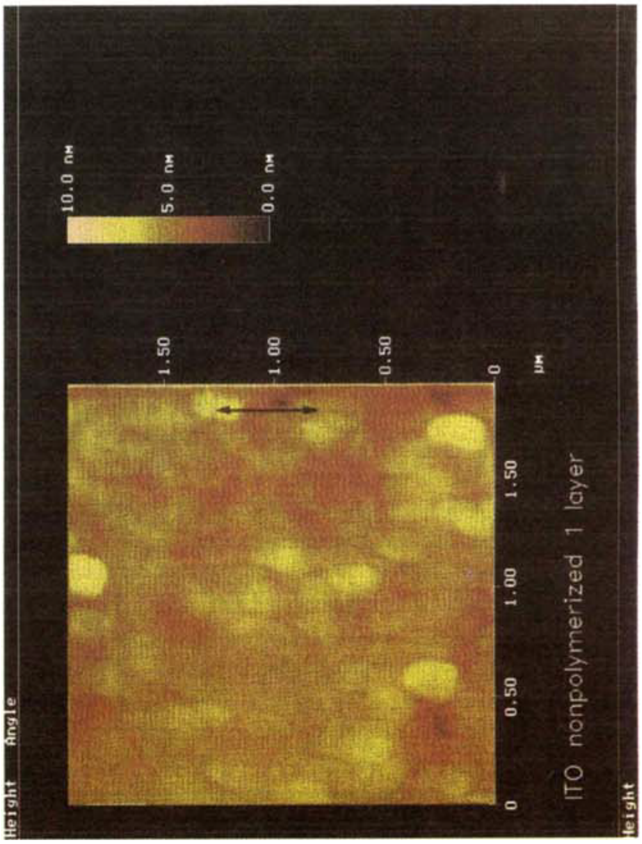


Figure 1.

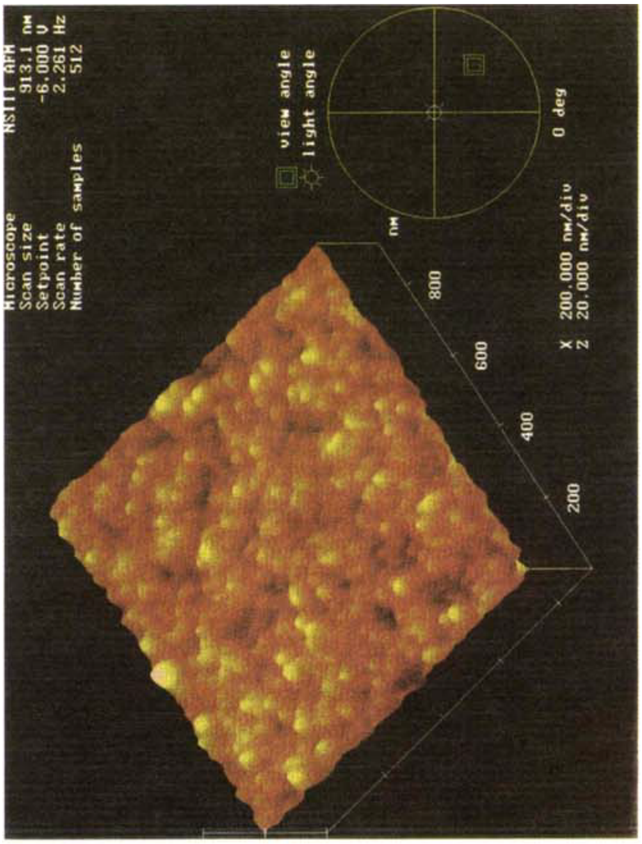


Figure 5.

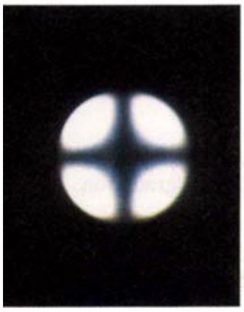
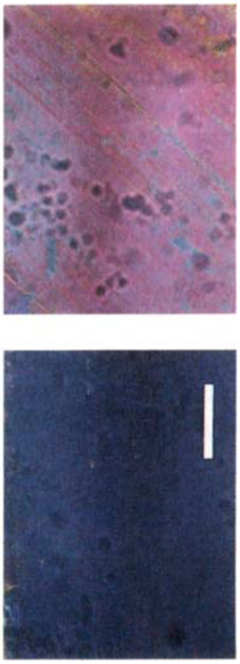


Figure 8.

Figure 9.



(*a*) (*b*)

Figure 2.

(*a*) (*b*)

Figure 6.

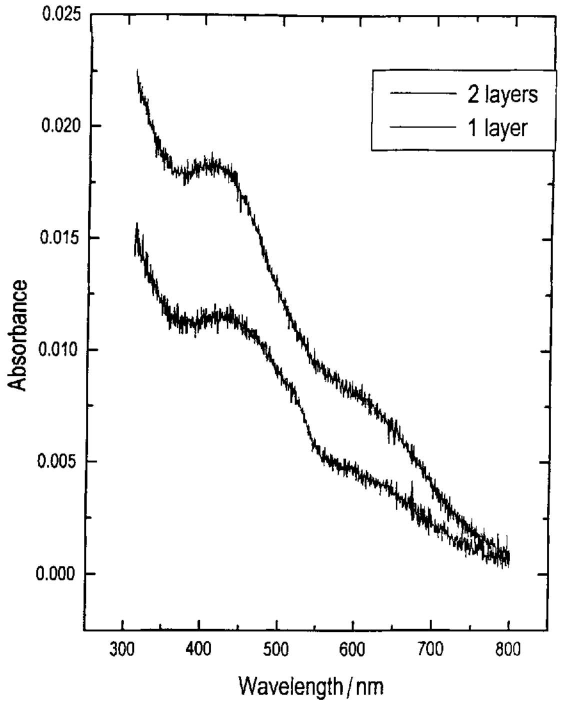


Figure 4. The *differential* absorption spectra between polymerized and unpolymerized LB films on ITO surface. Upper curve: two-layer film; lower curve: one-layer film.

with clean room paper. The typical effect of rubbing is shown in figure 3 (*b*). The star-like features emanating from various nucleation sites (cf. figure 3 (*a*)) appear to have been altered into parallel domain features. The roughness of the surface is also increased, presumably due to aggregation effects associated with rubbing. In the following, we will show that the rubbing can modify the aligning behaviour of the surface coated with polymeric LB films.

To confirm the formation of the polymerized LB film on ITO substrates, visible absorption spectroscopy was performed. The differential spectra between UV treated and untreated LB films are shown in figure 4. The weak but discernible absorption indicates the existence of the polymerized LB film on the ITO surface. Note that the magnitude of the absorption for two-layer film is only about 50 per cent higher than that of one-layer, possibly suggesting either incomplete coverage or some peeling off during the second dipping process.

Figure 1. AFM image of bare ITO surface. Note that the length scale in *z* direction is 20 nm/gradation.

Figure 2. AFM image of the ITO surface covered by diacetylene LB monolayer before polymerization. The dipping was along the vertical direction (as indicated by the arrow) and the dipping speed was 5 mm min^{-1}.

Figure 5. AFM image of an unpolymerized random DC$_{23}$PC film on an ITO surface.

Figure 6. AFM image of an UV polymerized random DC$_{23}$PC film on an ITO surface.

As a comparison to the LB film on the ITO substrates, we also performed AFM imaging of a *random* DC$_{23}$PC film which was formed by dipping the substrate into DC$_{23}$PC–chloroform solution. Figure 5 exhibits the image of an unpolymerized random DC$_{23}$PC film. Figure 6 exhibits the image of a random DC$_{23}$PC film which was UV polymerized. Figure 7 exhibits the image of a random DC$_{23}$PC film which was UV polymerized and hand-rubbed. Evidently, compared to bare ITO glass, the surface roughness is reduced by the dipping process, and the polymerization of the random film seems to make the surface structure even finer. Further buffing of the polymerized random film caused aggregation of the film in some areas, thus the surface again became rougher.

In practice, it may be desired that the orientation or the conformation of the polymeric segments on the substrates influence or control the alignment of liquid crystal molecules. By the same token, liquid crystal materials can be utilized to visualize or to amplify the structure of the underlying polymeric aligning surface, such as tilt angle, polymer chain propagation, and domain size. Bearing this in mind, we examined the alignment of the liquid crystal cells fabricated with DC$_{23}$PC coated ITO substrates. Before UV treatment, both the LB film and the random film coated substrates provide perfect homeotropic alignment; buffing of the substrates apparently has no effect on the alignment. An example is given in figure 8, which shows the conoscopic image of the buffed unpolymerized cell containing 5CB. Clearly, good homeotropic alignment is achieved. For the UV illuminated substrates, however, a dramatic difference in the liquid crystal alignment was observed. A tilted multidomain structure was obtained in both non-rubbed LB film coated cell and the random film coated cell. In figure 9, transmission pictures under cross polarizers are shown for liquid crystal cells whose LB film coatings (unrubbed) were prepared at different dipping speeds: (*a*) 2 mm min^{-1}, (*b*) 5 mm min^{-1} and (*c*) 20 mm min^{-1}. Apparently, the domain size depends on the dipping speed: 5 mm min^{-1} resulted in the largest domain size, and 20 mm min^{-1} in the smallest domain size. When the cells were rotated on the microscope stage by 45°, colour inversion between domains was observed. Note the length scale in figure 9 is much larger than that in figure 3, the connection between the formation of liquid crystal domains and domains of the polymerized LB films is not clear. Nevertheless, figure 9 demonstrates that the aligning behaviour of the LB film coated surface has been changed from homeotropic to tilted, and that the tilt domain size depends on processing conditions such as dipping speed. We found that further buffing of the LB film can provide a uniform orientation

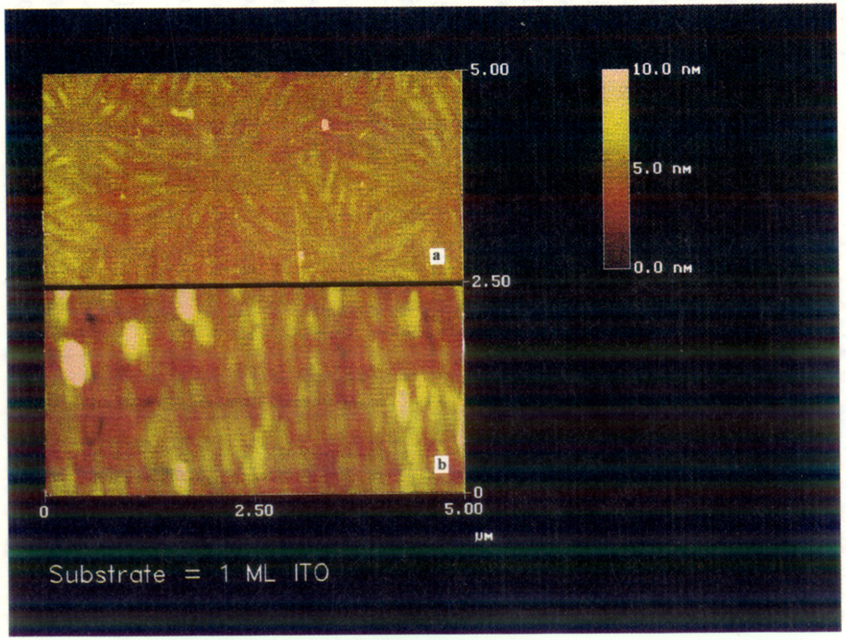


Figure 3.

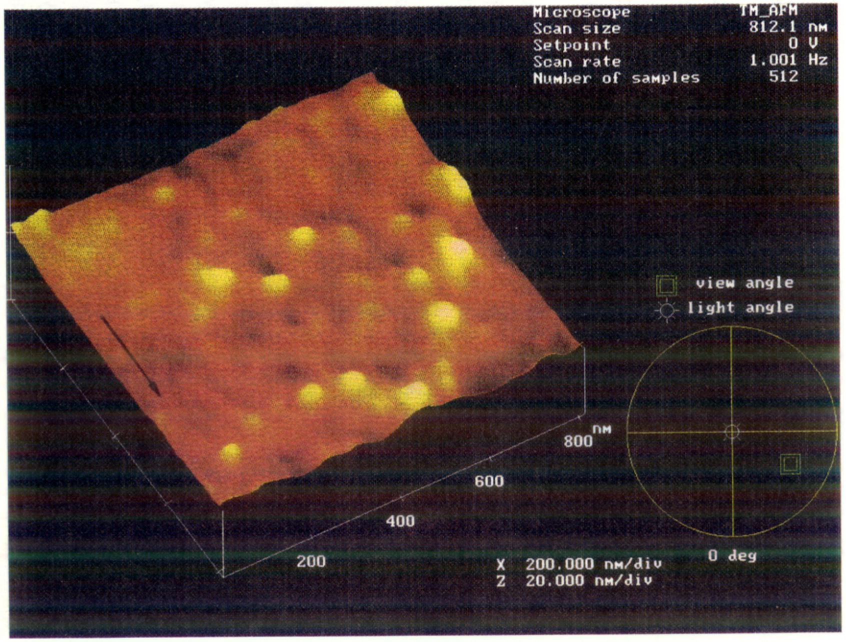


Figure 7.

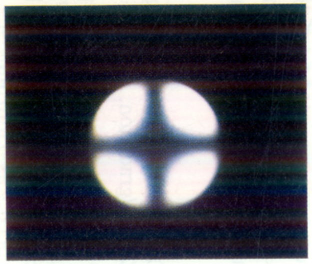


Figure 8.

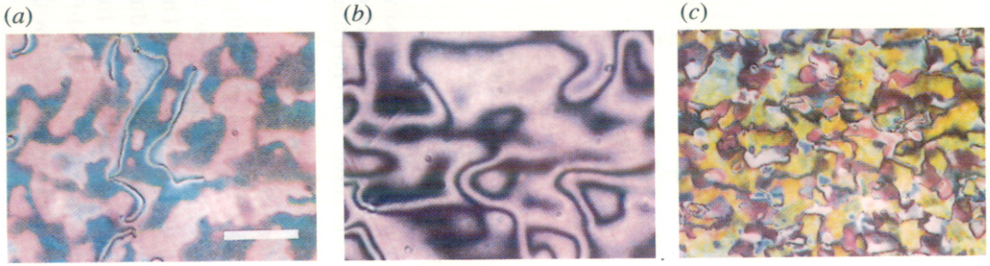


Figure 9.

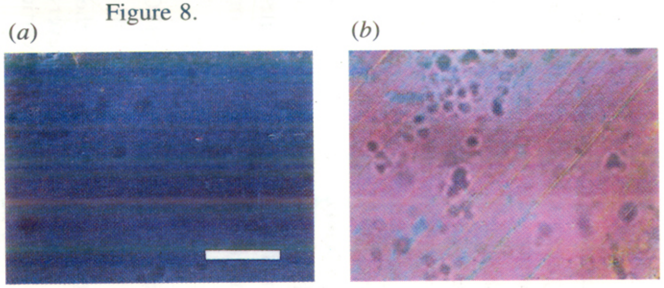


Figure 10.

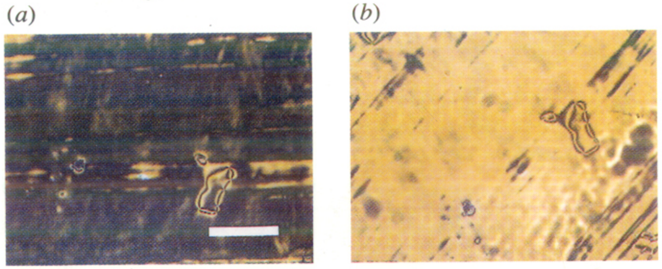


Figure 11.

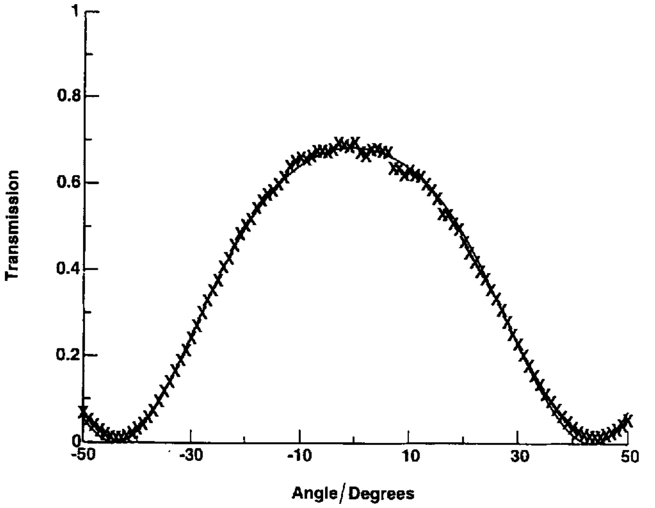


Figure 12. Crystal rotation measurement result exhibits a very symmetric transmission curve about the substrate normal, indicating a zero pretilt angle (0 ± 0·5)°.

of the liquid crystal. An example is given in figure 10, which shows that a monodomain planar orientation has been achieved and that the nematic director is along the rubbing direction. This result is qualitatively consistent with the AFM image of the rubbed polymeric LB film on ITO (shown in figure 3 (*b*)). Similar to cells coated with a rubbed polymeric LB film, cells coated with a rubbed random polymeric film also provide a planar alignment, as shown in figure 11. Note that the alignment effect of the random polymeric diacetylene film observed in this study is consistent with those reported by Li recently [21]. Further investigation of this homogeneously aligned cell indicates that the pretilt angle is zero. Shown in figure 12 is the result of crystal rotation measurement, which exhibits a very symmetric transmission curve about the substrate normal.

Figure 3. AFM image of polymerized diacetylene monolayer LB film on ITO surface, (*a*) unrubbed surface, (*b*) hand-rubbed surface. The dipping direction and the dipping speed are the same specified for figure 2.

Figure 7. AFM image of an UV polymerized and buffed random $DC_{23}PC$ film on an ITO surface. The rubbing direction is indicated by the arrow.

Figure 8. Conoscopic image of the rubbed unpolymerized liquid crystal cell. A good homeotropic alignment is apparent.

Figure 9. The transmission picture under cross polarizers for liquid crystal cells whose LB film coatings were prepared at different dipping speed: (*a*) $2\,\mathrm{mm\,min^{-1}}$, (*b*) $5\,\mathrm{mm\,min^{-1}}$, and (*c*) $20\,\mathrm{mm\,min^{-1}}$.

Figure 10. A monodomain planar orientation has been achieved by unidirectional rubbing of the polymerized LB film coated surface. The polarizers are placed along the vertical and horizontal directions. (*a*) The rubbing direction is placed parallel to the horizontal polarizer and (*b*) the rubbing direction is placed 45° between polarizers.

Figure 11. A monodomain planar orientation has been achieved by unidirectional rubbing of the random film coated surface. The positions of polarizers are as figure 10. (*a*) The rubbing direction is placed parallel to the horizontal polarizer and (*b*) The rubbing direction is placed 45° between polarizers.

The discussion now turns to the mechanism of the observed alignment transition from homeotropic to planar (or at least tilted) upon UV irradiation. Since the roughness of the ITO substrate and the resolution of the atomic force microscope prevented us from the probing the mechanism at subnanometer of molecular levels, the details of the final conformation of the lecithin array were difficult to determine. However, some mechanisms can be ruled out. Lecithin has a low surface tension, which tends to favour homeotropic alignment [31]. Given that the process here is solid state polymerization and that alkyl tails are flexible, the surface tension is unlikely to undergo much change. 5CB is noted for its high polarity, but lecithin induces homeotropic alignment for all types of liquid crystals, polar and nonpolar alike [31, 32]. Therefore, the dipolar interactions are likely not the cause of the orientation transition. Another possibility is that after UV radiation there is an increase in ionic concentration which could change the electric double layer, which is responsible for some observed tilt transitions [33, 34]. This is also unlikely because a similar tilt transition was observed in the liquid crystal material CCN-47, which has a fairly large *negative* dielectric anisotropy, $\Delta\varepsilon \approx -8{\cdot}5$ at 40°C [21].

Considering the star-like features observed in AFM image after the photopolymerization of the diacetylene LB film, the above discussion leaves us with conformation changes in the diacetylene molecules as the most plausible explanation for the observed transition. The tilting of the side chains of the polymer and the reduction of the alkyl chain length seem to contribute to this transition, such that this tilting does not favour a homeotropic alignment. Moreover, the UV induced polymer chains are located in the middle of diacetylene molecules, resulting in a small increase in the stiffness of the side chain. The presence of polymer chin also reduces the mobility of the side chains, making the vertical packing of the side chains more difficult. Therefore, a tilted orientation of the liquid crystal molecules will likely obtain.

4. Conclusions

We observed that when ITO substrates coated with $DC_{23}PC$ LB film or random $DC_{23}PC$ film were subjected to UV illumination, the aligning behaviour of the surface changes from homeotropic to tilted. AFM studies of the surface topological changes due to the photopolymerization of the diacetylene surfactant $DC_{23}PC$ deposited as LB films indicates that the mechanism of the liquid crystal alignment transition is the conformation change of the diacetylene array. A combination of tilting and shortening of the array could induce this transition. We intend to further investigate other aspects of this problem, such as modification of the molecular structure of the monomer and the influence of the processing condition of LB films, since this potential new way to control liquid crystal tilt angle could be of importance in many applications.

The authors are grateful to fruitful discussions with Drs Bruce Winker, Jerome Lando, and William Gunning. Dr Steven Eppel and Mr Chris Siedlecki helped with AFM measurements. Dr Hongying Wang helped with the preparation of LB films. Mr Don Rizzi and Mr Leonard Hale helped with the tilt measurement. Their assistance is greatly appreciated. This work is sponsored by Rockwell International Corporation and by the NSF's Advanced Liquid Crystalline Optical Materials Science and Technology Center under grant DMR-8920147.

References

[1] Nishikata, Y., Morikawa, A., Takiguchi, Y., Kanemoto, A., Kakimoto, M., and Imai, Y., 1988, *Jap. J. appl. Phys.*, **27,** L1163.

[2] (*a*) Ichimura, K., Suzuki, Y., Seki, T., Hosoki, A., and Aoki, K., 1988, *Langmuir*, **4,** 1214; (*b*) Seki, T., Sakuragi, M., Kawanishi, Y., Suzuki, Y., Tamaki, T., Fukuda, R., and Ichimura, K., 1993, *Langmuir*, **9,** 211; (*c*) Seki, T., Fukuda, R., Tamaki, T., and Ichimura, K., 1994, *Thin Solid Films*, **243,** 675.

[3] Baker, S., Seki, A., and Seto, J., 1989, *Thin Solid Films*, **180,** 263.

[4] Myrvold, B. O., 1989, *Liq. Crystals*, **4,** 637.

[5] Fang, J. Y., Wei, Y., Sun, Z. M., and Stroeve, P., 1991, *Phys. Lett. A.*, **154,** 369.

[6] Fang, J. Y., Lu, Z. H., Ming, G. W., Ai, Z. M., Wei, Y., and Stroeve, P., 1992, *Phys. Rev. A.*, **46,** 4963.

[7] Rupp, T., Eberhardt, M., and Gruler, H., 1992, *Jap. J. appl. Phys.*, **31,** 3636.

[8] Sasaki, T., Fujii, H., and Nishikawa, M., 1992, *Jap. J. appl. Phys.*, **31,** L632.

[9] Zhu, Y. M., Lu, Z. H., Wei, Q. H., Yang, X. M., Wei, Y., Chen, X. X., Tang, J. H., and Wei, Y., 1993, *Phys. Lett. A.*, **183,** 107.

[10] Akatsuka, T., Tanaka, H., Toyama, J., Nakamura, T., Matsumoto, M., and Kawabata, Y., 1991, *Chem. Lett.*, 1587.

[11] Fang, J. Y., Lu, Z. H., Ming, G. W., and Wei, Y., 1993, *Liq. Crystals*, **14,** 1621.

[12] Akatsuka, T., Tanaka, H., Toyama, J., Nakamura, T., Matsumoto, M., and Kawabata, Y., 1993, *Synthetic Metals*, **55,** 3859.

[13] Yang, Z. M., Gu, N., Lu, Z. H., and Wei, Y., 1993, *Phys. Lett.*, **183,** 111.

[14] Schadt, M., Schmitt, K., Kozinkov, V., and Chigrinov, V., 1992, *Jap. J. appl. Phys.*, **31,** 2155.

[15] Marussi, T. Ya., and Renikov, Yu, A., 1993, *Molec. Mater.*, **3,** 161.

[16] Hirshfeld, F. L., and Schmidt, G. M., 1962, *J. polym. Sci. Phys.*, *A*, **2,** 2181.

[17] Wegner, G. Z., 1969, *Z. Naturf.* (*b*), **24,** 824.

[18] Baughman, R. H., Gleiter, H., and Sendfeld, N., 1975, *J. polym. Sci. Phys.*, **13,** 1871.

[19] Yager, P., and Schoen, P. E., 1984, *Molec. Crystals liq. Crystals*, **106,** 371.

[20] Tredgold, R. H., 1994, *Order in Thin Organic Films* (Cambridge University Press), Chap. 5.

[21] (*a*) Li, Z., 1994, *Proceedings of International Display Research Conference*, Monterey, CA, U.S.A., p. 337; (*b*) Li, Z., 1995, *Liq. Crystals*, **19,** 307.

[22] Meyer, E., Howald, L., Overney, R. M., Heinzelmann, H., Frommer, J., Guntherodt, H. J., Wagner, T., Schier, H., and Roth, S., 1991, *Nature*, **349,** 398.

[23] Bourdieu, L., Silberzan, P., and Chatenay, D., 1991, *Phys. Rev. Lett.*, **67,** 2029.

[24] Weinsenhorn, A. L., Egger, M., Ohnesorge, F., Gould, S. A. C., Heyn, S. P., Hansma, H. G., Sinsheimer, R. L., Gaub, H. E., and Hansma, P. K., 1991, *Langmuir*, **7,** 8.

[25] Arisawa, S., Fujii, T., Okane, T., and Yamamoto, R., 1992, *Appl. Surf. Sci.*, **60,** 321.

[26] Lando, J. B., and Sudiwala, R. V., 1990, *Chem. Mater.*, **2,** 594.

[27] 1985, *Polydiacetylenes*, edited by D. Bloor and R. R. Chance (Martinus Nijhoff Publishers), Chap. 1.

[28] Tieke, B., Graf, H. J., Wegner, G., Naegele, B., Ringsdorf, H., Banerjie, A., Day, D., and Lando, J. B., 1977, *Coll. Polym. Sci.*, **255,** 521.

[29] Day, D., and Ringsdorf, H., 1978, *J. polym. Sci. polym. Lett.*, **16,** 205.

[30] Farris, G., Lando, J. B., and Rickert, S., 1983, *Thin Solid Film*, **99,** 305.

[31] Cognard, J., 1981, *Molec. Crystals liq. Crystals Suppl.*, **1,** 1.

[32] Hiltrop, K., Hasse, J., and Stegemeyer, H., 1994, *Ber. Bunsenges. phys. Chem.*, **98,** 209.

[33] Barbero, G., and Durand, G., 1990, *J. appl. Phys.*, **67,** 2678.

[34] Nazarenko, V., and Lavrentovich, O., 1994, *Phys. Rev. E.*, **49,** R990.