Molecular structure and pretilt control of photodimerized-monolayers (PDML)

Jawad Naciri,*[a] Devanand K. Shenoy,[a] Kirsten Grüeneberg[b]† and Ranganathan Shashidhar[b]

[a]Center for Bio/Molecular Science and Engineering, Naval Research Laboratory, 4555 Overlook Avenue SW, Washington DC 20375, USA
[b]Geo-Centers, Inc. 4640 Forbes Blvd., Street 120, Lanham, MD 20706, USA

We have studied the alignment of nematic liquid crystals on photo-sensitive chemisorbed monolayers. Surface modification and a single UV exposure at normal incidence resulted in photo-dimerized monolayers. A uniform, planar alignment of liquid crystals is realized on these surfaces. Chemical modification of the photo-sensitive chromophores of the monolayer allow fine-tuning of the pretilt. For a given alignment layer, there is a good correlation between the value of the pretilt and the polar properties of the liquid crystal used. Furthermore, the value of the pretilt depends on the chemical functionality at the outermost portion of the photo-alignment layer.

Introduction

With the growing demand for liquid crystal displays (LCD) for notebook computers, camcorders and digital cameras in the past few years, there has been a strong effort to improve production yields and display characteristics such as viewing angle and multiplexibility. A number of potential problems arise from the currently used rubbing techniques. The build up of dust and static charges during the rubbing process leads to failure of the devices.[1] The high curing temperatures required for polyimides can affect sensitive electronic parts such as color filters. Incorporating multi-domains with small pixel sizes into displays for high resolution and wide viewing-angle was found difficult when using mechanical rubbing. To overcome these problems, alternative alignment methods have been developed which are not based on rubbing and photo-alignment techniques. Several approaches have been reported: stretched polymer films,[2] Langmuir–Blodgett films,[3] micro-grooves[4] and stamped polymers.[5] However, photo-alignment methods have caught the most attention from LCD manufacturers in recent years due to the significant convenience of this non-contact approach which eliminates problems stated earlier.

Two approaches for photo-alignment have been reported so far. A guest–host approach was first reported by Gibbons et al.,[6] wherein dye molecules were incorporated into a liquid crystal. Illumination with laser light reorients the dye molecules and alignment of the liquid crystal molecules was achieved. In the second approach spin cast polymers were exposed to UV light. The photo-polymerized anisotropic surface yields planar alignment of LC molecules.[7–12]

Twisted nematic (TN) as well as super-twisted nematic (STN) devices require a finite pretilt in addition to the planar alignment of the LC molecules. The pretilt angle is defined as the angle between the optic axis of the LC molecules and the substrate surface. This pretilt is necessary to prevent reverse tilt domains in TN displays, stripe domains in STN-LCD and surface stabilized ferroelectric LCD.[13,14] Although most of the photo-alignment methods lack the achievement of a finite pretilt, recently published methods have solved this problem by varying the processing conditions.

Pretilt can be generated by the following schemes: double exposure with polarized UV light with different polarizations and angles of incidence,[15] with a single exposure using polarized UV light,[16] or with a single exposure of poly(coumarin) using an oblique incidence of polarized UV light.[8] Finite pretilts in photo-exposed polyimide films have also been reported.[17,18] A fine-tuning of the interactions between LC molecules and alignment layer molecules was first shown in rubbed polyimide films. Kobayashi et al.[19] describe how alkyl branches in polyimides contribute to the pretilt by interacting with the LC molecules. A systematic dependence between length of the branched alkyl chains and the pretilt was observed, longer alkyl chains leading to higher pretilts. Also, mixtures of polyimide with alkylamines gave finite pretilt angles.[20]

The use of polyimides with fluorinated substituents yielded high pretilts. The most successful substituents are fluorinated alkyl side chains,[21] trifluoromethyl groups[22] and diamine moieties containing hexafluoroisopropylidene groups with –O– or –CH$_2$– linkage.[23] The attachment of the trifluoro-group to the lateral benzene ring yielded higher pretilts compared to its attachment to the polymer backbone.[24]

The relationship between the chemical structure of the liquid crystal and the pretilt on polyimide was investigated by Myrvold et al.[25] When comparing cyano compounds and dialkyl compounds it was found that the core of the liquid crystal is tilted with respect to the surface in the first case and parallel in the latter. Therefore increasing the length of the core of the cyano LCs or increasing the longer alkyl chain in dialkyl LCs respectively led to an increase in pretilt. They also found that pretilts increase with increasing polarity of the liquid crystal. LC mixtures with a high number of cyano groups exhibit high polarity.

Fluorine and alkyl-substitutions were also used in photo-alignment layers. These groups increased pretilt values in poly(vinyl cinnamates) (PVCi), whereas unsubstituted PVCi systems only showed pretilts of the order of 0.3°.[26] UV irradiation of PI surfaces with alkyl side chains led to pretilts of the order of 6°.[27] The influence of hydrophobic alkyl moieties in the side chains of photo-aligned polysiloxanes on the generation of oblique alignment has also been recognized.[28]

We reported the first alignment process that combines (a) chemisorption of a self-assembled monolayer, (b) introduction

† Currently at: Oblon, Spivak and Associates, 1940 Duke Street, Alexandria, VA, USA

of an UV-sensitive chromophore and (c) irradiation with linearly polarized UV light to achieve uniformly planar alignment of liquid crystal molecules.[29–36] In this paper we will demonstrate how a fine-tuning of the pretilt is possible by varying the chemical structure of the chromophore in the monolayer. Introducing fluoro-, trifluoro-methyl-, nitro- and alkoxy- groups modifies the structure of the monolayer and its polar properties. We investigated the interaction of the liquid crystal mixtures E7 and ZLI 4792 with these monolayers. We find that the value of the pretilt correlates to the polarity of the liquid crystal for a given alignment layer.

Experimental

Materials

Cinnamic acid, 4-hydroxycinnamic acid, 4-methoxycinnamic acid, 4-nitrocinnamic acid, 3-nitrocinnamic acid, 2-nitrocinnamic acid, 4-fluorocinnamic acid, difluoro-3,5-cinnamic acid, 4-(trifluoromethyl)cinnamic acid, bromoalkanes (n = 1, 4, 6, 8, 10 where n is the number of carbons in the hydrocarbon chains), aminopropyl-triethoxysilane, anhydrous THF, triethylamine were obtained from Aldrich and used without further purification. The liquid crystals, ZLI 4792 and E7 were obtained from EM Industries and used as received. The ITO substrates with a coating of 1600 Å of SiO_2 (referred to as passivated ITO) were obtained from Applied Films, Inc. Water was purified with a Nanopure-Ultrapure water system to give a resistivity of 18 MΩ cm. The deionized water was used for the cleaning procedure, surface chemistry and static water contact angle measurements.
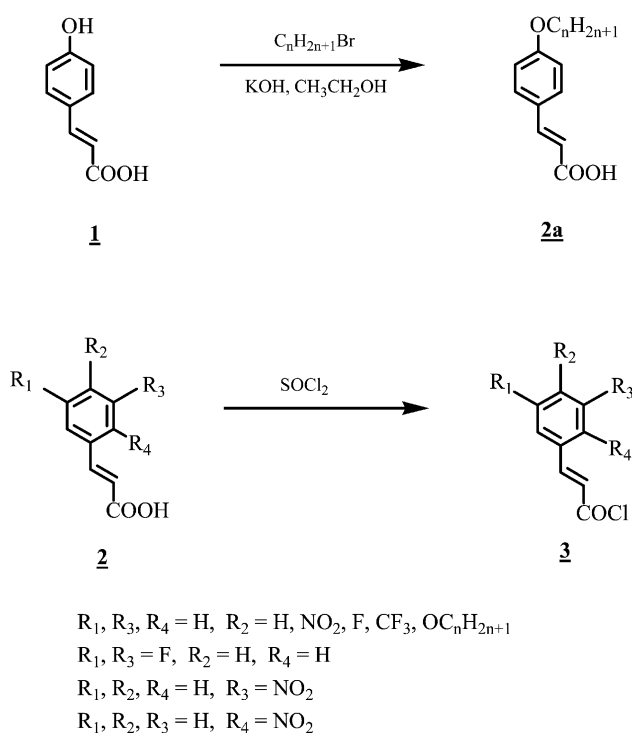
Techniques

Analytical TLC was conducted on Whatman precoated silica gel 60-F254 plates. 400 MHz ^{1}H NMR spectra were recorded on a Bruker DRX-400 spectrometer. All spectra were run in $CDCl_3$ or d-DMSO solutions. Infrared spectra were obtained by using an FT Perkin–Elmer 1800 spectrophotometer and KBr pellets. The static water (18 MΩ) contact angle was measured using a goniometer from Rame–Hart, Inc. (model # 100-00-115). An automated measurement system using National Instruments Labview (version 3.1) was used for the electro-optic measurements. A white light source or a low power He Ne laser was used as the source. The transmitted luminance in the normally black or normally white mode was measured using a detector from Graseby Optronics, Inc. (model S370 Optometer).

Synthesis

Typical synthesis steps leading to the preparation of 4-alkyloxy-cinnamoyl chloride are shown in Scheme 1.

4-Alkyloxy-cinnamic acid 2. 4-hydroxy-cinnamic acid **1**(1 mmol), KOH (3 mmol) and a catalytic amount of KI were dissolved in a mixture of ethanol/water (75/25%) and refluxed for 1 h. Alkyl bromide (1 mmol) was added and the reaction mixture was refluxed for 24 h. The solvent was removed and the precipitate was acidified with concentrated HCl. The crude product was filtered, washed with water, and recrystallized from a mixture of ethanol/water (75:25). The final product was dried under vacuum to yield **2a**as a white solid. Detail characterizations of each homologue are described below.

(2E)-3-[4-(butoxy)phenyl]-2-propenoic acid. Yield 80%; mp: 167–168 °C; ^{1}H NMR ($CDCl_3$) δppm): 0.99 (t, 3 H, CH_3), 1.50 (m, 2 H, CH_3(CH_2)), 1.75 (m, 2 H, OCH_2CH_2), 4.02 (t, 2 H, OCH_2), 6.40 (d, 1 H, CH=CHCOOH), 6.95 (d, 2 H, Ar–H),

Scheme 1 Reaction pathway for chromophores.

R_1, R_3, R_4 = H, R_2 = H, NO_2, F, CF_3, OC_nH_{2n+1}
R_1, R_3 = F, R_2 = H, R_4 = H
R_1, R_2, R_4 = H, R_3 = NO_2
R_1, R_2, R_3 = H, R_4 = NO_2

7.51 (d, 2 H, Ar–H), 7.74 (d, 1 H, Ci=CHCOOH). Elemental analysis, calculated for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.72; H, 7.45.

(2E)-3-[4-(hexyloxy)phenyl]-2-propenoic acid. Yield 78%; mp: 149.6–151 °C; ^{1}H NMR ($CDCl_3$) δppm): 0.9 (t, 3 H, CH_3), 1.32 (m, 4 H, CH_3(CH_2)$_2$), 1.45 (m, 2 H, O(CH$_2$)$_2$CH_2), 1.80 (m, 2 H, OCH$_2$CH_2), 4.02 (t, 2 H, OCH_2), 6.34 (d, 1 H, CH=CHCOO), 6.90 (d, 2 H, Ar–H), 7.51 (d, 2 H, Ar–H), 7.76 (d, 1 H, CH=CHCOO). Elemental analysis, calculated for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.65; H, 8.04.

(2E)-3-[4-(octyloxy)phenyl]-2-propenoic acid. Yield 82%; mp: 146 °C; ^{1}H NMR ($CDCl_3$) δppm): 0.96 (t, 3 H, CH_3), 1.32 (m, 4 H, CH_3(CH$_2$)$_2$), 1.35 (m, 4 H, (CH$_2$)$_2$), 1.45 (m, 2 H, O(CH$_2$)$_2$CH_2), 1.80 (m, 2 H, OCH$_2$CH_2), 4.02 (t, 2 H, OCH_2), 6.34 (d, 1 H, CH=CHCOO), 6.90 (d, 2 H, Ar–H), 7.49 (d, 2 H, Ar–H), 7.70 (d, 1 H, CH=CHCOO). Elemental analysis, calculated for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 73.70; H, 8.65.

(2E)-3-[4-(decyloxy)phenyl]-2-propenoic acid. Yield 80%; mp: 136 °C; ^{1}H NMR ($CDCl3$) δppm): 0.92 (t, 3 H, CH_3), 1.31 (m, 4 H, CH3(CH2)2), 1.36 (m, 8 H, (CH_2)$_4$), 1.45 (m, 2 H, O(CH$_2$)$_2$CH_2), 1.80 (m, 2 H, OCH$_2$CH_2), 4.02 (t, 2 H, OCH_2), 6.34 (d, 1 H, CH=CHCOO), 6.90 (d, 2 H, Ar–H), 7.51 (d, 2 H, Ar–H), 7.76 (d, 1 H, CH=CHCOO). Elemental analysis, calculated for $C_{19}H_{28}O_3$: C, 74.96; H, 9.27. Found: C, 74.88; H, 9.16.

Synthesis of the cinnamoyl chlorides 3. 1 mmol of the cinnamic acid **2**was dissolved in anhydrous benzene and stirred in an aluminum foil covered flask under nitrogen. 3 mmol of thionyl chloride was added and the mixture was refluxed overnight. The solvent was removed under vacuum and the product **3** recrystallized from hexane. The derivatives of cinnamoyl chloride were obtained in a 90% yield. The products were characterized by IR spectroscopy. All materials show no broad absorption in the region of 3300–2500 cm^{-1} typically

found in the acid derivatives. A strong absorption at 1778 cm^{-1} corresponding to the C=O stretch of the cinnamoyl chlorides was detected.

Cleaning of the substrate surfaces

ITO substrates with a coating of 1600 Å SiO$_2$ (referred to as passivated ITO) were cleaned by soaking in chloroform, then in a mixture of hydrochloric acid and water (50:50) solutions. Each step was performed for 20 min and followed by two rinses with methanol. The substrates were then soaked in concentrated sulfuric acid for 20 min. and washed with deionized water until the rinsing water shows a neutral pH. The substrates were than heated in deionized water for 20 min at 80–100 °C. The static water contact angle was measured to be approximately 0°.

Surface chemistry

The reaction solution was prepared as follows: 94% (by volume) of a 1 mM solution of acetic acid in anhydrous xylene were combined with 1% of the cinnamate silylating material. The freshly cleaned substrates **4** were treated with 3-aminopropyltriethoxysilane **5** solution at room temperature until saturation of the static water contact angle. The substrates **6** were rinsed twice with methanol, dried and baked for 4 min at 120 °C. After cooling the substrates were rinsed twice with anhydrous acetonitrile, treated with a solution of derivatized cinnamoyl chloride **3** (60 mM) and diisopropylethylamine (30 mM) in anhydrous acetonitrile and under the exclusion of light and moisture for 1 h. The substrates **7** were rinsed twice with acetonitrile and finally dried with a nitrogen stream and stored in Teflon containers.

Irradiation of the substrates

A 500 W Oriel Mercury arc lamp (power supply 68810, lamp housing 66033, bulb 6285) was used as the UV source. The UV beam was collimated in the set up. A grating monochromator (model# 77250) from Oriel was used to obtain the irradiation wavelength of 280 nm with a bandwidth of 2.5 nm. A sheet polarizer (model # 27320) from Oriel was used to linearly polarize the UV light.

Fabrication of liquid crystal cells

Planar cells (20 μm) were fabricated using substrates treated with the alignment layer. Mylar or glass spheres were used as spacers. The substrates were mounted antiparallel and filled with liquid crystals E7 or ZLI 4792 in the isotropic phase. The liquid crystal cells were cooled to room temperature with a temperature gradient of 0.5 °C min^{-1}.

Results and discussion

Synthesis of the chromophores

Scheme 1 illustrates the synthetic pathway used to obtain derivatized cinnamic acid chlorides. 4-Hydroxy-cinnamic acid **1** is reacted with a series of alkyl bromide and twofold excess of potassium hydroxide to yield the corresponding 4-alkyloxy-cinnamic acids **2a**. The acid chlorides of the chromophores **3** are obtained by reaction of the substituted cinnamic acids **2** with an excess of thionyl chloride in benzene. The other acid chlorides obtained from the commercially available starting materials were prepared following the same procedure described above. We synthesized a variety of chromophores that enabled us to control the pretilt for a given liquid crystal. An overview of their structures is given in Scheme 2.

n = 1, 4, 6, 8, 10
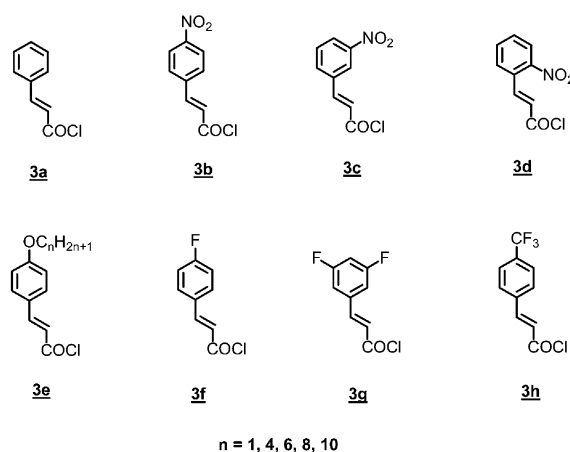
Scheme 2 Overview of chromophores.
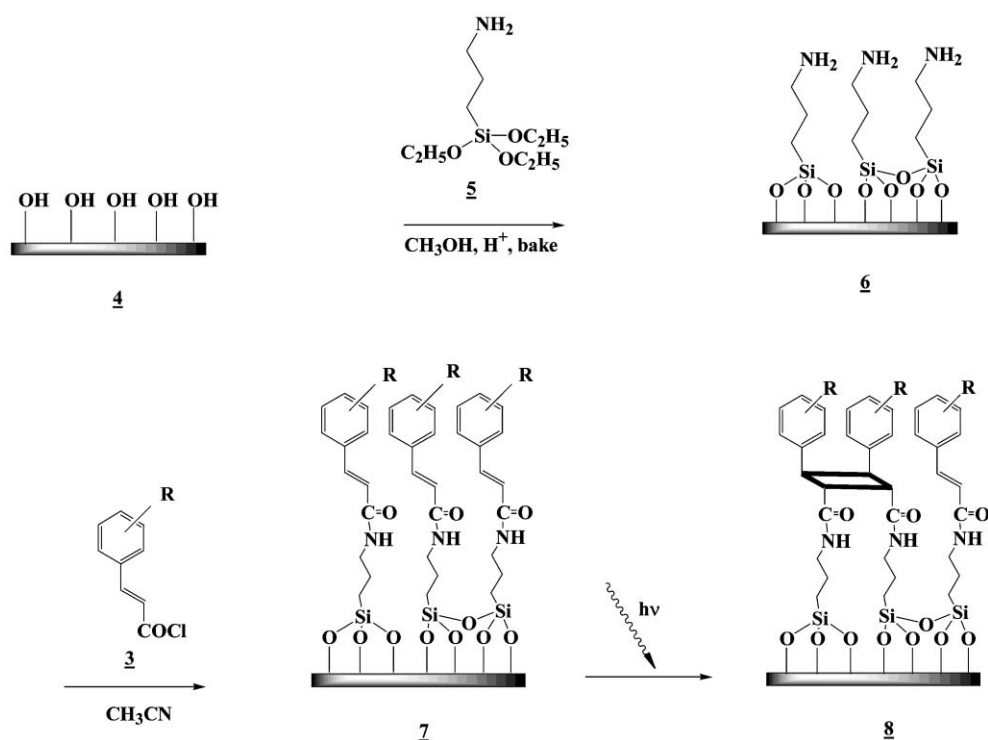
Chemisorption and irradiation process

The freshly cleaned passivated ITO plates were used for the three step procedure consisting of chemisorption, modification of the monolayer and irradiation (Scheme 3). The self-assembly process starts at the substrate surface **4** containing the hydroxyl-groups. After formation of the 3-amino-propyl-triethoxysilane (APS) monolayer **6**, the substrates are washed and thermally cured. In the next step the photosensitive chromophore **3** reacts with the monolayer to give **7**. The final step consists of dimerization of adjacent monomers using linearly polarized UV light λ = 280nm at normal incidence. The incident intensity was measured to be 1 mW cm^{-2} and all substrates were subjected to the same amount of light intensity for a fixed time of 20 min which we found was sufficient to cause a saturation of the pretilt measured. The photo-dimerized monolayer (PDML) **8** gives rise to uniform planar alignment of liquid crystal molecules with the alignment direction orthogonal to the direction of polarization of incident light.[32,33]

We have already reported studies of the monolayer growth of APS and subsequent attachment of 4-octyloxycinnamoyl chloride on silicon.[37] One important finding was the fact that the deposition time of APS was an important control parameter for the formation of functionalized aminosilane films. In this work we have determined the saturation value of the surface coverage of passivated ITO with APS by measuring the static water contact angle for different deposition times on passivated ITO. The contact angle saturates after 30 min (Figure 1). The contact angle for different substituted alignment layers was measured (Table 1). As expected, the contact angle increases with alkyl chain length.

After UV exposure, the substrates were mounted antiparallel and filled with liquid crystals E7 or ZLI 4792 in the isotropic phase.

Pretilt

The crystal rotation method[38] is used to determine the pretilt angle when the pretilt is small (0–10°).[38] The pretilts were measured using 20 μm thick planar samples. The method relies on the determination of the optical phase retardation and the transmitted intensity as a function of the angle of incidence of the laser beam with respect to the normal to the cell walls. The cell itself is rotated around an axis perpendicular to the optic axis. The transmitted intensity oscillates as the angle of incidence is changed. The intensity curve is symmetric about a certain angle called the symmetry point, which is related to the pretilt angle. Thus if the ordinary and the extraordinary refractive indices and the cell thickness are known, the pretilt angle can be calculated. The accuracy of the method is of the order of 0.3°. A typical pretilt curve is shown in Fig. 2.

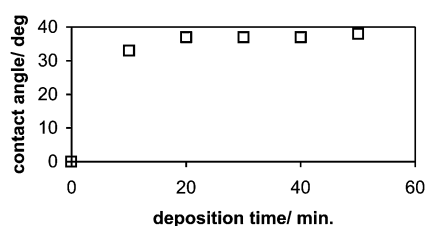**Scheme 3** Chemisorption and irradiation process.

Fig. 1 Growth curve of the 3-amino-propyltriethoxysilane: time dependence of the static water contact angle for passivated ITO.

Table 1 Static water contact angle of different substituted alignment layers illustrates the different degrees of hydrophobicity of the monolayers

Chromophore substituent	Contact angle/°
3a, R = H	64.5
3b, R = 4-NO$_2$	54.9
3c, R = 3-NO$_2$	58.8
3d, R = 2-NO$_2$	63.3
3e, R = OCH$_3$	71
3e, R = OC$_4$H$_9$	80.1
3e, R = OC$_6$H$_{13}$	83.4
3e, R = OC$_8$H$_{17}$	88.1
3e, R = OC$_{10}$H$_{21}$	92.2
3f, R = 4-F	67.6
3g, R = 3.5-(F)$_2$	52.8
3h, R = 4-CF$_3$	60.1

Fig. 2 Pretilt curve.

Earlier studies have shown that molecular interactions responsible for the alignment and pretilt of liquid crystal molecules are complex. Typically these are polar, van der Waals and steric interactions.[7,8] The pretilt angle depends not only on the alignment layer but on the liquid crystal itself. In view of these parameters, we conducted four sets of experiments. We systematically varied the structure of the chromophore of the alignment layer as well as the type of liquid crystal. The liquid crystal mixture E7 contains cyanobiphenyl groups with a strong dipole moment. However, the liquid crystal mi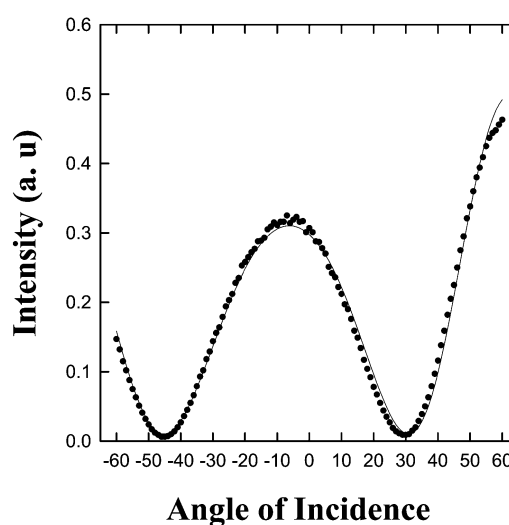xture ZLI 4792 consists of materials with less polar substituents such as fluorine, trifluoro-methyl or difluoro-methyl instead of the cyano group.

In the first set of experiments, altering the longitudinal dipole moment of the alignment layer molecule varies the pretilt. This can be illustrated by comparing the pretilt values of the liquid crystal E7 on alignment layers with decreasing polarity as shown in Table 2. To create a finite pretilt suitable for TN applications (2–5°), it is useful to utilize the polar interactions between cyano groups and nitro groups as is done in the alignment layer with a nitro-substitution in the 4-position of the phenyl ring. This results in a pretilt of 2° ± 0.3. By changing the attachment of the nitro-substituent in the *ortho* and *meta* positions (3-NO$_2$, 2-NO$_2$) the polarity of the alignment layer decreases and so does the pretilt. An unsubstituted chromophore (R = H) yields the least polar alignment layer and therefore exhibits the smallest pretilt of 0.5° ± 0.3. The opposite trend is observed for the liquid crystal mixture ZLI 4792 (Table 3). It should also be pointed out that

Table 2 Dependence of pretilt on the polarity of the chromophore substituent for liquid crystal mixture E7

Chromophore substituent	pretilt/° for E7
R = 4-NO$_2$	2
R = 3-NO$_2$	1.5
R = 2-NO$_2$	0.9
R = H	0.5

Table 3 Dependence of pretilt on the polarity of the chromophore substituent for liquid crystal mixture ZLI 4792

Chromophore substituent	pretilt/° for ZLI 4792
R = 4-NO$_2$	0
R = 50% 4-NO$_2$, 50% H	0.3
R = H	0.6

such variations in the dipolar interactions do not lead to any significant pretilt values for ZLI 4792.

For the generation of a pretilt using the liquid crystal mixture ZLI 4792 a different class of chromophores had to be synthesized. We attached alkoxy chains to the chromophores and utilized the concept of van der Waals interactions between the substituents and the liquid crystal. Table 4 shows the suitability of different alkoxy substituted alignment layers for ZLI 4792. The pretilt increases as the chain length of the alkoxy group increases. This trend reverses in the case of the polar liquid crystal mixture E7 (Table 4).

It has been reported that fluorine substitution of photo-polymers leads to high pretilts.[17] As illustrated in Table 5, we observe the same effect in the photo-dimerized monolayer. The measured pretilts are of the order of 2° and compare to those achieved by introduction of alkoxy chains of lower chain length. It is important to note that these correlations between liquid crystal properties and pretilt were observed with LC mixtures consisting of many components. To make clear cut correlations of such a nature would require single component liquid crystals. Nevertheless, it is encouraging to see that the general trends are consistent in both mixtures as observed.

It must be stated that the origin of the uniformity of pretilt is not yet established. It is conceivable that because the surfaces of the glass onto which these chemisorbed materials are deposited are not atomically smooth, that surface roughness may be causing a preferential bias of the tilt of molecules. We have shown earlier that in those situations where a degeneracy does arise, one could eliminate the non-uniformity of pretilt through an electric field treatment.[35] Besides pretilt, which is the focus of this manuscript, other characterizations of such alignment layers with display relevant liquid crystal mixtures as well as single component liquid crystals have been performed.

Table 4 Dependence of pretilt on the hydrophobicity of the chromophore substituent for liquid crystal mixture ZLI 4792 and E7

Chromophore substituent	pretilt/° for E7	pretilt/° for ZLI 4792
R = OCH$_3$	1	0.1
R = OC$_4$H$_9$	0.2	0.5
R = OC$_6$H$_{13}$	0	1.7
R = OC$_8$H$_{17}$	0	2.5
R = OC$_{10}$H$_{21}$	0	3.5

Table 5 Pretilts of alignment layers with fluorinated substitution

Chromophore substituent	pretilt/° for ZLI 4792
R = 4-F	2.1
R = 4-CF$_3$	1.7
R = 3.5-(F)$_2$	1.5

For instance, we have also shown earlier that these chemisorbed layers used for obtaining a uniform alignment have polar surface anchoring energies that are considered adequate for device applications. Further, a systematic and detailed study of the polar anchoring energies of such photo-dimerized mono-layers have been published elsewhere.[39] In this work, we show how specific chemical substitutions at the outermost portion of the photo-alignment layer correlate with the polar anchoring energy.

Conclusion

We have developed a molecular level understanding of the origin of pretilts in new photo-dimerized monolayers that are irradiated at normal incidence. This understanding was based on a study using two different classes of liquid crystal mixtures, *viz.* the cyanobiphenyl based E7 class and the fluorinated mixture ZLI 4792. We have demonstrated that, by introducing substituents of different structure and polarity into the chromophore of the self-assembled photo-alignment layer, a pretilt is achieved. The pretilt is systematically tuned by altering the molecular interactions at the interface between the alignment layer and the liquid crystal molecules. These pretilts are sufficient for some liquid crystal display modes used in the display industry. Detailed characterization work has been carried out on liquid crystal cells fabricated with these photo-alignment layers. These results indicate that these photo-alignment techniques are promising for device applications.

Acknowledgements

References

1 Y. Imura and S. Kobayashi, *Oyo Butsuri*, 1995, **64**, 1007.
2 H. Aoyama, Y. Yamazaki, N. Matsuura, H. Mada and S. Kobayashi, *Mol. Cryst. Liq. Cryst.*, 1981, **72**, 127.
3 Z. Lu, H. Deng and Y. Wei, *Supramol. Sci.*, 1998, **5**(5/6), 649.
4 Y. Katawa, K. Takatoh, M. Hasegawa and M. Sakamoto, *Liq. Cryst.*, 1994, **16**, 1027.
5 Y. Kawata, K. E. S. Lee, P. Vetter, T. Miyashita, T. Uchida, M. Kano, M. Abe and K. Sugurawa, *Jpn. J. Appl. Phys.*, 1993, **32**, L1436.
6 W. Gibbons, P. J. Shannon, S. T. Sun and B. J. Swelin, *Nature*, 1991, **351**, 49.
7 M. Schadt, K. Schmitt, V. Kokinkov and V. Chigrinov, *Jpn. J. Appl. Phys.*, 1992, **31**, 2155.
8 M. Schadt, H. Sieberle and A. Schuster, *Nature*, 1996, **381**, 212.
9 J. L. West, X. Wang, Y. Ji and J. R. Kelly, *SID Dig.*, 1996, 634.
10 J. Chen, D. L. Johnson, P. L. Bos, X. Wang, J. L. West and Y. Reznikov, *SID Digest*, 1996, 654.
11 T. Yamamoto, M. Hasgwawa and H. Hatoh, *SID Dig.*, 1996, 642.
12 X. Wang, D. Subacius, O. Lavrentovich, J. L. West and Y. Reznikov, *SID Dig.*, 1996, 654.
13 T. J. Scheffer and J. Nehring, *Appl. Phys. Lett.*, 1984, **45**, 1021.
14 N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.*, 1980, **36**, 899.
15 Y. Imura, T. saitoh, S. Kobayashi and T. Hashimoto, *J. Photopolym. Sci. Tech.*, 1995, **8**, 257.
16 K. Y. Han, B. H. Chae, S. H. Yu, J. K. Song, J. G. Park and D. Y. Kim, *SID Dig. Tech.*, 1997, **28**, 707.
17 M. Nishikawa, B. Taheri and J. L. West, *SID Dig.*, 1998, 131.
18 J. L. West, M. Nishikawa and Y. Reznikov, *Proc. SPIE–Int. Soc. Opt. Eng.*, 1999, **3635**, 16.
19 R. Arafune, K. Sakamoto and S. Ushioda, *Appl. Phys. Lett.*, 1997, **71**(19), 2755.
20 H. Fukuro and S. Kobayashi, *Mol. Cryst. Liq. Cryst.*, 1988, **163**, 157.

21 S. Ishibashi, M. Hirayama and T. Matsuura, *Mol. Cryst. Liq. Cryst.*, 1993, **225**, 99.
22 D. S. Seo, S. Kobayashi and M. Nishikawa, *Appl. Phys. Lett.*, 1992, **61**(20), 2392.
23 C. Nozaki, N. Imamura and Y. Sano, *Jpn. J. Appl. Phys.*, 1993, **32**, 4352.
24 D. S. Seo, M. Nishikawa and S. Kobayashi, *Liq. Cryst.*, 1997, **22**(4), 515.
25 B. O. Myrvold and K. Kondo, *Liq. Cryst.*, 1995, **18**(2), 271.
26 Y. Iimura, S. Kobayashi, T. Hashimoto, T. Sugiyama and K. Katoh, *IEICE Trans. Electron.*, 1996, **E79C**(8), 1040.
27 D. S. Seo and J. H. Choi, *Liq. Cryst.*, 1999, **26**(2), 291.
28 Y. Reznikov, O. Yaroshchuk, I. Gerus, A. Homuth, G. Pelzl, W. Weissflog, K. J. Kim, Y. S. Choi and S. B. Kwon, *Mol. Cryst. Liq. Cryst.*, 1998, **9**(4), 333.
29 R. Shashidhar, K. Grüneberg, D. Shenoy, U. Karkarla and J. Naciri, *SID Dig. Tech.*, 1997, **28**, 315.
30 D. Shenoy, K. Grüneberg, J. Naciri, M. S. Chen and R. Shashidhar, *SID Dig. Tech.*, 1998, **29**, 731.
31 A. Herrmanns, C. Wilson, K. Grüneberg, J. Patel, K. Nelson, A. Townsend-Booth and B. Ratna, *Proc. SPIE–Int. Soc. Opt. Eng.*, 1998, **3297**, 73.
32 K. Grüneberg, D. Shenoy, J. Naciri, M. S. Chen and R. Shashidhar, *Proc. SPIE–Int. Soc. Opt. Eng.*, 1998, **3475**, 35.
33 K. Grüneberg, D. Shenoy, J. Naciri, M. S. Chen and R. Shashidhar, *IDRC Proc.*, 1998, 199.
34 D. Shenoy, K. Grüneberg, J. Naciri and R. Shashidhar, *Jpn. J. Appl. Phys.*, 1998, **37**(11A), L1326.
35 D. Shenoy, J. V. Selinger, K. Grüneberg, J. Naciri and R. Shashidhar, *Phys. Rev. Lett.*, 1999, **82**(8), 1716.
36 D. Shenoy, K. Grüneberg, J. Naciri, R. Shashidhar, Y. Nastishyn and O. Lavrentovich, *Proc. SPIE–Int. Soc. Opt. Eng.*, 1999, **3635**, 24.
37 P. Heiney, K. Grüneberg, C. Dulcey and R. Shashidhar, *Langmuir*, 2000, **16**, 2651.
38 T. J. Scheffer and J. Nehring, *J. Appl. Phys.*, 1977, **48**, 1783.
39 D. Shenoy, L. Beresnev, D. Holt and R. Shashidhar, *Appl. Phys. Lett.*, 2002, **80**, 1538.