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Smectic and Chiral Liquid Crystals

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Orientation of Ferroelectric Liquid Crystals by Self-Assembled Bilayer Molecular Assembly

Sukhmal C. Jain, Vivechana Dixit, Vinod K. Tanwar and S. M. Shivaprasad
Polymeric and Soft Materials Division, National Physical Laboratory,
Dr. K.S. Krishnan Road, New Delhi-110012, India

ABSTRACT

Molecular films of amino propyl triethoxy silane (APTES) attached with cinnamoyl moieties were deposited on indium tin oxide (ITO) coated glass and quartz substrates by self-assembly technique. The deposition of the monolayer films resulted in a large change in the wettability of the substrates. X-ray photoelectron spectroscopy (XPS) and UV-spectroscopy were used to study the structure and properties of the grown films. The molecular assembly was photodimerized by irradiating it with a linearly polarized UV-light. Thus created polymer-solid interface has been shown to produce good, stable planar orientation of ferroelectric liquid crystal mixtures. The electro-optical and switching properties of the ferroelectric liquid crystal cells have been investigated and found to be quite similar to those prepared in conventional manner.

INTRODUCTION

The field of self-assembled (SA) monolayers and multilayers of various organic surfactants have witnessed a phenomenal growth in last one decade due to increasing level of sophistication in their synthesis and characterization [1-8]. The SA technique provides for the needed designed flexibility, both at the individual molecular level and the material level and thus presents unique opportunities to create interfaces with desired structure and properties at different substrates. In this technique, the molecules are directly chemisorbed on a hydroxylated substrate under controlled environmental conditions leading to the formation of a two-dimensional ordered molecular assembly.

The monolayers of alkoxy-alkyl-amine-silanes have been used for wide ranging applications including [1-3] surface modification of silica and alumina, chromatography, adhesion promoters between polymer and silica or glass surfaces, immobilization of the enzymes etc. Recently, a new technique based on photodimerization of the self-assembled bilayer molecular assembly to orient nematic liquid crystals has been reported [11-14]. Photo-alignment techniques [11-20] are finding great favor, as they do not require any mechanical rubbing of the substrates, which can be a source of dust, and electrostatic charge buildup that can be detrimental to the life and quality of the liquid crystal displays. In the present work, we wish to report on the uniform planar orientation of ferroelectric liquid crystals utilizing anisotropic polymer-solid interfaces created by photodimerization of the molecular films of APTES attached with cinnamoyl moieties. The growth of the molecular films has been monitored by i) contact angle measurement, ii) XPS and iii) UV-spectroscopy. The optical polarizing microscopy and electro-optical measurements were used to study the alignment and switching behavior of photo-aligned liquid crystal cells.

EXPERIMENTAL DETAILS

Clean hydrophilic polar surfaces, that are a primary requirement for the rapid formation of quality compact films by self-assembly technique, were prepared by an elaborate cleaning procedure described earlier [14]. APTES used in the present investigations was procured from M/S Sivento, Germany under the trade name DYNASYLAN-AMEO. XPS measurements were made on a Perkin-Elmer 1257 X-ray photoelectron spectrometer with MgK$_\alpha$ source (1253.6 eV). The instrument was operated at the base pressure of 5×10^{-7} torr. The secondary electron detector was hemispherical of 279.4mm with an angular resolution of 25 milli eV. UV-spectroscopy was done on Shimadzu UV Spectrophotometer UV-2401 PC.

The bilayer molecular assembly was irradiated with a linearly polarized UV-light beam of ~0.1 W/cm^2 (ELC-700 from Electro-Lite Co., USA). A Glan-Thompson polarizing prism was used to produce linearly polarized light. The liquid crystal cells were prepared in sandwich configuration from the photodimerized substrates using 4 micron glass beads as spacers and were filled with commercial liquid crystal mixtures ZLI#4237 (K→<-30° S_c^* →62° S_a→76°Ch →86°C iso.) and ZLI#3654 (K→<-20° S_c^* →63° S_a→76°Ch →79°C iso.), respectively, in their isotropic phases. A Carl-Zeiss Universal Polarizing Microscope (Nμ) along with a photomultiplier setup, a digital function generator and a digital storage oscilloscope were used to study the alignment and electro-optical properties of liquid crystal cells.

PROCESS, RESULTS & DISCUSSION

The formation and growth of monolayers of APTES molecules on solid substrates and their subsequent functionalization with photochromophores involve many steps. As a first step, the cleaned ITO glass and quartz substrates were cleaned and checked for their high wettability by contact angle measurement. Typically the contact angle was ≤ 40°. In the second step, the substrates were immersed in a 0.01-0.1M solution of APTES in GR grade methanol containing 0.1% acetic acid for an optimum period of time at temperature (≤ 25°C) and relative humidity (40-50%) to form a monolayer of APTES molecules. As a next step, the cinnamoyl moieties were attached to the APTES molecules by immersing the APTES coated substrates in the cinnamoyl chloride solution (0.01-0.1M) in HPLC grade acetonitrile containing a small quantity of triethylamine (TEA) and N, N´-dicylo hexyl carbodiimide (DCC) in base catalytic conditions. Immidization of the APTES monolayer is most successfully done when the temperature of the solution is ≤ 20°C and relative humidity (45-50%). Subsequently, the bilayer molecular assembly was irradiated with a linearly polarized UV-light to create anisotropic ordered surface structure, which has been shown to promote good planar orientation of liquid crystals.

Deposition of APTES molecules led to a large change in the wettability of the substrates. The surface contact angle of the double distill water increased rapidly initially as a function of time of immersion of the substrates in the solution and then plateau off suggesting the complete coverage of the surface with APTES molecules. Typically, the contact angle saturated to ~65° after a period of 30 minutes in 0.05M silane solution. The saturation time, however, may vary considerably with the concentration of silane in the solution, the moisture therein, temperature and humidity of the ambient etc. The contact angle could be much higher (~80°), if the substrates are exposed to water for some time. The high contact angle has been found to be undesirable for good alignment. The high contact angle represents a non-polar surface and would require the APTES to be adsorbed with electron pair on the nitrogen atom oriented towards glass surface [5].

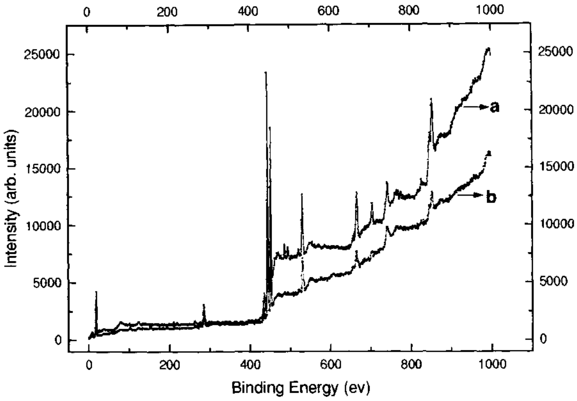

Figure 1: Binding energy of different elements on ITO coated substrates with and without APTES coating.

The formation and structure of the monolayer was examined with XPS. It was observed that the formation of the monolayer of APTES molecules resulted in the appearance of N 1s (398.0 eV) and Si 2p(102 eV) peaks in the XPS spectra, corresponding to amine and silicon of the APTES molecules. The amine peak at 398 eV is a singlet and can be easily protonated and take part in immidization [3]. Figures 1a and 1b show the XPS Spectra of ITO coated substrates with and without APTES layer, respectively. The XPS spectra for various elements were recorded with much higher resolution. On comparing the intensities of the various peaks (Table I), one finds that the N1s peak was non-existent and Si 2p peak was very weak in the base ITO coated substrate. However, the deposition of the APTES molecules on it, resulted in the appearance of the nitrogen peak and an increase in the intensities of silicon and carbon peaks. Consequently, the intensities of the indium and tin peak decreased due to the formation of the monolayer on the surface. It was further observed (Fig.2) that the intensities of the nitrogen and silicon peaks increased with increasing time of immersion of the substrate in the silane solution, showing sign of saturation at long period of time. This behavior is similar to the wettability behavior and suggests the complete formation of the monolayer.

Table I: Normalized intensities of the various elements in the XPS spectra on different substrates.

	Indium (In) 443.7 eV	Tin (Sn) 484.7 eV	Carbon (C) 284.6 eV	Nitrogen (N) 398.0 eV	Silicon (Si) 102 eV
ITO substrate	31.0	1.7	26.4	0	5.7
APTES coated ITO substrate	16.8	0.7	49.4	2.2	7.1
APTES layer functionalized with cinnamoyl moieties	7.3	0.7	63.9	1.8	7.5

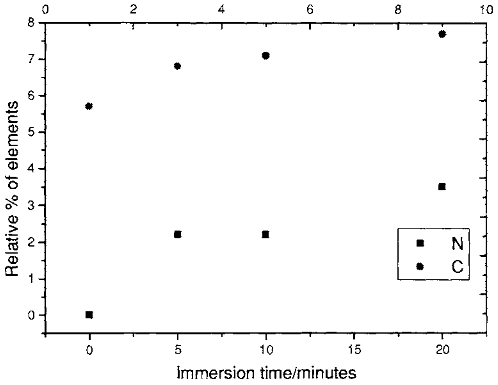

Figure 2: Normalized intensity of nitrogen and silicon (from XPS spectra) with increasing time of immersion in 0.05M APTES solution.

The attachment of cinnamoyl moieties to the APTES molecules led to some modification in the surface wettability and in the XPS spectrum. The contact angle increased and saturated to ~75° suggesting the more hydrophobic nature of the substrate. The XPS spectra showed a decrease in the intensities of nitrogen and indium peaks while silicon peak showed little variation (Table I). This was only to be expected as cinnamoyl group be not expected to give any new peak and significant modification in the XPS spectrum.

The attachment of the cinnamoyl moieties to the APTES molecules on a quartz substrate resulted in an UV-absorption band at 278nm [14]. The intensity of the UV peak showed saturation after some time, corresponding to the full coverage of the APTES molecules with cinnamoyl moieties. On irradiation with linearly polarized UV-light, the UV-absorption band peak decreased and became very small on completion of the photodimerization. The photodimerization resulted in creation of a highly ordered anisotropic surface structure [14]. The substrates thus prepared were used to prepare liquid crystal cells in sandwich configuration. The cells were filled with commercial liquid crystal mixtures ZLI# 3654 & 4237 in their respective isotropic phases and then cooled very slowly into their liquid crystalline phases. The portions of the cells irradiated with linearly polarized light exhibited a good, stable, uniform planar orientation of liquid crystals in their various liquid crystalline phases. The planar oriented cells showed a strong variation in their transmission when rotated between crossed polarizer. As such one observes four successive maxima and minima in the transmission intensity when the cell is rotated through an angle of 360°. The transmission is minimum when the planar orientation axis of the cell lies parallel to one of the polarizing axes of the two polarizer and maximum when it is at 45° to the polarizing axis. Figure 3 shows a typical set of microphotographs of a planar oriented liquid crystal cell containing ZLI# 3654 (T=55°C) at its different orientation with respect to the polarizing axis of the polarizer. In Fig.3a, the black portion corresponds to the planar oriented FLC cell with the orientation direction lying parallel to one of the polarizing axes while the fan texture shows the unoriented portion of the cell. On rotating the cell through 45°, black portion becomes highly transparent (fig.3b) which on further rotation to 90° becomes black again (Fig3c). These observations confirm the planar orientation of ferroelectric liquid crystal mixture. The planar orientation is maintained even well below the room temperature. Such planar orientation was also observed in other LC cells containing ZLI# 4237 mixture. It was further observed that the direction of planar orientation is governed by the direction of the electric field vector of the polarized light and is at right angles to it. The planar aligned cell in the SmC* phase could be switched between dark and bright states under crossed polarizer by low voltage positive and negative pulses. Figure 4 shows the variation in contrast ratio between bright and dark states as a function of voltage at 1 Hz at 36°C. Similar behavior was observed at other temperatures. The cell showed a threshold behavior with a full switching voltage ~1.5V. Figure 5 shows the variation in the contrast ratio as a function of temperature (from room temperature to the SmC*-SmA phase transition). The contrast decreases rapidly as one approaches the SmC*- SmA transition. The switching times were in the range of a few milliseconds and increase somewhat

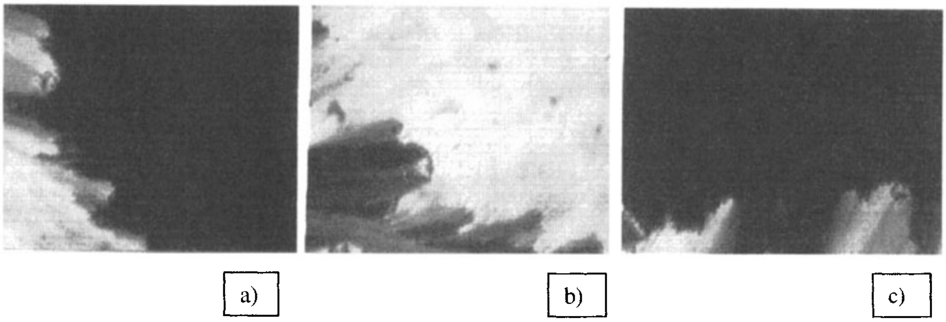

Figure 3: Set of optical micrographs of one such cell in chiral smectic C phase of ZLI# 3654 at T=55°C between crossed polarizer at different orientations.

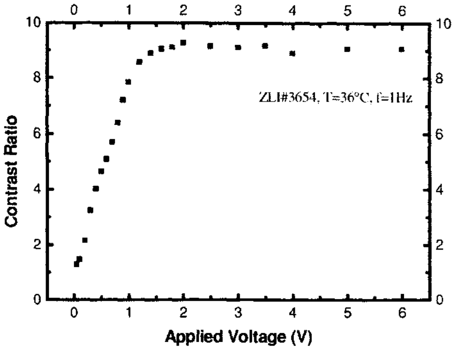

Figure 4: Contrast ratio versus applied voltage.

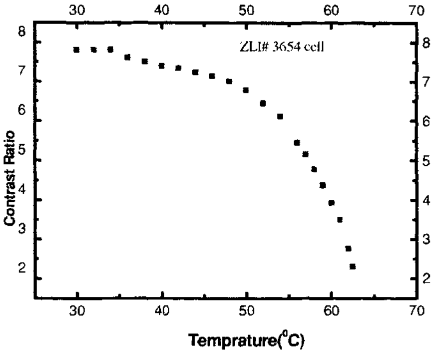

Figure 5: Contrast ration versus temperature at 2V,1Hz.

with decreasing temperature. These switching characteristics are very similar to the ones observed in FLC cells prepared in conventional manner.

CONCLUSIONS

In conclusion we have been able to show that the photodimerized bilayer molecular films of APTES molecules attached with cinnamoyl moieties can be used to produce stable, uniform planar orientation of ferroelectric liquid crystals. The electro-optic and switching properties of the prepared FLC cells have been investigated and found to be quite similar to those prepared in conventional manner. The growth and structure of the monolayer and bilayer films have been monitored and investigated by contact angle measurement, XPS and UV spectroscopy.

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Imprinting the Quasi Bookshelf Texture of a Ferroelectric Liquid Crystal into Nano-scaled Polymer Fibrils

S. H. Kim, S. Suresh, and L.-C. Chien
Chemical Physics Interdisciplinary Program and Liquid Crystal Institute
Kent state University, Kent, Ohio 44242

ABSTRACT

Polymer-stabilized ferroelectric liquid crystals (PSFLCs) are made by photopolymerizing 3% reactive mesogenic monomer on a quasi bookshelf texture of a ferroelectric liquid crystal (FLC). We observe the formation of nano-scaled polymer fibrils templated by the two dimensionally ordered host. The polymer fibrils capture the orientation of the host with thin polymer fibrils interweaving the smectic layers. The SEM study highlights the difference in morphology of the polymer fibrils depending on polymerization conditions; that is, polymerizing with or without the presence of an electric field. The polymer networks suppress the cone of rotation of FLC and thus, facilitate the switching and shorten the response time of the PSFLCs. We observed the threshold-less switching behavior in PSFLCs from samples polymerized with and without the field.

INTRODUCTION

Polymer stabilized liquid crystals (PSLCs) have rapidly developed into a unique class of electro-optical materials and play an important role in display[1,2] and photonic[3,4] technologies. The polymer network morphology of PSLCs, unique among these applications, plays a critical role in the performance of each device.[5,6] The polymer network is typically formed via a controllable photopolymerization process using a wide variety of optical pattern forming states of liquid crystal hosts. The resultant polymer networks not only mimic the phase and structures of liquid crystals but also, under applied external field, control the reorientation of liquid crystal molecules in the surrounding area of polymer network. The polymer morphology itself is of considerable interest in the study of polymerization-induced phase separation in orientationally-ordered media. Despite reports on polymer stabilized ferroelectric liquid crystals,[7-10] the specific morphology of the polymer network and its precise connection to the electro-optical properties of ferroelectric liquid crystal (FLC) system remain open issues. In this paper, we report the study of polymer networks formed in a FLC and the influences of network morphology on electro-optical properties of the composite system.

EXPERIMENTAL DETAILS

The CS1024 FLC obtained from Chisso Japan was used as the host (96.85wt%). A mesogenic monomer 1,4'-{bis[4-(6-acryloyloxy)hexoxy] benzoate}-2-methyl-benzene (BBMB6) (3wt%) was used to form polymer networks in CS1024. A small amount of photo initiator Irgacure 369 (0.15wt%) was added to the mixtures of monomer/liquid crystal. The mixtures of FLC/monomer/photoinitiator were loaded into commercial LC cells (with 4 μm

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spacing between anti-parallel rubbed polyimide alignment layers and ITO electrode area of 0.9x0.9 mm^2) by capillary action. The FLC mixtures were photopolymerized by UV illumination (the light source has a wavelength of 365 nm and 0.4 mW/cm^2) at room temperature with (4V/μm 34 Hz triangle wave) or without an applied field. The sample to be polymerized under the electric field, was first heated to isotropic and then cooled to the desired polymerization temperature under the applied field. Polarizing microscopy study indicated that the transition temperatures of FLCs decrease with the addition of reactive monomers. The spontaneous polarization measurements on pure FLC, FLC/monomer mixture, and polymer-stabilized samples were carried out using the triangular wave method. The samples were placed in a Mettler FP 5 hot stage for temperature control within 0.1 degree Celsius and electric field applied by HP33120A function generator in combination with a HP6824A power amplifier. The polarization reversal current data were measured across a 30-Ohm resistor and detected with a HP54600 digital oscilloscope and recorded with a PC. For each temperature, multiple measurements were taken to reduce statistical errors. The quality of alignment was evaluated with a Nikon polarizing microscope.

We prepared PSFLC samples with a LC diacrylate monomer BBMB6 and studied their electro-optical properties including spontaneous polarization and switching characteristics using cells with a 4μm cell gap. The temperature dependence of spontaneous polarization of the PSFLC sample (CS1024/BBMB6 polymerized with the triangular wave, 8V/μm, 34Hz, at 25°C) was studied under the applied field of 8V/μm. Figure 1a shows the maximum spontaneous polarization (Ps) value of 35 nC/cm^2 at 25°C. There is a slight decrease in Ps value compared with that of the pure CS1024 because of a smaller tilt angle caused by the formation of polymer network.

Figure 1b shows the field dependence of spontaneous polarization of the PSFLC samples prepared from CS1024/BBMB6. As shown in 1b, we observed a slight decrease in Ps value of PSFLC compared with the pure FLC because of the smaller tilt angle as a result of the formation of polymer network. A faster switching time was observed (Figure 1c, 80μs at 8V/μm, 34 Hz, triangular wave) for the PSFLC sample compared with that of the neat CS1024.

Figures 2a and 2b show the PSFLC switched between the bright and dark state under the applied electric field of square wave, 8V/μm, 1 Hz. The PSFLC displays a stripe texture observed from a polarizing optical microscopy study. A distinct optical contrast was observed between the two different optical states. The SEM study highlights the difference in morphology of the polymer fibrils depending on polymerization conditions; that is, polymerizing with or without the presence of electric field. The cells of PSFLCs were immersed in hexane and dichloromethane at a mixture ratio of 8:2 to extract the liquid crystal. The cells were kept in solvent for several days and fresh solvent was used each day. After the FLC was removed, the cells were opened carefully. The SEM images highlight the difference in polymer morphology for the PSFLC samples from CS1024 polymerized with or without the presence of electric field. Nano-scaled thin and uniaxially aligned polymer fibrils with lateral brushes are observed for the CS1024 sample polymerized without the presence of electric field (Figure 2c). The fibrous networks formed without the application of electric field are tilted with respect to the rubbing direction (up-down arrow direction), indicating that the polymer network formed parallel to the smectic layers. In the case of CS1024 polymerized with the presence of electric field, we observed thicker polymer fibrils (Fig. 2d). The polymer fibrils from the sample polymerized with applied electric field possess a pattern of crossed stripes. The crossed polymer fibrils separate with