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A novel photoalignment film for ferroelectric liquid crystal based on self-assembled monolayer method

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A novel strategy based on self-assembly technology was devised for design of photosensitive material as a ferroelectric liquid crystal (FLC) alignment layer. This development offers new tools for the study and control at the molecular level of the interaction of FLCs with solid surfaces. The photoreactive material was self-assembled to the substrate by covalent bond linkage due to a special chemical adsorption reaction. Through ester bond linkage, a cyano group with strong polarity was introduced to be terminus of the film. Under irradiation of linearly polarised ultraviolet light, an optically anisotropic self-assembled film was easily obtained. The irradiated film was demonstrated to result in homogenous alignment of FLC by optical transmittance measurements and polarising optical microscopy images of a FLC cell at different rotation angles. The alignment quality of the FLC on this self-assembled monolayer film is comparable to that of commercial rubbed polyimide film. Furthermore, it was also found that the fine alignment of the FLC may be related to the smoothness of the self-assembled film surface owing to its polar end.

Keywords: ferroelectric liquid crystal; photoalignment; self-assembled monolayer

1. Introduction

Ferroelectric liquid crystal (FLC) displays, in comparison with the widely used nematic liquid crystal displays, show some important advantages, such as fast response time and wide viewing angle (*1*). A major problem that hinders the application of FLC displays is the difficulty of obtaining good orientation. Commercial FLC displays mainly use a rubbed polyimide film (*2, 3*). However, the rubbing method shows many shortcomings unsolved until now, such as sample contamination, static charge generation and mechanical damage.

Photoalignment, which avoids many drawbacks of traditional rubbing techniques for LC alignment (*4*), is a promising technology for manufacturing a variety of liquid crystal displays. Several researchers have reported FLC displays fabricated with photoalignment techniques with spin-coated photosensitive polyimide material (*5, 6*). As to the spin-coating process, certain adhesion problems exist for photosensitive alignment layers on some surfaces, which would degrade the film-forming ability and further the optical quality of a FLC device. Furthermore, the degree of order in spin-coated films was low. Previous work has shown that a self-assembled film with organosilane material exhibits a high degree of order and stability (*7, 8*). A self-assembled film is a system of supramolecular hierarchical organisation, which is more stable than the Langmuir-Blodgett film and more ordered than the spin-coating film (*9*). In this work, a novel photoalignment layer for FLCs based on the self-assembled monolayer (SAM) method with an end group of strong polarity was investigated. During the self-assembly process, the aligned material was chemisorbed onto a substrate. Under linearly polarised ultraviolet light (LPUVL) irradiation, homogeneous alignment, comparable to that achieved by rubbing, of the FLC on the SAM film was obtained. The relationship of the surface roughness of the irradiated SAM film and the alignment of the FLC is also discussed.

2. Experimental

Film and FLC cell preparation

The photosensitive material was synthesised using a conventional method based on an esterification reaction, as developed in previous work (*10*). After immersion of pretreated substrate in solution of photosensitive material for certain time, a self-assembled monolayer (SAM) film was successfully prepared. The self-assembled monolayer film was vertically irradiated at room temperature by LPUVL. The LPUVL was obtained from a collimated light source of 300 W Hg–Xe lamp, with a Glan–Thomson prism, used as polariser. The intensity of the LPUVL was 0.80 mW cm^{-2} at 297 nm ($\pm$5 nm).

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FLC cells were fabricated as sandwich-type cells between two substrates coated by self-assembled films and the thickness was about 2 μm. The FLC, Felix F171 (I 87°C N* 77°C SmA 73°C SmC* −28°C Cr, Clariant), was heated into its isotropic phase, drawn into the cell by capillary action and cooled to room temperature, at which the FLC medium is in the chiral smectic C (SmC*) phase, with a cooling rate of 0.1°C min^{-1}.

Measurement techniques

The water contact angle of the film surface was measured during the self-assembly process using a contact angle analyser (JJC-I, Changchun No.5 Optical Instrument Co., China). The contact angles along the four directions every 90° to the horizontal direction were measured and averaged to obtain the result. The UV absorption spectrum of the SAM film was detected by UV-3101PC spectroscopy (Shimadzu Co.). The topography of the film was detected with AFM method (Dimension 3100s, Digital Instrument Co.) on a quartz substrate. The alignment behaviour of the FLC was evaluated by using a polarised optical microscope (BX-51, Olympus) with crossed polarisers.

3. Results and discussion

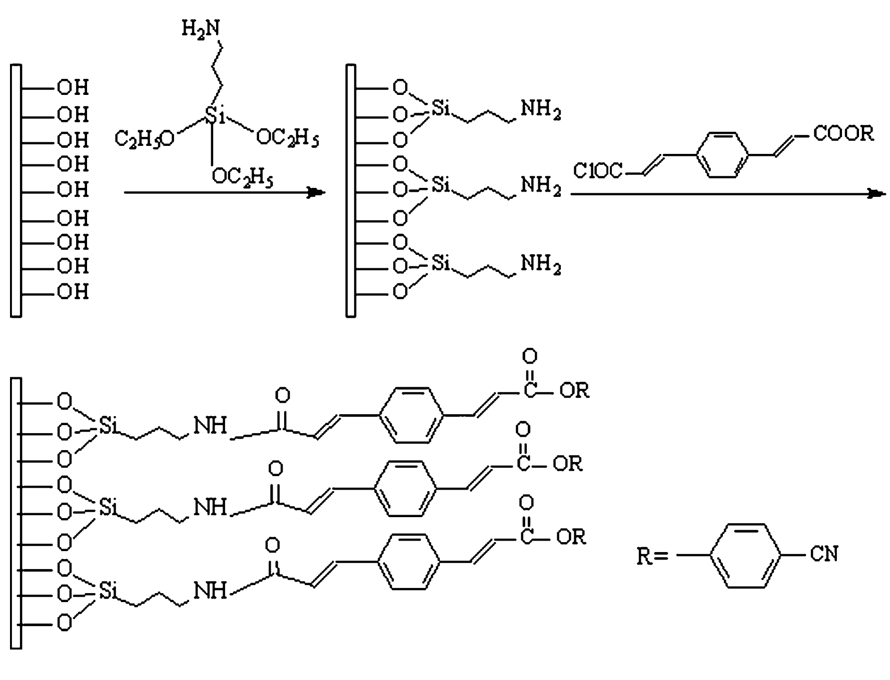
Formation of the self-assembled film

Clean quartz plates (25 mm × 20 mm × 1 mm) were used as substrates. The surface of the cleaned substrate was modified with aminopropyltriethoxysilane using the method described by Haller (*11*). Then the substrate decorated with the amino group was immersed in 1% solution of the photosensitive material used in this study in anhydrous toluene at room temperature. The substrates were then cleaned in toluene, ethanol and deionised water in an ultrasonic bath for 2 min and finally dried in a nitrogen stream. The detailed illustration of the self-assembly process is shown in Scheme 1. When the substrate containing the amino group was immersed in the solution of photosensitive acyl chloride, a self-assembly reaction occurred. As shown in Scheme 1, the electrophilic acyl group in solution in excess easily reacted with the nucleophilic amino group on the substrate. Thus, a photosensitive SAM film was obtained.

During this process, the water contact angle was used to analyse the kinetics of the self-assembly reaction. Figure 1 plots the contact angle as a function of the adsorption time. It can be seen that the contact angle reaches a saturated value in a very short deposition time, which indicates fast kinetics of monolayer formation.

UV–visible spectroscopic inspection of SAMs

In order to study the photoreaction process of the photosensitive group in the SAM film, UV–visible spectroscopy was used to investigate the irradiated film. Figure 2 shows the UV absorption spectra of the monolayer film with increasing exposure energy. The



Scheme 1. Schematic illustration for formation of photosensitive self-assembled film on quartz substrate.

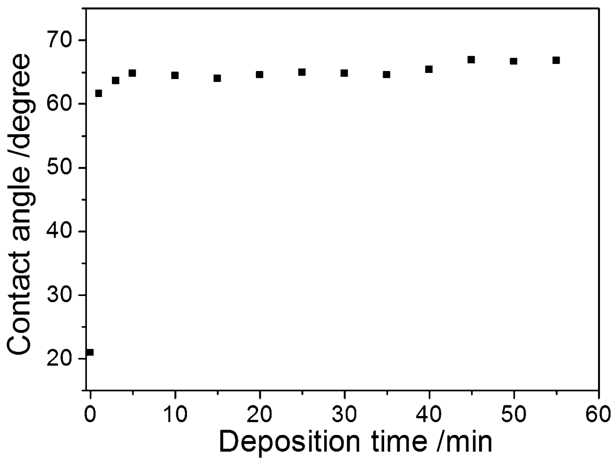


Figure 1. Contact angle of SAM film as a function of deposition time.

peak at 305 nm was attributed to the absorbance of photosensitive double bonds in the SAM film. The intensity of the UV peak exhibited an obvious decrease with increase of irradiation within 10 min. After 10 min of irradiation by LPUVL, the absorbance intensity of the peak no longer decreased, which indicated that the photochemical reaction involving photosensitive double bonds had completed. With evaluation by a UV spectrophotometric method, about 60% double carbon bonds was consumed, which revealed that the photosensitive self-assembled film has a high efficiency of the photoreaction. Similar studies showed that the photosensitive double bonds in the film mainly undergo [2+2] photocyclisation (*12*). Moreover, by exposure of LUVPL, macromolecules might be generated along the polarised direction of LPUVL via [2+2] cycloaddition for two double bonds in each unit. The possible

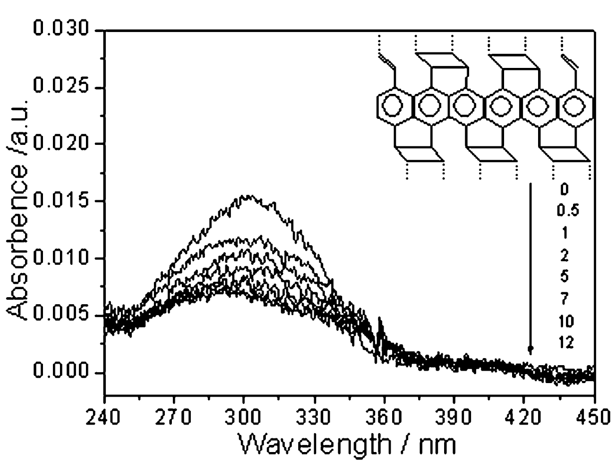


Figure 2. UV spectra of photosensitive self-assembled film as a function of LPUVL irradiation time; the inset shows a schematic illustration of photocrosslinkage of photoalignment film.

configuration of the reacted film is schematically illustrated in the inset to Figure 2. Thus, an anisotropic photoalignment film was achieved.

LC alignment behaviour

Via rotation on the object stage, the alignment behaviour of the FLC cell based on irradiated SAM film was evaluated using a polarising optical microscope with crossed polarisers. An obvious dark state (when the optical axis of the FLC aligns with either the polariser or the analyser) and bright state (when observed with polariser or analyser kept at 45° to the optical axis) were found, as shown in Figure 3. All images were obtained using a 50 × objective lens with a 200 μm field of view. It can be seen that the FLC on SAM film results in a very good dark state, indicating defect-free alignment of the FLC.

Figure 4 shows the transmittance curve of the FLC cells based on SAM film and rubbed polyimide (PI) film as a function of rotation angle. Here, a static contrast ratio (CR) of the FLC cell is introduced to analyse the results. It is defined as the ratio between intensity of the brightest state and that of darkest

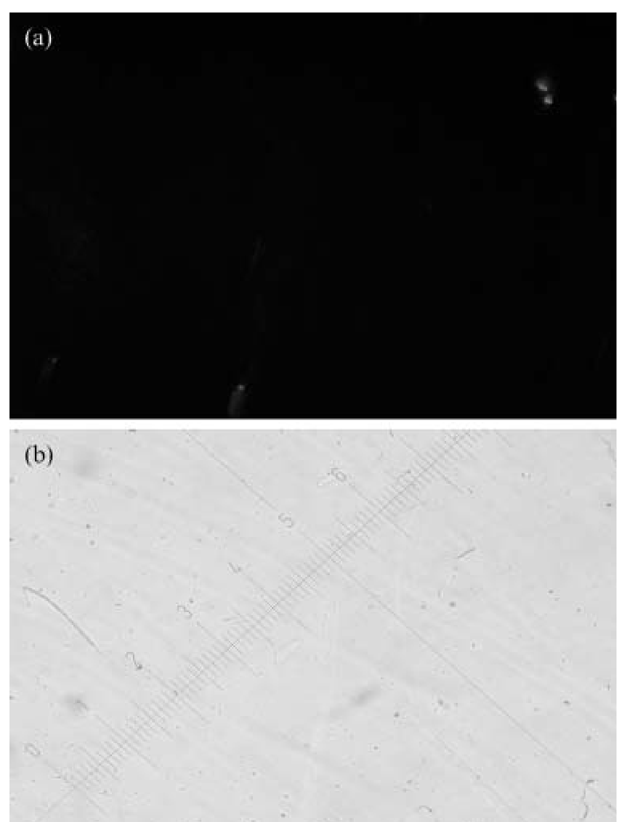


Figure 3. Optical micrographs of FLC cells fabricated with photosensitive self-assembled film: (a) image of dark state; (b) image of bright state.

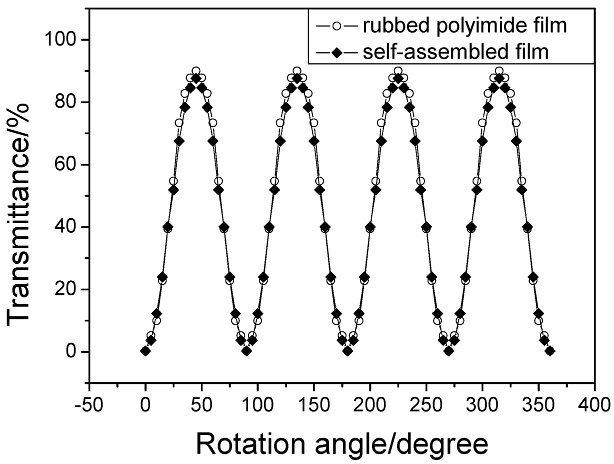


Figure 4. Transmittances of FLC cells with photosensitive self-assembled film and rubbed polyimide film depended on rotational angle of polarised microscope.

state when the FLC cell was rotated on the object stage of the polarising microscope (CR$=I_{max}/I_{min}$), with a large CR value corresponding to a good alignment performance of the FLC. The CR value of the FLC cell on SAM film is as high as 350, which is comparable with that achieved on rubbed polyimide film (*13*). This indicates that a fine photoalignment of FLC is obtained on this novel self-assembled film.

Morphology observation with AFM

In order to determine why the FLC exhibited a fine alignment on this SAM film, the characterisation of irradiated film was conducted by observing surface morphology using atomic force microscopy (AFM). Figures 5 a and 5 b show the surface morphologies of the irradiated SAM film and rubbed PI film, respectively. The corresponding root-mean-square roughness values are 0.504 nm detected in 3 µm × 3 µm area and 0.712 nm detected in 2 µm × 2 µm area, respectively. This shows that the scale and number of undulations on SAM film surfaces are much less than those of rubbed PI film, even averaged in a larger detected area. Organic molecules in a SAM are densely immobilised on the surface with their molecular orientation and arrangement depending on molecular interactions. The polar terminus of this SAM film may be responsible for its smooth surface due to a strong static repulsion effect. This effect could avoid entanglement of hydrocarbon chains in SAM, which would result in a coarse surface. Moreover, rugged surface may produce high pretilted angle locally and zigzag defects would appear in FLC cell. Hence, it is concluded that the wonderfully flat surface of SAM film may be one of the favourable features for fabricating FLCs free of zigzag defects. Furue *et al.* also has found that smooth surface is suitable for forming a fine alignment that produces a very good dark state without zigzag defects (*14*). This conclusion is also in agreement with that obtained by Watson *et al.* (*15*).

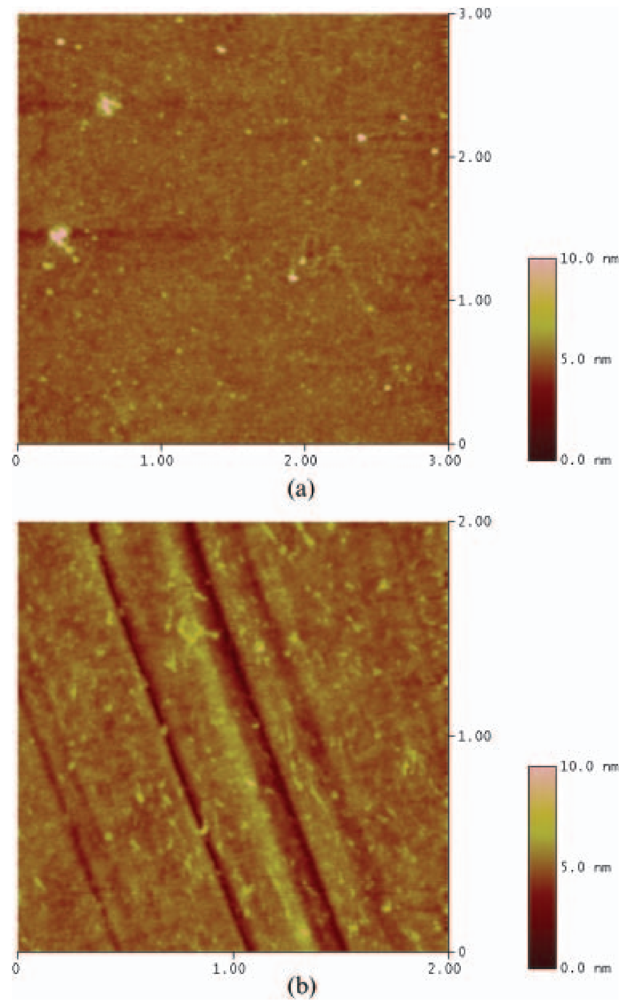


Figure 5. Surface morphologies of irradiated SAM film (a) and rubbed PI film (b).

4. Conclusions

A novel self-assembled alignment film for ferroelectric liquid crystals is reported in this work. The photosensitive material was chemisorbed onto a substrate by covalent bond linkage with fast formation kinetics involving a deposition time of a few seconds. After LPUVL irradiation for about 10 min, an optically anisotropic SAM film was easily obtained. The irradiated film could induce ferroelectric liquid crystal to align homogeneously, and the alignment quality is comparable to that with conventional rubbed film. Static repulsion among polar ends in SAM film may be responsible for resulting smooth surface observed by AFM. It is concluded that the smooth surface of irradiated SAM film may be one favourable factor for fabricating FLC cells with good dark state without zigzag defects. Because the self-assembled film is easily built on quartz and silicon substrates, this novel SAM photoalignment film will be useful in ferroelectric liquid crystal-on-silicon displays.

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References

(1) Clark N.A.; Lagerwall S.T. *Appl. Phys. Lett.* **1980**, *36*, 899–901.
(2) Koden M.; Katsuse H.; Tagawa A. *Jap. J. appl. Phys.* **1992**, *31*, 3632–3635.
(3) Williams D.; Davis L.E. *Appl. Phys.* **1986**, *19*, L241–L245.
(4) Schadt M.; Schmitt K.; Kozenkov V.; Chigrinov V. *Jap. J. Appl. Phys.* **1992**, *31*, 2155–2164.
(5) Kang W.S.; Kim H.W.; Kim J.D. *Liq. Cryst.* **2002**, *29*, 583.
(6) Walba D.M.; Liberko C.A.; Shao R.; Clark N.A. *Liq. Cryst.* **2002**, *29*, 1015.
(7) Jin S.H.; Lee J.C.; Park D.K. *Polym. Bull.* **1996**, *37*, 799.
(8) Naciri J.; Fang J.Y.; Moore M.; Shenoy D.; Dulcey C.S.; Shashidhar R. *Chem. Mater.* **2000**, *12*, 3288.
(9) Ulman A. *Chem. Rev.* **1996**, *96*, 1533.
(10) Yao L.S.; Peng Z.H.; Zhang L.L.; Xuan L. *Mol. Cryst. liq. Cryst.* **2006**, *461*, 3.
(11) Haller I. *J. Am. chem. Soc.* **1978**, *100*, 8050.
(12) Egerton P.L.; Trigg J.; Hyde E.M. *Macromolecules* **1981**, *14*, 100.
(13) Furue H. *Jap. J. appl. Phys.* **2003**, *42*, 2759.
(14) Furue H.; Iimura Y.; Miyamoto Y.; Endoh H.; Fukuro H.; Kobayashi S. *Jap. J. appl. Phys.* **1998**, *37*, 3417.
(15) Watson P.; Bos P.J.; Pirs J. *Phys. Rev. E* **1997**, *56*, R3769.