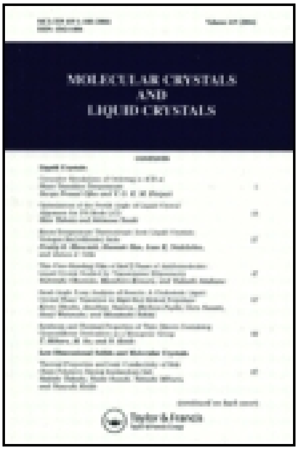

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Investigation of Photoalignment Films of Liquid Crystal Based on a Photosensitive Self-Assembled Monolayer Film

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Version of record first published: 31 Jan 2007

To cite this article: Lishuang Yao, Lingli Zhang, Chunhong Fei, Fengzhen Lv, Zenghui Peng & Li Xuan (2006): Investigation of Photoalignment Films of Liquid Crystal Based on a Photosensitive Self-Assembled Monolayer Film, Molecular Crystals and Liquid Crystals, 461:1, 3-13

To link to this article: http://dx.doi.org/10.1080/15421400600912860

Mol. Cryst. Liq. Cryst., Vol. 461, pp. 3–13, 2007
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400600912860

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A photoalignment film derived from photosensitive self-assembled monolayer with a p-phenylenediacrylate group is reported. The precursor film was prepared by self-assembled reaction of chemical adsorption, and then the film was irradiated by linearly polarized ultraviolet light. The photoalignment film induces nematic liquid crystal to align homogeneously, and the alignment direction of the liquid crystal molecules is perpendicular to the polarized direction of incident ultraviolet light. By variation of the length of the alkane chain and the different functional group at its terminus, the self-assembled photoalignment films with different polarity were prepared and determined. The film with n-alkyl benzene moieties showed better alignment performance than the others.

Keywords: liquid crystal; photoalignment; photosensitive; self-assembled

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1. INTRODUCTION

Alignment films of liquid crystals (LCs) are important components of liquid crystal displays (LCDs). The fabrication of commercial LCDs mainly uses a rubbing polyimide film. However, the rubbing method leads to many shortcomings, such as mechanical damage of the substrate, electrostatic charge, and dust contamination [1,2]. Recently, photoalignment technology has attracted great interest by virtue of the touch-free process [3]. When irradiated by linearly polarized ultraviolet light (LPUVL), the photoalignment film can undergo a polarized photoreaction and will exhibit the ability to align the LC. There are three principal types of photoalignment materials that have been extensively studied: (1) photoisomerizable materials [4], (2) photo-cross-linking materials [3], and (3) photodegradable materials [5]. The photoisomerizable materials involve a polymer with a group of azobenzenes, spiropyrans, *etc*., which can exhibit E/Z transition under LPUVL irradiation. The second type shows $[2+2]$ photodimerization of materials such as cinnamates and coumarins. The photodegradable materials are usually polyimides, which can be degraded in a polarizing direction by deep LPUVL. Though polyimide film possesses better thermal stability than the others, the product of photodegradation is unstable and can bring a flicker phenomenon to LCDs and impair the performance of the LC device. Many research results indicate that the photo-cross-linking materials are more suitable for permanent alignment films of LCDs. A systematical review of photoalignment materials was given by Ichimura [6].

The precursor films of photoalignment are normally prepared by three methods: the spin-coating method, Langmuir–Bolodgett (LB) method [7], and self-assembled method [8]. The first two methods have been widely studied, but little investigation for photoalignment films has been undertaken of the self-assembled film method. The self-assembled film is a system of supramolecular hierarchical organization, which is more stable than the LB film and more ordered than the spin-coating film [9]. Appropriate chemical reactions enable the self-assembled films to be carried out efficiently.

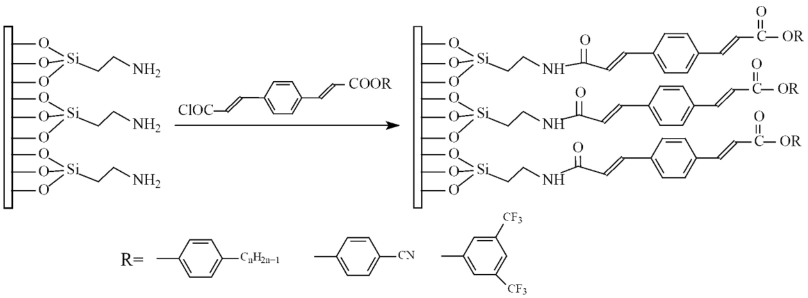
In this article, a photo-cross-linkable self-assembled monolayer film with p-phenylenediacrylate chromophores was prepared. The p-phenylenediacrylate group has two photosensitive double bonds and exhibits good photoactivity. These groups can undergo photo-cross-linking and be converted to a high molecular polymer [10]. In the experiment, under LPUVL irradiation the p-phenylenediacrylate moieties were cross-linked along the polarized direction of LPUVL *via* $[2+2]$ cyclization, and the self-assembled photoalignment film was obtained. By variation of the length of the alkane chain and the different functional group at its terminus, the photoalignment films with various polarities were prepared, which exhibited different alignment performance. The experimental results were discussed through UV-vis absorption spectroscopy and atomic force microscope (AFM) analysis.

2. EXPERIMENTAL

2.1. Film and LC Cell Preparation

Clean quartz plates (25 mm × 20 mm × 1 mm) were used as substrates in this study. The substrates were cleaned in piranha solution (70:30 v/v mixture of conc. H_2SO_4 and 30% H_2O_2) for 20 minutes at 80°C, then rinsed with deionized water and blown dry. The surface of the quartz substrate was modified with aminopropyltriethoxysilane in the way described in Ref. [11]. Then the substrate was immersed in a 1% solution of photosensitive materials in anhydrous toluene at room temperature. The photosensitive materials were synthesized by conventional organic methods, and the chemical reaction route is illustrated in Scheme 1. Then the substrates were cleaned in toluene, ethanol, and deionized water in an ultrasonic bath respectively for 2 min and finally dried in a nitrogen stream. A photosensitive self-assembled film was successfully prepared on the quartz substrate.

The self-assembled monolayer film was vertically irradiated at room temperature by linearly polarized UV light. The LPUVL was obtained from a collimated light source of a 300-W Hg-Xe lamp, and a Glan–Thomson prism was used as polarizer. The intensity of LPUVL is 0.80 mw/cm^2 at 297 nm.



SCHEME 1 Schematic illustration of the formation of photosensitive self-assembled film (with 4-alkyl benzene end group, with 4-cyano benzene end group, and with 3,5-trifluoromethyl benzene end group) on quartz substrate.

Two similar substrates with the irradiated films were assembled to form sandwich-type parallel LC cells with a gap of 40 μm. The nematic LC 5CB (Slichem Co. Ltd., China) was filled into the cells in the isotropic state at 40°C, and then the cells were naturally cooled to the nematic phase of 5CB.

2.2. Methods of Measurements

The water contact angle was measured in the process of film formation by a contact-angle analyzer (JJC-I, Chang Chun No. 5 Optical Instrument Co. Ltd.). The UV absorption spectrum of the self-assembled film was detected by UV-3101PC spectroscopy (Shimadzu Co.) on a quartz substrate. The LC alignment direction was determined by polarized Fourier transform infrared (FT-IR) spectroscopy (BIO-RAD FTS-3000, USA). The topography of the film was analyzed with the AFM method (Dimension 3100s, Digital Instrument Co.) on a quartz substrate.

3. RESULTS AND DISCUSSION

3.1. Formation of Self-Assembled Photoalignment Film

In this work, a photosensitive self-assembled monolayer was prepared by a chemical reaction on a quartz substrate surface. When the substrate containing an amino group was immersed in the solution of photosensitive acyl chloride, a self-assembled reaction was carried out, and then a photosensitive self-assembled monolayer film was obtained. The reaction route is illustrated in Scheme 1. In this process, the water contact angle was used to analyze the kinetics of the self-assembled reaction. Figure 1 plots the contact angles as a function of the adsorption time. In all cases, the contact angle reaches a saturated value in a very short reaction time, which indicates the formation of the monolayer is a fast kinetic process. Also, the contact angle value of each photoalignment film was different, which was mainly caused by the different hydrophobicity of the film surface structure.

Figure 2 shows the UV absorption spectra of the monolayer film with exposure energy increasing, and the self-assembled film has 4-ethyl benzene moieties. The peak at 305 nm was attributed to the absorbance of photosensitive double bonds. The intensity of the UV peak decreased with increase of irradiation time. When LPUVL irradiation exceeded 10 min, the absorbance intensity of the peak would be a constant. The reaction ratio of photosensitive group was 60% as evaluated by UV spectrophotometric method, which revealed that the self-assembled films have a high photosensitive efficiency.

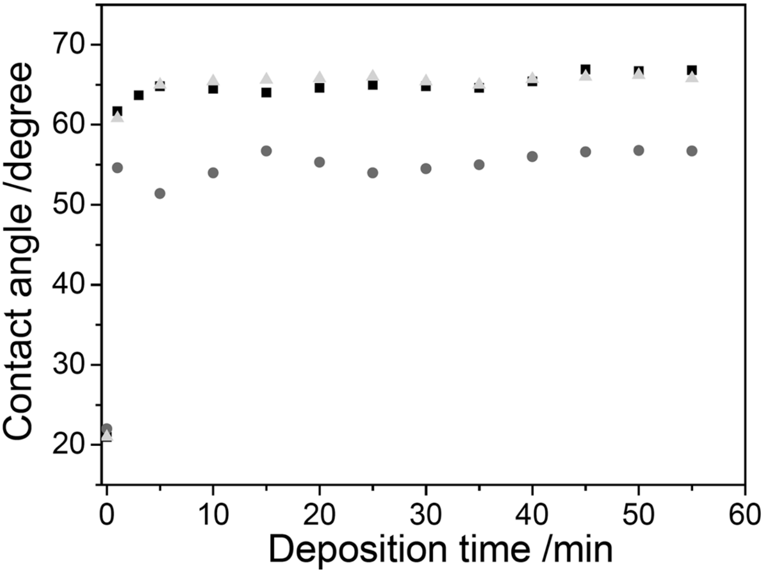


FIGURE 1 Contact angles of self-assembled monolayers as a function of depositon time (▲: film with trifuloromethyl benzene end, ■: film with cyano benzene end, and ●: film with ethylic benzene end).

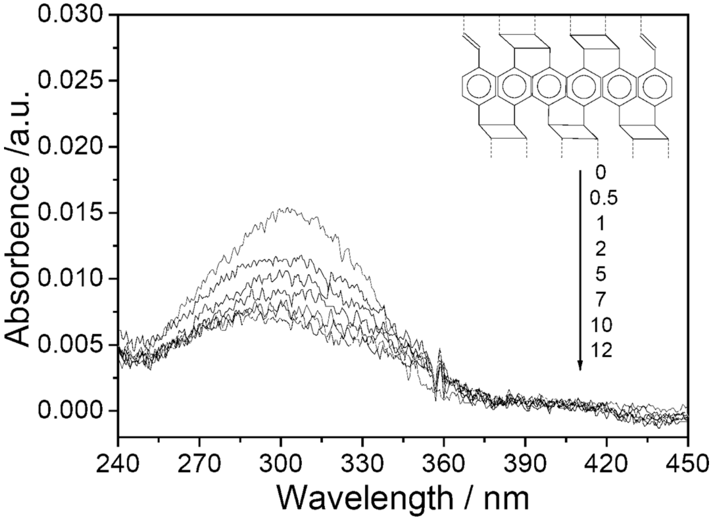


FIGURE 2 UV spectra of photoalignment material with 4-ethyl benzene as a function LPUVL irradiation time; the inset is the schematic illustration of photo-cross-linkage of photoalignment film.

Some similar research shows that the photosensitive double bonds in the film mainly undergo [2 + 2] photocyclization [12]. Moreover, by LUVPL exposure, macromolecules might be generated along the polarization direction of LPUVL via [2 + 2] cyclization. The possible configuration of the reacted film is schematically illustrated in Fig. 2. Then an anisotropic photoalignment film was achieved.

3.2. LC Photoalignment Behavior

The alignment behavior of LC cells with different types of photoalignment films was evaluated by optical microscope with crossed polarizers. Obvious dark and bright states were found in the field of vision when the object stage was rotated. Figure 3 shows photomicrographs of the dark and bright states of the cells fabricated with films attached to the 4-ethyl benzene group. Figure 4 shows the transmittance curve of LC cells with different alignment films as a function of rotating angle. It indicated that the self-assembled film could induce the LC to align homogeneously in a planar state. To investigate the influence of the terminal group, a static contrast ratio (CR) of LC cell was introduced. It was defined as the ratio between light intensity of the brightest state and that of the darkest state when the LC cell was rotated on the objective stage of the polarizing microscope [$CR = I_{max}/I_{min}$], and large CR value means a good alignment performance of the LC. The CR values of trifluoromethyl benzene, cyano benzene, and 4-ethyl benzene end groups were 9, 13, and 50 respectively. It indicated that the photoaligned performance of trifluoromethyl and cyano benzene film is inferior to the film attached the 4-ethyl benzene end with weaker

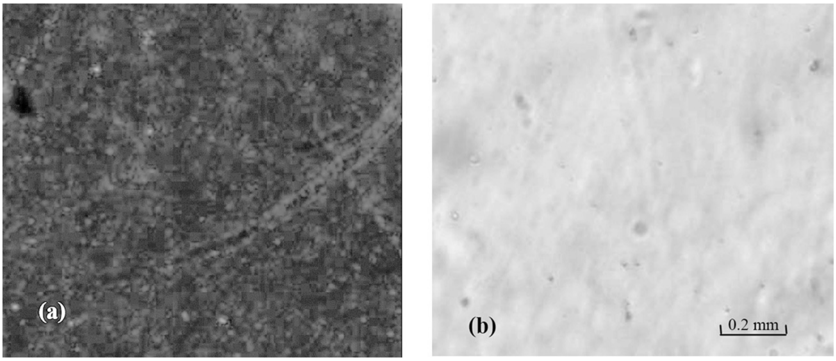


FIGURE 3 Optical micrographs of cells fabricated with ethylic benzene end film: (a) dark state, (b) bright state.

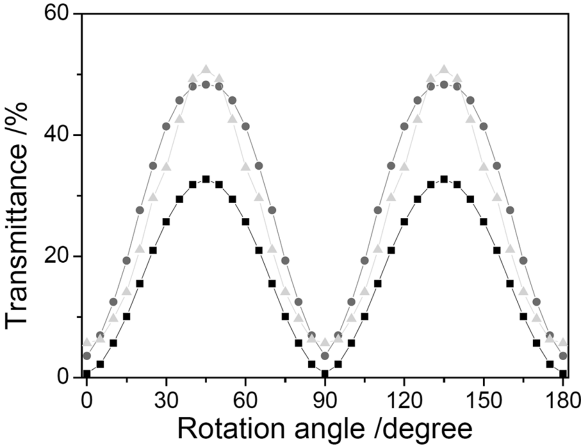


FIGURE 4 Transmittance of LC cell with different photoalignment film depending on rotational angle of polarized microscope (●: cyano benzene terminal group, ▲: trifluoromethyl benzene terminal group, and ◆: ethyl benzene terminal group).

polarity. Therefore, the alignment performance can be affected by structural modification of self-assembled monolayer film.

For further research, four more types of photoalignment film with phenyl, *n*-pentyl benzene, *n*-octyl benzene, and *n*-dodecyl benzene groups were prepared. The five types of self-assembled films with different lengths of alkyl moieties are named C0, C2, C5, C8, and C12 (n = 0, 2, 5, 8, 12 in Fig. 1). Figure 5 shows the transmittance curves of the LC cells with different kinds of photoalignment films. With an increase of the alkyl chain length, the CR value of LC cell became large, and the alignment performance became better. When the alkyl length was C8, the alignment quality attained saturation and gave the best result.

To investigate why the photoalignment films with different terminal alkyl groups have different alignment properties, the AFM technique was used as a probe of the uniformity of the surface morphology. Table 1 shows the root-mean-square (RMS) roughness values of the films with alkyl values of C0, C2, C5, and C8, and these numbers are the averages of five samples. After irradiation, the RMS values of photoalignment film with all lengths of alkyl chain became larger. Moreover, the difference in values of RMS between irradiated and unirradiated film become smaller with the increase of alkyl length, and it was similar to the previous result [13,14]. When the length is C8, the change of RMS value is very slight. Figure 6 shows the AFM photograph of the photoa-

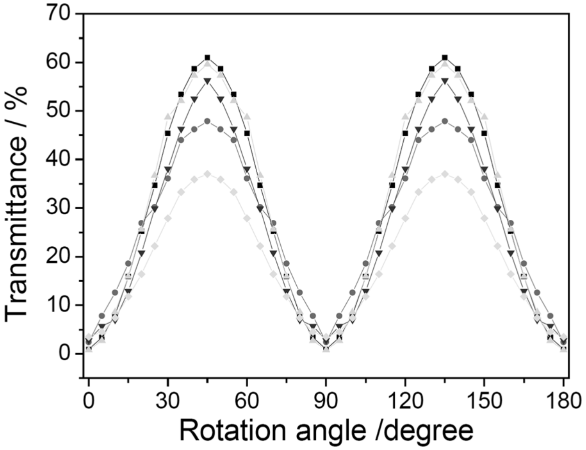


FIGURE 5 Angular transmittance of five types of LC cells with alignment film containing different groups (■: *n*-dodecyl benzene, ▲: *n*-octyl benzene, ◆: *n*-pentyl benzene, ●: *n*-ethyl benzene, and ▼: benzene).

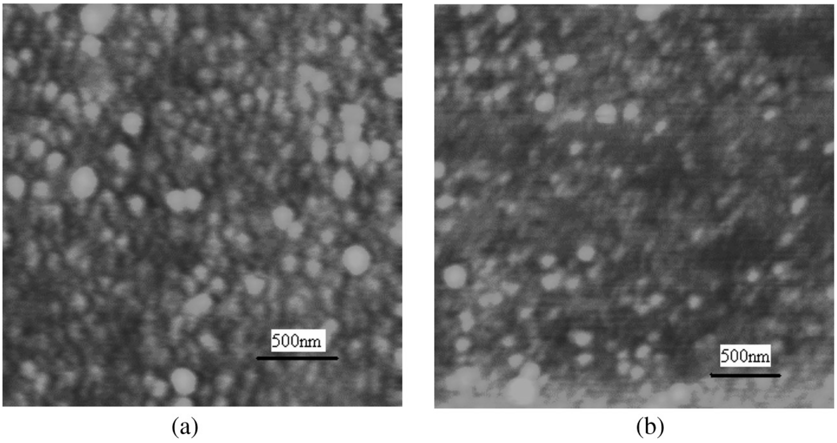
lignment film containing a C8 moiety. The difference of irradiated and unirradiated RMS value is probably caused by the selective photoreaction. As to the film with the longer alkyl chain, the long alkyl chain with flexibility could adjust its spatial arrangement and minimize the surface energy of the film, which promotes the formation of a close-packed, ordered monolayer structure [15]. The ordered photoalignment film with a C8 alkyl chain would induce a fine alignment of LC.

3.3. Direction of LC Alignment

The LC alignment direction can be determined by polarized FT-IR spectroscopy. When polarized IR adsorptions of 5CB in the LC cell are measured at a variational angle between the polarized direction of IR beam and that of LPUVL, the maximal absorption direction of the C≡N group

TABLE 1 RMS Roughness Values of Films with Alkyl Chain of C0, C2, C5, and C8 Before and After LPUVL Irradiation

Roughness (RMS value)	C0	C2	C5	C8
Before irradiation	0.182	0.144	0.134	0.130
After irradiation	0.210	0.221	0.159	0.139



(a) (b)

FIGURE 6 Topographic images of C8 self-assembled photoalignment film (a) before and (b) after irradiation.

(2231 cm^{-1}) represents the LC alignment direction. Figure 7 illustrates the angular absorption intensity of the 2231 cm^{-1} peak by the alignment film containing 4-ethyl benzene groups, and the arrow in Fig. 7 is the polarization direction of LPUVL. It indicates that the alignment direction of 5CB LC molecules is perpendicular to the polarization direction of the LPUVL. All types of photoalignment film in this work had the same results, which might come from the interactions between LC molecules and the unreacted photosensitive moieties.

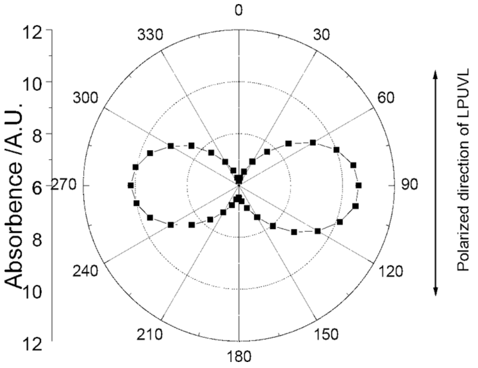


FIGURE 7 Polar diagrams of the IR polarized absorption by LC cell fabricated with 4-ethyl benzene self-assembled film, as a function of the angle of rotation of the LC cell. (Arrow line is the polarized direction of the LPUVL.)

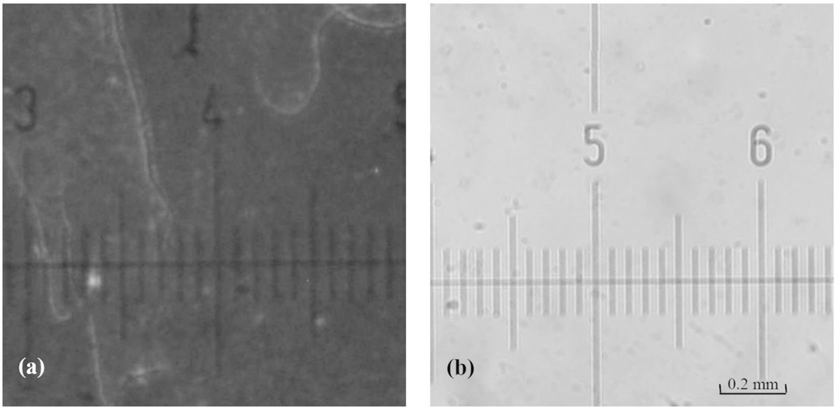


FIGURE 8 Optical micrographs of cells fabricated with octyl material after thermal anneal: a) dark state, b) bright state.

3.4. Thermal Stability of the Photoalignment Film

At the request of industrialized manufacturing, we evaluated the thermal stability of the film with an alkyl length of C8. Figure 8 shows the dark and bright state of the cell after heating at 120°C for 30 min. A high temperature of 120°C hardly damaged the alignment effect. The film with an alkyl length of C8 still gave a good alignment, with a CR value of 66. The thermal stability of this material against heat was very close to the commercial requirement.

4. CONCLUSIONS

A new photosensitive self-assembled monolayer film was prepared in this work. After LPUVL irradiation, the macromolecular product might be generated via [2 + 2] cycloaddition in the polarized direction. The alignment result of different terminal structural modification of the film was investigated. The material with an alkyl end group of weaker polarity than the others referred to in this article exhibited preferable alignment behavior. Furthermore, when the structure of the terminal alkyl chain in self-assembled film was C8, the alignment effect of the LC could reach the best result. AFM results indicate that the film with a longer alkyl terminal chain (longer than an 8-hydrocarbon chain) could maintain its preferable order of the exposed film and showed better alignment. Because the self-assembled film is easily built up on quartz and silicon substrate, the photoalignment films will be useful in the liquid-crystal-on-silicon display.

ACKNOWLEDGMENT

The authors are grateful to the National Natural Science Foundation of China (Grant Nos. 50473040, 60578035) and the Natural Foundation of Jilin Province (Grant No. 20050520, No. 20050321-2) for financial support.

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