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Alignment of liquid crystals induced by a photopolymerized self-assembled film

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An alignment film derived from a photopolymerized self-assembled film may be used to orient nematic liquid crystals after irradiating the film with linearly polarized UV (LPUV). A photosensitive cationic amphiphile was first synthesized containing two double bonds and which could be polymerized by UV. A layer-by-layer self-assembled multilayer film was next prepared in an aqueous solution of the cationic amphiphile and poly(sodium 4-styrenesulphonate); the UV-Vis spectra showed that each layer of the LBL multilayer film was uniform. When the film was irradiated by LPUV, the photosensitive double bonds underwent [2+2] cycloaddition along the vector direction of LPUV. The polarized UV-Vis absorption spectra also provided evidence that the film was anisotropic, i.e. the photopolymerization was along a certain direction. The anisotropic film was used as an alignment layer for nematic liquid crystals, and observations under a polarizing microscope indicated that the alignment of the liquid crystals was good, as expected, and that the orientation direction of the liquid crystals was always perpendicular to the electric vector of the irradiating LPUV.

1. Introduction

Most liquid crystal devices (LCDs) require alignment layers to achieve a preferential orientation direction of the liquid crystals. In recent years, the photoalignment technique has become a promising method to replace the conventional rubbing method. Photoalignment is a non-contact alignment technique, which avoids the shortcomings of rubbing, such as substrate contamination by dirt and scratching of the thin film transistor (TFT); and with the photoalignment technique multi-domain liquid crystal displays can be fabricated with improved viewing angles [1].

Photoalignment research began in the 1990s. In 1992, Schadt [2] found that poly(vinylcinnamate) films could induce liquid crystals to orient after irradiating by linearly polarized ultraviolet radiation (LPUV). The mechanism of photoalignment is that polarized photochemical reactions in the polymer film generate anisotropy at the interface of the film, and this anisotropic interface can induce the orientation of the liquid crystals. Since then, many photosensitive polymeric systems for photoalignment have been reported. These materials can be classified into three major categories. The first involves, for example azobenzenes [3], and stilbenes, which can undergo *E*/*Z* photoisomerization. Materials of the second category undergo [2+2] photocyclozation, for example cinnamates [2] and coumarins [1]. The third category are polyimides [4] which can be degraded by LPUV. Amongst these materials, the photodimerizable materials are more suitable for the permanent alignment of LCDs because of their stability. Ichimura has written a systematic review [5] of these materials.

The three major methods of forming photoalignment films are the spin-coating method, the LB film method and the self-assembled film method. The first two methods have been widely studied; however, little investigation on photoalignment has been undertaken for the self-assembled films method. A self-assembled film is an ordered reorganizing system, in which special chemical reactions may be performed in high yield. Naciri *et al*. [6, 7] fabricated photosensitive self-assembled monolayers using silane-based photodimerizable cinnamate materials; the photoalignment was excellent and the anchoring energy comparable to that from rubbing treatments.

In this work, a new self-assembled multilayer deposition film based on a photocycloaddition was prepared for photoalignment studies. A photosensitive quaternary ammonium salt (DIPY08) was synthesized, and then a layer-by-layer (LBL) self-assembled deposition

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multilayer film prepared in aqueous solution of DIPY08 and poly(sodium 4-styrenesulphonate) (PSS). After irradiation with LPUV, anisotropy was generated in the UV-Vis absorption measurement. It was found that the anisotropic LBL multilayer film could induce liquid crystals to align homogeneously, disclinations were hardly found in the liquid crystal cell under polarizing microscopy, and the contrast ratio of the device was about 100. Finally, the irradiation dosage was optimized and the mechanisms of liquid crystals alignment explored.

2. Experimental

2.1. *Synthesis*

PSS ($M_w \approx 70\,000$, 30 wt% aq.) was purchased from Aldrich Co. while DIPY08 was synthesized by a four-step procedure as described in reference [8], see the scheme.

2.1.1. p-Phenyleediacrylic acid (I). In a typical synthesis, terephthaldialdehyde (5 g) and malonic acid (8.5 g) were dissolved in pyridine (17 ml); aniline (0.75 g) was added as catalyst. The solution was stirred at 90°C, and carbon dioxide was generated as a by-product. When solution stopped producing gas, it was poured into 100 ml 1 M hydrochloric acid. A large quantity of white precipitate was generated; the product **I** was obtained by filtration. After dissolving in sodium carbonate solution the product was converted to the sodium salt; this was recrystallized from water, then redissolved in distilled water, and the pH adjusted to about 2 with hydrochloric acid added dropwise. After filtration, the final product (**I**) was obtained in 70% yield, m.p.>300°C. FTIR (powder, KBr, cm^{-1}): 984(=CH, δ), 1228(C–O, ν), 1626(C=C, ν), 1683 (C=O, ν), 3061(=CH, ν).

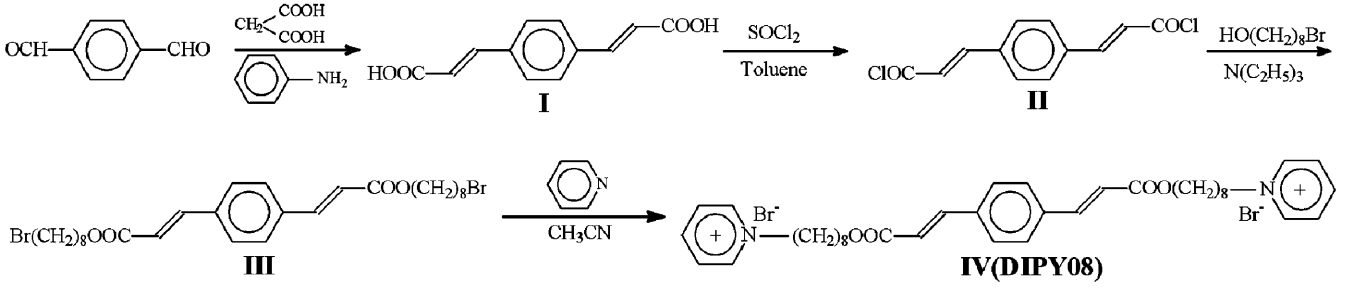
2.1.2. p-Phenyleediacrylic acid dichloride (II). Compound **I** (3.4 g) and 10 ml thionyl chloride (freshly distilled) were heated under reflux in 50 ml toluene for 4 h, with the addition of a few drops of DMF as catalyst. The resultant solution was cooled, and yellow needle-like crystals of **II** were produced. After filtering, the crude product was recrystallized from dry toluene, yielding 60% of final product, m.p. 170°C. FTIR (powder, KBr, cm^{-1}) 977(=CH, δ), 1229(C–O, ν), 1624(C=C, ν), 1718(C=O, ν), 3064(+CH, ν).

2.1.3. p-Phenylenediacrylic acid bis(11-bromoundecyl ester) (III). In a typical synthesis, the ester was prepared by a conventional esterification procedure from 8-bromo-1-octanol and compound **II** in dichloromethane in the presence of triethylamine. After evaporation of dichloromethane the crude residue was dissolved in ethyl acetate, and the white solid (triethylamine-hydrochloride) filtered off. The filtrate was washed by 0.1 M HC1, 0.1 M Na_2CO_3 solution and water. $MgSO_4$ was used to dry the organic layer, and the ethyl acetate was evaporated. The crude product **III** was purified via column chromatography (SiO_2, dichloromethane), yielding 30% of final product, m.p. 92–93°C. FTIR (powder, KBr, cm^{-1}): 645(C–Br, ν), 989(=CH, δ), 1205(C–O, ν), 1469(>CH_2, δ), 1632(C=C, ν), 1717(C=O, ν), 2859(>CH_2, ν), 2941(>CH_2, ν).

2.1.4. p-Phenylenediacrylic acid bis(11-pyridinium-N-ylundecyl ester)dibromide (IV) (DIPY08). The diester **III** (0.9 g) and pyridine (3 ml) were stirred in 30 ml acetonitrile at 80°C for 48 h; the mixture then was poured into 400 ml of dry ether. The insoluble white product **IV** was filtered off and vacuum dried giving 90% yield of final product, m.p. 177–179°C. FTIR (powder, KBr, cm^{-1}): 991(=CH, δ), 1202(C–O, ν), 1475(>CH_2, δ), 1635(C=C, ν), 1707(C=O, ν), 2867(>CH_2, ν), 2959(>CH_2, ν).

2.2. *Preparation of LBL multilayer film, cell fabrication and physical measurements*

2.2.1. Surface modification, layer-by-layer deposition and irradiation process. Quartz substrates were cleaned



Scheme. Method of preparation of photosensitive di-quaternary ammonium salt (DIPY08).

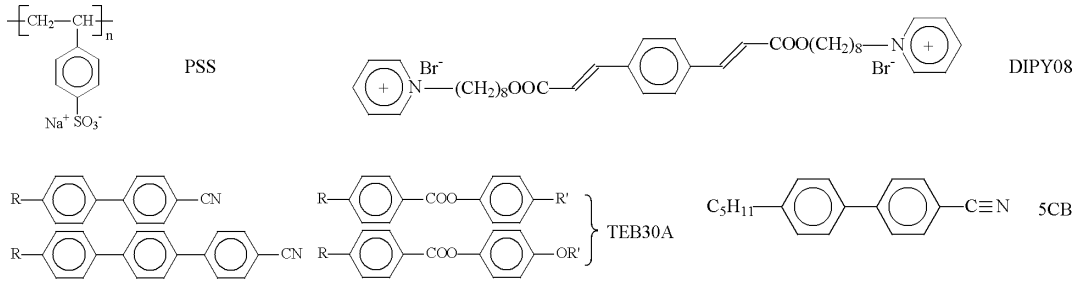


Figure 1. Chemical structures of reagents used in the experiment.

by first soaking in a surfactant solution and then in a heated Piranha solution, each step was performed for 20 min. The substrates were then washed by de-ionized water and dried on a Teflon shelf in an oven at 110°C for 30 min. The substrates were then treated with a solution of aminopropyltriethoxysilane (Aldrich Co.) in xylene [9], and rinsed twice, successively, with xylene, methanol and water. They were then soaked in 0.1 M HCl. By this process, the surface of quartz substrates was covered with ammonium cations for the following deposition process.

The self-assembled LBL deposition on the substrate was achieved using a well reported procedure [10]. The substrates were inmmersed in PSS solution ($1.0\,mg\,ml^{-1}$) and then DIPY08 solution ($1.0\,mg\,ml^{-1}$); the chemical structures of these materials are given in figure 1. After 20 min immersion time the substrates were washed using de-ionized water and blown dry using nitrogen gas. The cycle was repeated until the desired numbers of bilayers were obtained. The DIPY08 layer was always deposited last, see figure 2.

With the LBL multilayer film perpendicular to the incident light path, the substrate was irradiated by light from a 300 W Hg-Xe lamp at room temperature. LPUV was obtained by combination of a filter at 300 nm (Model 53370, Oriel Co.) and a Glan–Talor lens. The intensity of LPUV light on the surface of the film was $2.95\,mW\,cm^{-2}$ ($\lambda=296$ nm). After exposure, the substrates were used to measure UV-Vis and IR spectra or in the assembly of liquid crystal cells.

2.2.2. Preparation of liquid crystal cells. Liquid crystal cells with a gap of 20 μm were fabricated with two substrates fixed by acrylic ester glue, both substrates parallel with polarized direction of the LPUV. The commercial liquid crystal material 5CB ($T_c=35.4$°C, Aldrich Co.) was injected into the cells at 38°C. The cells were then cooled to room temperature at which 5CB exhibited the nematic phase.

2.2.3. Spectroscopic measurements. UV-Vis absorption spectra of the LBL multilayer films fabricated under different conditions on quartz substrates were measured by a Shimadzu UV-3101PC spectrophotometer; polarized UV-Vis absorption spectra were measured by using special polarizing accessories. IR spectra were recorded with a Bio-Rad FTS3000

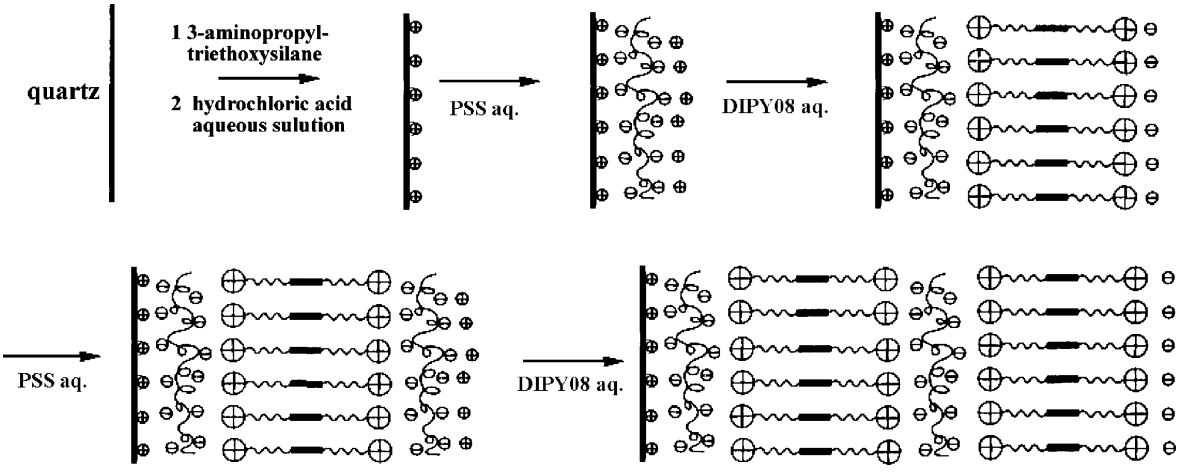


Figure 2. Schematic diagram of cationic amphiphile (DIPY08) and anionic polyelectrolyte (PSS) multilayer self-assembly on a quartz substrate.

spectrophotometer equipped with an IR polarizer (Graseby Specac Co., UK). Polarizing microscopy (FOIC-2, China) with a digital camera was used to evaluate the alignment quality of the liquid crystal and to measure the transmittance; the two microscopy polarizers were crossed.

3. Results and discussion

3.1. *Deposition of a LBL multilayer film*

Figure 3 shows the UV-Vis absorption spectra of the LBL multilayer films. The spectra were obtained 0, 1, 2, …, 6 bilayers. The absorption spectra displayed two broad bands centered at 305 and 225 nm. The band centered at 305 nm arises from the π–π^* transition of double bonds conjugated with the phenyl group in DIPY08, and the band centered at 225 nm corresponds to the absorption of the phenyl group in PSS [11]. The intensity of the two peaks increased linearly with the numbers of layers, indicating that the molecular quantities of DIPY08 (or PSS) of each layer were similar, and that the deposition procedure was indeed uniform.

3.2. *Photochemical reaction in a LBL multilayer film*

In order to analyse the photoreaction procedure in the LBL multilayer film, UV-Vis absorption spectra were measured for different irradiation times. As shown in figure 4, the broad band centered at 305 nm decreased rapidly with increasing irradiation time. The peak intensity decreased by 85% after 10 min irradiation, which indicated that the photosensitive double bonds in DIPY08 (the double bonds conjugated with the phenyl group) were consumed. Egerton *et al.* [12] reported that when a solid phase polyester with cinnamate groups was irradiated by UV, two reactions could occur: *E* to *Z* isomerization and photocycloaddtion. They also reported that isomerization produced less than 10% of the photoproducts, but [2+2] photocyclization took place in most of the nearby chromophores. Thus, photocycloaddtion played the most important role in the reactions in the LBL multilayer films. Investigations by Mao *et al.* [8] also showed this reaction route. Thus the products of the photochemical reaction were derivatives of cyclobutane. Figure 5 shows a schematic diagram of the photocycloaddition. Because the film

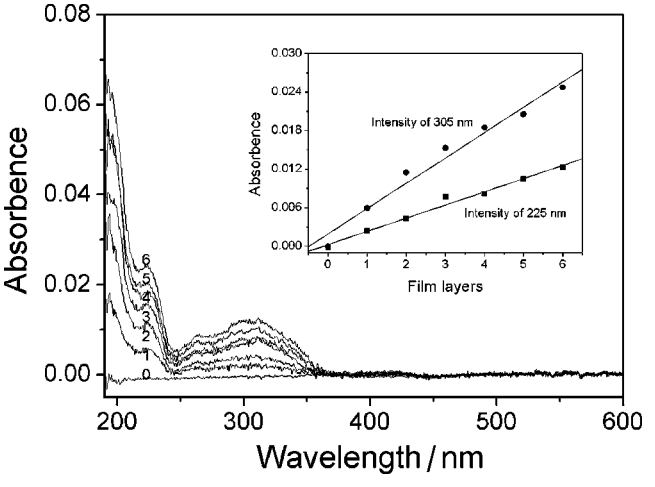


Figure 3. UV-Vis absorption spectra of a PSS/DIPY08 multilayer film with various numbers of layers on quartz substrates. A diagram of peak intensity (305 and 225 nm) depending on layer numbers is also shown (inset).

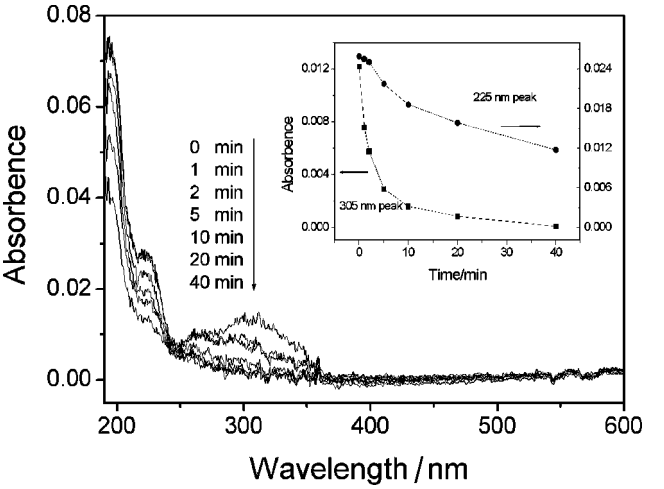


Figure 4. UV-Vis absorption spectra of a LBL multilayer film with 6 bi-layers irradiated by linearly polarized UV light. A diagram of peak intensity (305 and 225 nm) versus irradiation time is also shown (inset).

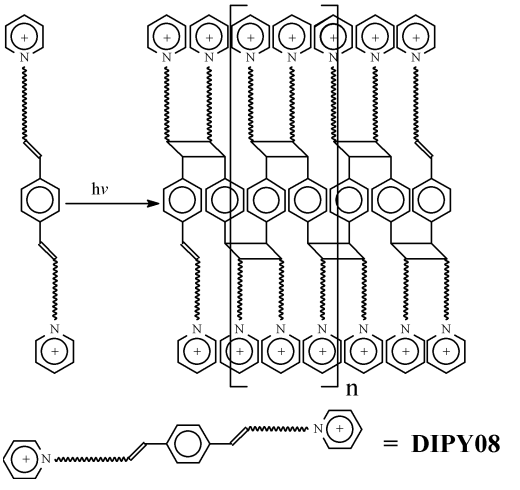


Figure 5. Schematic diagram of photocycloaddition of DIPY08 in LBL multilayer films.

was irradiated with LPUV, the product of the photocyclization was distributed along a particular direction, which generated anisotropy at the interface of the film.

As shown in figure 4, the intensity of the peak centered at 225 nm also clearly changed; in the inset figure the absorbance intensity as a function of irradiation time is given. When the exposure time was less than 5 min, the absorbance centered at 225 nm shows no obvious change, indicating that the phenyl groups in PSS were unaffected by LPUV, but that the photosensitive double bonds undergo the photocyclization. When the irradiation time exceeded 10 min, the 225 nm peak decreased in a stepwise fashion. Because the phenyl group in PSS has no photosensitive bond, the decrease perhaps results from decomposition of the benzene group in PSS under UV irradiation. In this decomposition reaction, PSS would generate carboxylic acid and aldehyde, causing the LBL multilayer film to be come unstable. Based on such observations an irradiation time of 5 min was considered appropriate for cell fabrication.

3.3. *Anisotropy of UV-Vis absorption of a LBL multilayer film*

In the field of LCDs, film anisotropy is very important because the orientation of the liquid crystal is governed by anisotropic interactions with the alignment layers, the greater anisotropy yielding the more uniform alignment [13]. In this work, it was shown that photoinduced dichroism accurred in the LBL multilayer film. Dichroism of the film was measured by polarized UV-Vis absorption spectra, because the IR peaks (such as IR vibration of double bonds at 1600 cm^{-1}) were too weak to be detected. The result for a 16 bi-layer LBL multilayer film irradiated for 5 min are given in figure 6. The polarized absorbence, A_0 (or A_{90}), was measured at 0° (or 90°) from the direction of polarization of the LPUV. The irradiated film had a small value of A_0 (A_0=0.015), and a large value of A_{90} (A_{90}=0.018) at 305 nm, indicating obvious dichroism. The result suggested that LPUV induces angular selective photodimerization; the photosensitive double bonds parallel with the LPUV direction of polarization reacted with each other, and photodimerization took place. The remaining double bonds (almost all *E* isomers) are maximized perpendicularly to the LPUV of direction polarization.

The dichroic ratio (DR), defined as $(A_{90}-A_0)/(A_{90}+A_0)$, was measured for different irradiation times see figure 7. The DR value of the LBL multilayer film first increased and then decreased, with the exposure time increasing to 40 min. At about 5 min the DR reached a maximum; when the time exceeded

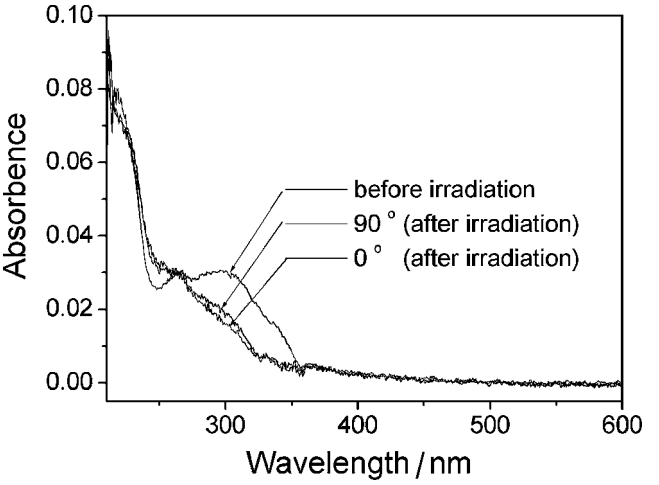


Figure 6. Polarized UV-Vis absorption spectra of a 16 bi-layer LBL multilayer film before and after irradiation (5 min) with LPUV.

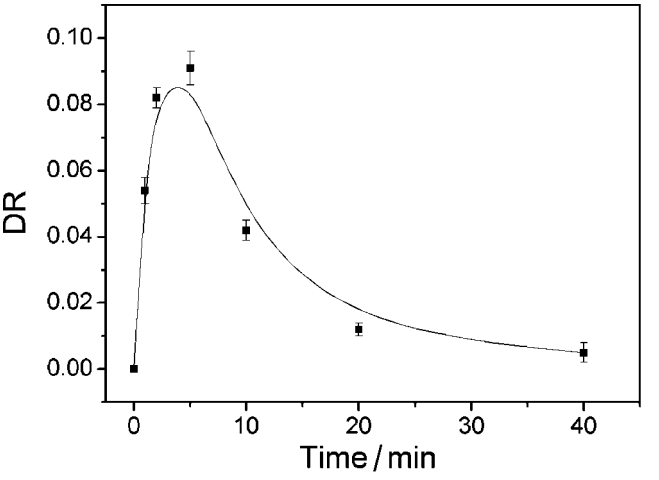


Figure 7. Dichroic ratio of LBL multilayer film depending on irradiation time (the line is the fitting result of the experimental data points).

40 min, the DR value was very small. The proposed mechanism is as follows. In the first stage of irradiation, the velocity of photocyclozation is greater than photodecomposition; and since photodecomposition is a non-angular selective reaction, this causes the DR to increase. With increasing irradiation time the photosensitive double bonds are consumed, and the double bond concentration in the film falls. Thus the velocity of photocyclization is less than decomposition, and prolonged irradiation results in a decreasing DR value; a similar result has been described by Ionescu [14].

3.4. *Photoalignment characteristics of a LBL multilayer film*

In this section the photoalignment effect of nematic liquid crystals is discussed. First, we evaluated the overall photoalignment property using polarizing microscopy; transmittance curves as a function of rotating angle were used to quantify the photoalignment effect; Second, polarized IR spectra were used to determine the liquid crystals alignment direction; finally, the thermal stability and pretilt angle of the LBL multilayer was measured.

3.4.1. Photoalignment effect. The liquid crystal alignment effect for LBL films with different numbers of bi-layers (1, 2, …, 8) was investigated. We found that all the LBL multilayer films gave uniform planar alignment, but when the bi-layer number was 1 the liquid crystal alignment containd a few defects (disclinations). When the bi-layer number exceeded 1, it appeared defect-free. It appears that the single bi-layer self-assembled film does not screen the defects of the surface of the quartz substrates. However, when the bi-layer number increased, the polymer (PSS) simply covers the underlying defects, and makes the film more homogeneous [10], so that the alignment effect of multilayer films becomes more uniform. Figure 8 shows micrographs of the liquid crystal cell with a 6 bi-layer multilayer film. Figure 8 (*a*) is the micrograph of a liquid crystals cell whose substrates with LBL multilayer were not irradiated with LPUV. A random multi-domain pattern is seen, which indicates that the liquid crystal in the cell was disordered. Figures 8 (*b*) and 8 (*c*) are micrographs of a parallel liquid crystal cell with a LBL multilayer film irradiated for 5 min by LPUV; 8 (*b*) is the dark state when one of the polarizers was parallel to the LPUV vector direction, 8 (*c*) is the bright state when the polarizer was kept at 45° to the of LPUV of polarization direction. The micrographs of the dark and bright states contain few defects and disclinations, indicating that excellent alignment was obtained; the contrast ratio (T_{max}/T_{min}) of the cell is about 100: 1. In the experiment described, 5CB was injected into the cell; the operation was repeated with the liquid crystals material TEB30A (Slichem Co. China, chemical structure is shown in figure 1), and a similar result was obtained.

The photoalignment of a liquid crystal induced by a 6 bi-layer LBL self-assembled film was further studied by recording the transmittance of visible light (400–700 nm) through the liquid crystal cell between crossed polarizers using polarizing microscopy with a power spectrometer, see figure 9. The transmittance of the liquid crystal cell with the un-irradiated alignment film (curve a) is almost constant, and does not display a regular change, whereas the parallel liquid crystal cell with an alignment film irradiated by LPUV shows a clearly regular period of 90° (curves b, c, d), in indicating that the irradiated LBL multilayer films induce the alignment of the liquid crystal. Moreover, the contrast ratio (T_{max}/T_{min}) increased with increasing exposure time; when the irradiation time exceeded 10 min the contrast ratio decrease. Again (the result for 10 min is not given in figure 9), which is in accord with the result of film anisotropy (figure 7), and indicated that the larger anisotropy of the LBL multilayer film induced the liquid crystal to orient more homogeneously.

3.4.2. Liquid crystal alignment direction. In order to determine the liquid crystal alignment direction on the LBL multilayer film, polarized IR spectra were measured. An IR polarizer and liquid crystal cell (5CB injected) were placed in the light path of the IR instrument. In the IR spectra, the peak associated with the nitrile group (–C≡N) at 2254 cm^{-1} was cleasly located. Figure 10 shows a circular diagram of peak intensity at 2254 cm^{-1} depending on the polar angle

Figure 8. Photomicrographs of a liquid crystal cell under polarizing microscopy: (*a*) liquid crystal cell with un-irradiated 6 bi-layer LBL multilayer film (random alignment); (*b*) parallel cell with photoalignment film irradiated 5 min with polarizers parallel to the optical axis of the sample (planer alignment); (*c*) parallel cell with irradiated film with polarizers at 45° to the optical axis of the sample.

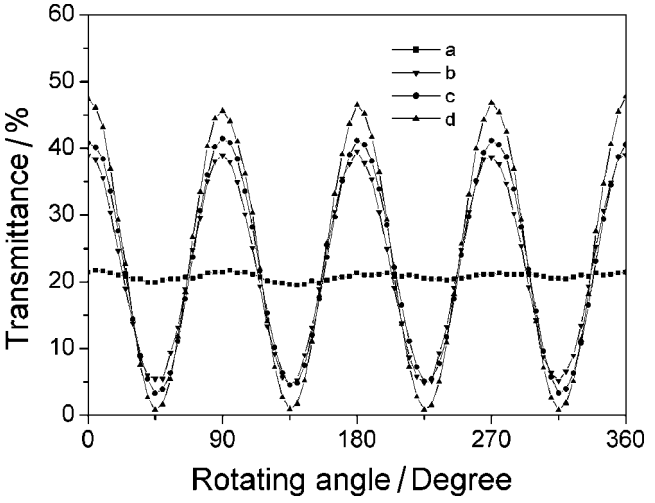


Figure 9. Angular transmittance intensity of a liquid crystal cell under polarizing microscopy with a 6 bi-layer multilayer film: (*a*) unirradiatied; (*b*) 1 min, (*c*) 2 min and (*d*) 5 min irradiation by LPUV.

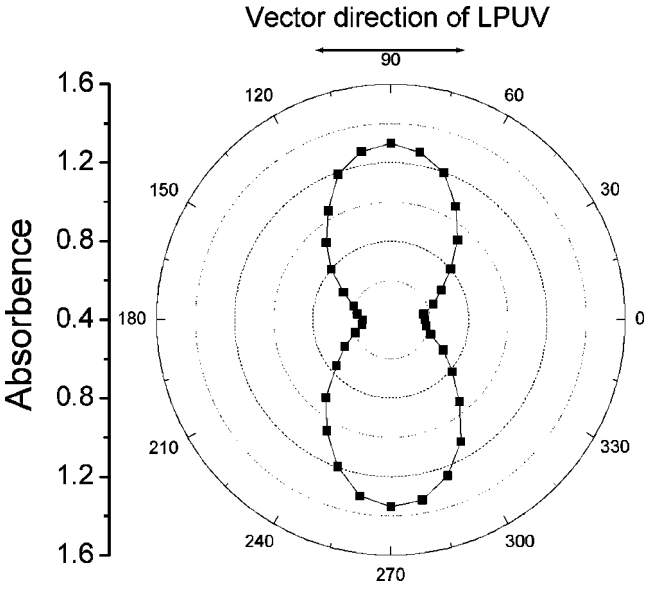


Figure 10. Angular absorbence intensity of IR peak at 2254 cm^{-1} (nitrile group) of a liquid crystal cell containing 5CB.

between the polarization plane of the IR light source and the polarization direction of the LPUV. The absorbence of the nitrile group has a maximum intensity at the perpendicular direction of LPUV vector, and given that the IR vibration direction of the nitrile group is the same as the alignment direction of 5CB, the alignment direction of most 5CB molecules was perpendicular to the LPUV electric vector. A possible mechanism for this behaviour is as follows. At the alignment film surface, the *E* isomer can induce liquid crystals molecales to align homogeneously, the *Z* isomer and the photo-cycloaddition product have little effect on alignment. After irradiation by LPUV, the quantity of *E* isomers in the parallel direction is less than in the perpendicular direction (figure 5 shows this). Thus LPUV irradiation generated an anisotropic field in the perpendicular to the LPUV, and resulted in the liquid crystal alignment in the perpendicular direction. This result was in accord with a spin-coated photoalignment polymer film [15].

Thermal stability is another important factor for LCDs, and was measured as follows: After 5 min irradiation substrates with LBL multilayer films were cured for half an hour under various thermal conditions, and then liquid crystal cells were fabricated. It was found that a liquid crystal cell held its contrast ratio up to 100°C. The pretilt angle of a LBL multilayer film was about 1° when 5CB was injected into a liquid crystal cell, as measured using the crystal rotation method [16].

4. Conclusion

In this work, a photopolymerized self-assembled multilayer film was used as photoalignment film for nematic liquid crystals. The LBL multilayer film was prepared from a photosensitive quaternary ammonium salt and PSS. After irradiation under linearly polarized UV light, the LBL multilayer film became anisotropic, which was shown by polarized UV-Vis absorption spectra. An increase in DR was observed in the early stages of the linearly polarized UV irradiation, followed by a decrease in DR upon long time irradiation. The high contrast between dark and bright states seen using polarizing optical microscopy indicated that the liquid crystal alignment was quite uniform. The alignment direction of a nematic liquid crystal on a LBL multilayer film was perpendicular to direction of polarization of incident LPUV, as determined by polarized IR absorption; the pretilt angle of the film was small.

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