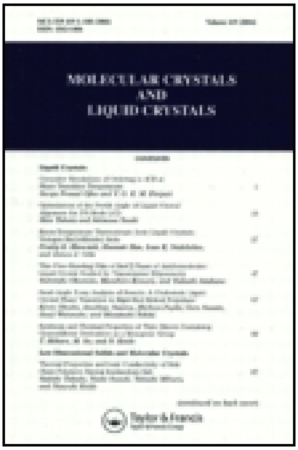

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Alignment Properties of Photoinduced Alignment Films for Liquid Crystals based on Self-assembled Multilayer Films

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A photoalignment film of liquid crystals based on a photosensitive self-assembled multilayer film was investigated. The precursor film was prepared by an alternate deposition method in aqueous solution, and when irradiated by linearly polarized ultraviolet light (LPUVL), the photosensitive double bonds in the film underwent photocycloaddition preferentially along the polarized direction of the LPUVL. The photoalignment film exhibited obvious anisotropy and could induce nematic liquid crystals to align uniformly in the planar state. The azimuthal anchoring energy of the film raised up to $1.5 \times 10^{-5}\,J/m^2$*. Atomic Force Microscopy (AFM) indicated that the surface of the multilayer film became slightly rougher with increasing thickness of the film layer but the alignment effect became more homogeneous.*

Keywords: layer by layer; liquid crystal; photoalignment; self-assembled

INTRODUCTION

Liquid-crystalline devices (LCDs) play an important role in the field of information display and optical communication because the liquid crystal (LC) has optical anisotropy and can be modulated by an electric field. Most LCDs require alignment films to give the LCs a

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preferential orientation. Photoalignment is a newly developed alignment method for LCs in recent years [1]. The photoalignment films are typically fabricated by a spin-coating method using polymer solutions, then irradiated by linear polarized ultraviolet light (LPUVL). This avoids contamination from dust particles and the generation of static charges as in the traditional rubbing method. The materials of photoalignment films are normally photosensitive polymers, such as polymers with cinnamate groups [1], coumarin groups [2], azobenzene groups [3], photodegradable polyimide (PI) [4], *etc*. Among these materials, the photoalignment films fabricated by photocycloaddition polymers are more stable than the others [5].

Similar to the other types of LC alignment films, photoalignment films are also required to possess some properties, such as thermal stability, uniformity, anchoring energy, *etc*. With respect to photocycloaddition materials, the dichroism value of the photoalignment film is as small as about 0.01 as determined by the polarized IR spectroscopic method [6]. The small anisotropy probably results in poor alignment of LCs. Moreover, the azimuthal anchoring energy of the LC on photoalignment film is less than $10^{-5}\,\mathrm{J/m^2}$ [7]. Recently Naciri reported a photoalignment film fabricated by self-assembled monolayer of silane-based cinnamate moieties [8]; the photoalignment film has a high anchoring energy and good thermal stability. It is clear that polarized photocycloaddition reactions could be carried out efficiently in the self-assembled film. Therefore, photosensitive self-assembled film is suitable for fabrication of photoalignment film. We have prepared photoalignment films based on photosensitive layer-by-layer self-assembled multilayer films, and the photoalignment film could induce LCs to align uniformly in the planar state [9,10].

In this article, we studied the alignment properties of the self-assembled photoalignment film and found that the number of film layers and irradiation dose could affect the alignment properties.

SAMPLES AND MEASUREMENTS

The materials for the self-assembled film are poly(sodium 4-styrenesulphonate) (PSS, $M_w < 70000$, 30 wt% aq., Aldrich Co.) and *p*-phenylenediacrylic acid bis(8-pyridinium-N-yl octyl ester) dibromide (DIPY08). DIPY08 was synthesized by a conventional synthetic method [9,11] and has two photosensitive double bonds. The chemical structures are given in Fig. 1.

The precursor film was prepared as follows: cleaned quartz plate was used as substrate, and then the surface was modified to

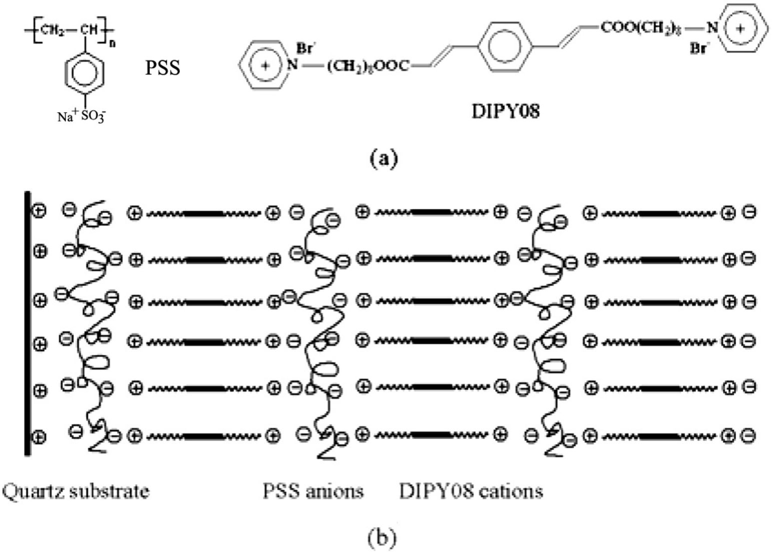

FIGURE 1 (a) Chemical structures of deposition materials and (b) schematic diagram of the self-assembled multilayer film.

ammonium cations by a chemical process [12]. The self-assembled multilayer films on the substrates were prepared using Decher's procedure [13]. First, the substrates were immersed in a PSS solution (1.0 mg/mL) for 20 min, and then the substrates were washed using de-ionized water and blown dry by nitrogen gas. Second, the substrates were immersed in a DIPY08 solution (1.0 mg/mL), then washed and blown as in the previous step. The two steps were repeated, and the self-assembled multilayer films were obtained. The DIPY08 layer was always deposited last.

In the experiments, a UV-vis spectrometer (UV-3101PC, Shimazu Co.) was used to analyze the film-forming process and photoreaction process. The self-assembled multilayer film was vertically irradiated at room temperature by LPUVL with an intensity of 2.5 mW/cm^2 at 297 nm. The topography of the film was analyzed with AFM (Dimension 3100s, Digital Instrument Co.) on a quartz substrate. Contact-mode AFM measurements were carried out using triangular Si_3N_4 cantilevers in air and room temperature, the resonant frequency of the instrument was around 100 kHz, z-range of AFM detection was 5.0 nm. The alignment behaviors of LC cells with photoalignment films were evaluated by optical polarizing microscopy (BX-51, Olympus Co.).

RESULTS AND DISCUSSION

Photoreaction in the Self-assembled Film

In a previous experiment, we found that the intensity of the two UV peaks increased linearly with the numbers of the layers in deposition process. It indicates that the amount of molecules (PSS, DIPY08) of each layer were similar. Therefore, a uniform self-assembled multilayer film was obtained [9]. Figure 1 shows a schematic diagram of the multilayer film. UV-vis absorption spectra were measured for the multilayer film before (Fig. 2a) and after (Figs. 2b,c) exposure to LPUVL. The peak at 305 nm can be attributed to the π–π^* transition of the photosensitive double bonds in DIPY08. After irradiation of LPUVL, the peak decreased remarkably due to the [2 + 2] photocycloaddition of the double bonds [11], and the absorption in the parallel direction ($A_{||} = 0.015$) of the polarized direction of the incident LPUVL was smaller than that in the perpendicular direction ($A_{\perp} = 0.018$). This result may indicate that the photocycloaddition preferentially took place in the parallel direction. The dichroic ratio [$DR = (A_{\perp} - A_{||})/(A_{\perp} + A_{||})$] was calculated as 0.09, which was larger than that of spin-coating photoalignment films [6]. This observation suggests that the polarized photoreaction may proceed more efficiently than in common spin-coating films because of the order of the DIPY08 molecules in the self-assembled

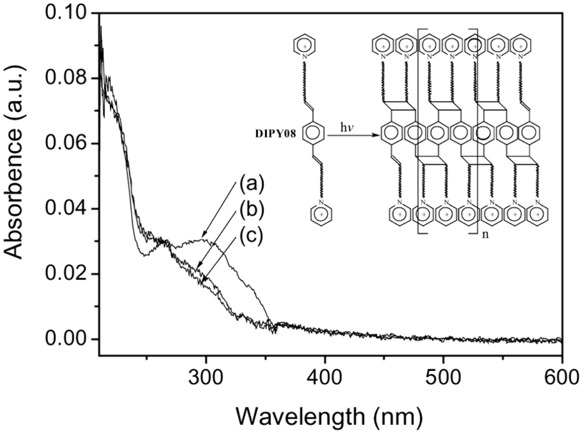

FIGURE 2 UV-vis absorption spectra of the self-assembled 32-layer film: (a) the spectrum of unexposed self-assembled film, (b) the spectrum of parallel direction to polarized direction of LPUVL (exposed energy was 750 mJ/cm^2), and (c) the spectrum of perpendicular direction.

film. Finally, after irradiation, some macromolecules were formed in the parallel direction in the self-assembled film (the schematic diagram is illustrated in Fig. 2), and an anisotropic photoalignment film was obtained.

LC Alignment Behavior

Two similarly irradiated substrates with a two-layer film were assembled as a sandwich-type parallel LC cell. Commercial nematic LC 5CB was injected to the LC cell in the isotropic state, and then the LC cell was cooled to room temperature. Obvious bright and dark states were found under a microscope with crossed polarizers. Therefore, the photoalignment multilayer films give homogeneous alignment for LCs in the planar state, but a few disclinations were found in the viewfield of the microscope, and the photograph of dark state is given in Fig. 3a. When the layer number increases, the alignment property became more uniform. While the layer number is six, the disclinations in LC cell could hardly be found (Fig. 3b).

To investigate the reason why the films with different layer numbers have different alignment effects, surface morphology of the photoalignment film was characterized by AFM (Di3100s, DI Instrument Co.). Figure 4 shows AFM images of quartz substrates deposited with 2-, 4-, 6-, and 10-layer self-assembled films. The morphology of the film surface is composed of depressions and ridges, and the root-mean-square (RMS) roughness values are 0.280, 0.301, 0.385, and 0.598 nm, respectively. This indicates that the surface topography of the multilayer became rougher with increasing layer numbers, but the degree of change was slight. The RMS value of two layers of film

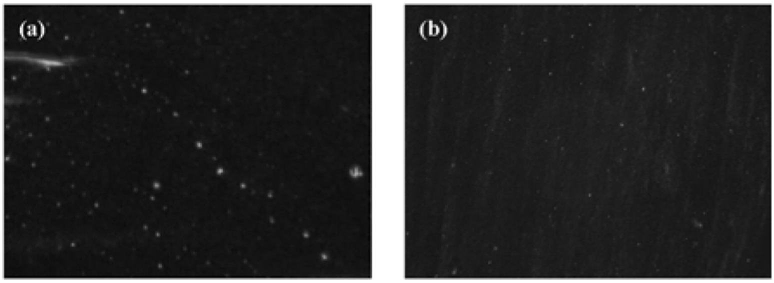

FIGURE 3 Optical micrographs of LC cell fabricated with self-assembled photoalignment films: (a) photograph of dark state for two-layer film and (b) photograph of dark state for six-layer film. Magnification of the microscope was 100.

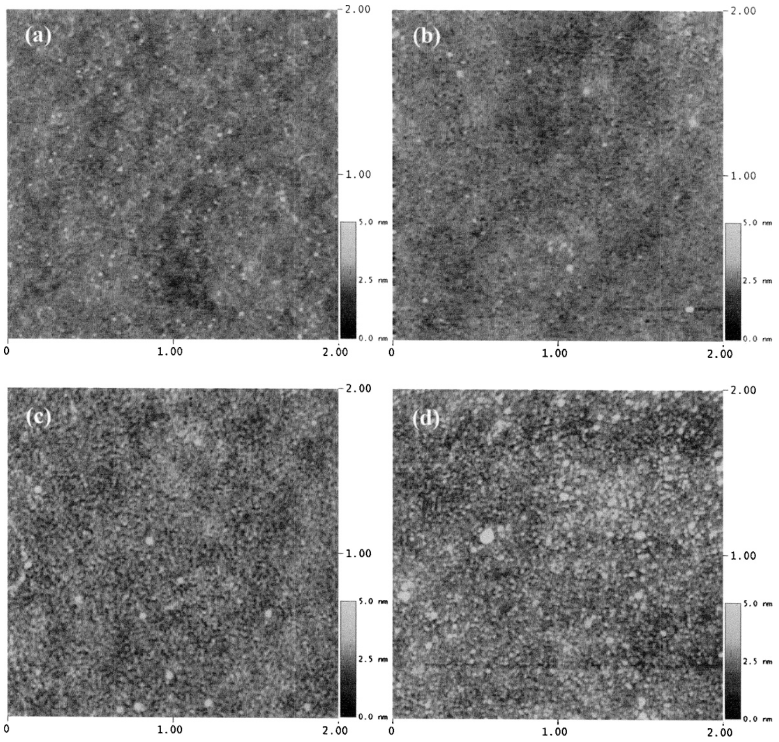

FIGURE 4 AFM images of the multilayer films at increasing film layers: (a) two layers, RMS = 0.280 nm; (b) four layers, RMS = 0.301 nm; (c) six layers, RMS = 0.385 nm; (d) 10 layers, RMS = 0.598 nm. Z range of the images is 5 nm.

is the same as the quartz substrate (0.267 nm). In the first stage of film formation, there may be some defects in the film–substrate interface from the substrate. When the layer number increases with the deposition cycles being repeated, the polymer (PSS) in the multilayer film could cover the defects formed in the first stage, which will make the film more homogeneous over a large range [13]. Therefore, the more homogeneous the multilayer film became, the better the alignment performance of LC cell that was obtained.

Azimuthal Anchoring Energy Result

Azimuthal anchoring energy W_a of the photoalignment film was measured using the Cano wedge cell method [14]. The anchoring energy

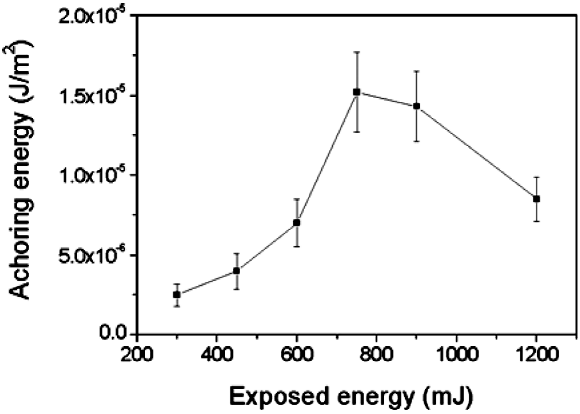

FIGURE 5 Azimuthal anchoring energy of six-layer self-assembled photoalignment film as a function of exposed dose.

(W_a) can be calculated from deviation angle (θ), cell gap (d), and twist elastic constant (k_{22}):

$$W_a = k_{22}\frac{\pi - 2\theta}{d\sin\theta}.$$

In the experiments, the commercial LC material (SLC7611 + 0.15% CB15) was used. The deviation angle θ was detected by polarizing microscopy method. Figure 5 shows the dependence of W_a on a UV irradiation dose of the photoalignment film. The anchoring energy once increased and then decreased with the rise of irradiation dose. The maximal value of W_a was observed at $750\,\mathrm{mJ/cm^2}$ exposure, where the corresponding anchoring energy value is $1.5\times10^{-5}\mathrm{J/m^2}$, which is similar to the rubbed PI alignment film. These results suggest that the high anchoring energy comes from interactions between the highly anisotropic film and the nematic LC. However, excessive irradiation would cause W_a to decrease, which may be due to the photodegradation of macromolecule products under LPUVL [15].

CONCLUSIONS

In summary, a LC photoalignment film derived from a photosensitive self-assembled multilayer film was prepared. From the UV-vis spectra measurement, it can be seen that the irradiated film became obviously anisotropic, which indicated that the [2 + 2] photocycloadditon was carried out efficiently along the polarized direction of LPUVL. The photoalignment film could induce nematic LCs to align uniformly in a planar state, and the film with more layers could give more homogeneous alignment. The azimuthal anchoring energy of the film was up to $1.5 \times 10^{-5} \mathrm{J/m^2}$ in the optimum experimental condition. An AFM test indicated that the roughness of the multilayer film increased slightly with the increasing number of layers. Because the self-assembled film could be fabricated conveniently on quartz (or silicon glass) substrate, the photoalignment film may have great potential in LCDs.

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