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Photoinduced liquid crystal alignment by layer-by-layer ultrathin films with dual photoreaction moieties

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A novel layer-by-layer (LBL) film containing dual photoreaction groups, cinnamoyl and azobenzene, was prepared from poly(diallyldimethylammonium chloride) (PDDA) and a photosensitive polyanion, PCAzo, in aqueous solution via electrostatic attraction. The film was able to induce uniform alignment of liquid crystals (LCs) with good stability and 2.3° pretilt angle by oblique irradiation with linearly polarised ultraviolet light (LPUVL). UV absorption and FTIR spectroscopic results indicate that the photoreactions of the two photoreactive groups jointly participate in generating the anisotropy of the film. The dichroic ratio of the film was found to depend on the number of adsorbed layers. The thicker film has the larger dichroic ratio after the LPUVL irradiation. The reorientation behaviour of the LC molecules was found to be associated with the LBL film thickness. Experiment results revealed that the photo-crosslinking of the cinnamoyl groups was responsible for the stability of the anisotropic orientation, and the isomerisation of the azobenzene chromophores led primarily to the appropriate pretilt angle.

Keywords: LBL ultrathin film; dual photoreaction moieties; liquid crystal photoalignment; pretilt angle

1. Introduction

Photoinduced orientation control of nematic liquid crystals (LCs) is an intriguing research topic from a technological point of view because of its application to optical data storage, anisotropic optical elements, display devices, etc. (1–3). The orientational directions of LC molecules are controlled by the photogenerated optical anisotropic photoreaction films, which have been referred to as “command surface” (4). There are many ways for the fabrication of “command surface”, e.g. the spin-coating (5), Langmuir–Blodgett (6) and self-assembled monolayers methods (7). Recently, much attention has been devoted to the development of multilayer assemblies of thin film based on an alternate layer-by-layer (LBL) adsorption of oppositely charged polyelectrolytes from aqueous solution (8, 9). LBL assembly of oppositely charged polyelectrolytes is a simple and powerful method for the construction of composites that are self-assembled planar ordered on a nanometre scale. In 2002, Park and Advincula prepared photochromic azobenzene polymer ultrathin films using the LBL approach and used the LBL polyelectrolyte films firstly for in-plane photoalignment of LCs with read/write capabilities (10). From previous research results, it was also found that azobenzene-containing films often have a higher degree of tilted orientation (2, 11), which was prerequisite for the LC displays to prevent from reverse tilt disclinations upon exerting an external electric field. However,

this type of azobenzene-containing film was not suitable for permanent LC-alignment films of displays due to the reversible isomerisation reaction of azobenzene. A large decrease in transmittance intensity was observed after two weeks. Our previous investigations showed that ordered cinnamate LBL ultrathin films can be used as photoalignment films, which have good stability due to the photo-crosslinking of cinnamate chromophores (12–14).

The purpose of this study was to fabricate a new LBL ultrathin film that possessed a large pretilt angle and good stability. A LBL polyelectrolyte film containing dual photoreaction groups, cinnamoyl and azobenzene, was prepared for photoalignment studies. The film design was based on the following considerations: (1) cinnamate materials exhibit thermally stable because of the irreversible [2+2] photodimerisation of cinnamoyl groups (5); (2) the azobenzene-containing polymer films have the ability of tilted orientation and good photosensitivity (11, 15); (3) both the photodimerisation and photoisomerisation of the dual photoreaction groups would take place cooperatively after proper irradiation and most likely result in better alignment. The ultrathin films were fabricated using poly(diallyldimethylammonium chloride) (PDDA) as polycation and photosensitive PCAzo as polyanion (the chemical structures of which are shown in Figure 1), via a self-assembly technique. As expected, both the photodimerisation

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and photoisomerisation of the neighbouring dual moieties took place collaboratively after linearly polarised ultraviolet light (LPUVL) oblique irradiation and resulted in a better alignment of LCs. The orientation behaviour of the film was studied using polarisation UV-visible spectroscopies and FTIR spectroscopies. The stability of the film was good and a pretilt angle of up to 2.3° was achieved.

2. Experimental

Materials and synthesis

PDDA ($M_w=200\,000\text{--}350\,000$, 20 wt% aq.) was purchased from Aldrich and used without further purification. The polyanion PCAzo was synthesised according to the reaction scheme in Figure 2. All reagents were obtained from Shanghai Chemical Inc, and directly used. Dry solvents were freshly distilled under anhydrous conditions.

Compounds I (4-acryloyloxyxinnamic acid chloride) (12) and II (4-hydroxyazobenzenesulfonic acid sodium salt) (16) (as shown in Figure 2) were synthesised according to literature methods. For the synthesis of III (CAzo), compound II (2.79 g, 10 mmol) and NaOH (0.8 g, 20 mmol) were dissolved in water (40 ml) and tetrahydrofuran (THF) (40 ml), and cooled to $0\text{--}5^\circ\text{C}$. Then, compound I (4.73 g, 20 mmol) in THF (10 ml) was added dropwise while stirring at the same temperature. After stirring at room temperature for 24 h, some of the solvent was removed by vacuum distillation. The precipitate was filtered, washed with water and dried under vacuum. The crude product was purified by re-precipitation from *N,N*-dimethylformamide (DMF) solution into water, and

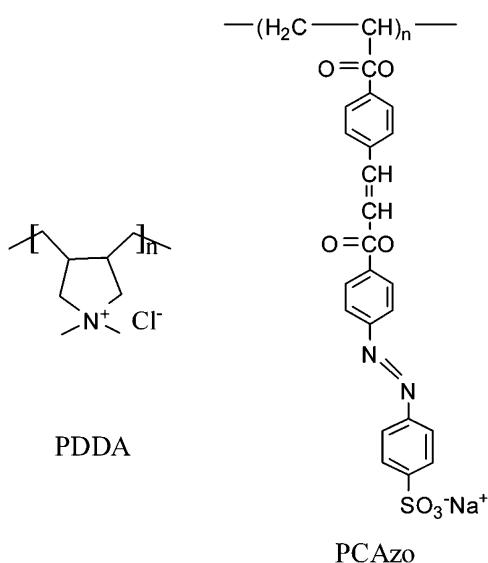


Figure 1. Chemical structures of PDDA and PCAzo.

dried under vacuum. Yield: 30%. FTIR (powder, KBr, cm^{-1}): 979 (=CH, δ), 1168 (C=O, v), 1178 (S=O, v), 1633 (C=C, v), 1742 (C=O, v), 3042(=C-H, v).

Compound III (CAzo) (1 g) was polymerised in 20 ml DMF with 0.01 g azobisisobutyronitrile (AIBN) as initiator at 70°C under nitrogen atmosphere. The polymer IV (PCAzo) was isolated after polymerisation for 12 h by adding the reaction solution to the ice water, purified by re-precipitation from THF solution into petroleum ether, and dried under vacuum. Yield: 60%. FTIR (powder, KBr, cm^{-1}): 1168 (C=O, v), 1178 (S=O, v), 1600, 1575, 1506 (aromatic C=C), 1635 (C=C, v), 1740 (C=O, v), 2965 (C-H, v).

Preparation of LBL multilayer film

The self-assembly films were constructed on quartz wafers for UV-visible measurement, on CaF_2 wafers for Fourier-transform (FT) IR spectroscopy and on indium-tin oxide (ITO) glasses for the assembly of LC cell. Before film construction, the quartz wafers were treated in fresh piranha solution (v/v=1:3, 30% H_2O_2 :98% H_2SO_4) for 1 h, then washed carefully with deionised water and dried. The CaF_2 wafers and ITO glasses were cleaned with deionised water. The substrates were soaked in PDDA solution (1 wt%) for 20 min to render a positively charged surface. The electrostatic LBL deposition on the substrates was performed using well-reported procedures (9). The substrates were immersed in aqueous solution of PCAzo (1.0 mg ml^{-1}) and PDDA (1.0 mg ml^{-1}) for 10 min alternately, each time rinsing with deionised water and blowing dry using nitrogen gas. The cycle was repeated until the desired number of bilayers was obtained. The last deposition was always done with PCAzo.

Cell fabrication

The polyelectrolyte-deposited substrates were obliquely irradiated by LPUVL with an incident angle of 30° , which is schematically depicted in Figure 3. The LC cells were assembled with substrates antiparallel to the LPUVL irradiation directions and the cell gap was $20\text{ }\mu\text{m}$. The commercial liquid crystal material TEB30A (Slidchem Co, China, $T_c=61^\circ\text{C}$) was injected into the cell at 70°C . Then the cell was cooled to room temperature slowly to remove any flow-induced memory that had been induced by the LC injection process.

Characterisation

LPUVL was obtained from a 300 W Hg-Xe lamp system with an optical filter ($297\pm 5\text{ nm}$) and a Glan-Taylor prism. The intensity of LPUVL on the surface

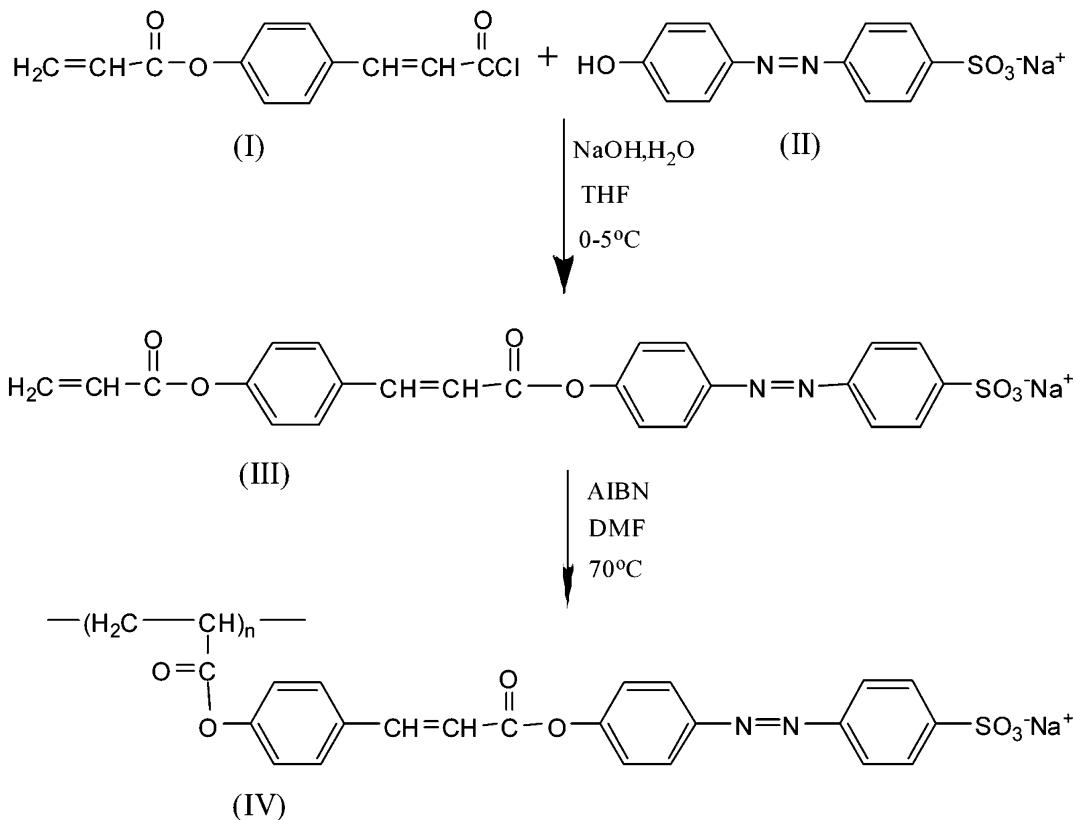


Figure 2. Synthetic route to the polyanion PCAzo.

of the film was 0.58 mW cm^{-2} ($\lambda=297 \text{ nm}$). The FTIR spectra of the materials were recorded using a Bio-Rad FTS3000 spectrophotometer. The quantity of material deposited at each step was deduced from its absorption spectrum, which was determined on a Shimadzu UV-3101PC spectrophotometer. Polarised UV-visible absorption spectra were measured by

using special polarising accessories. LC alignment behaviour was also evaluated by polarising optical microscopy under crossed polarisers. The pretilt angles were measured using the crystal rotation method (17).

3. Results and discussion

LBL multilayer film formation

The prepared films were clear, transparent and uniform, with good optical quality as seen by the naked eye. UV-visible spectroscopy was primarily used to investigate the assembly process of the multilayer film and aggregation phenomena. Figure 4 illustrates the UV-visible absorption spectra of PDPA/PCAzo films on quartz substrate with different number of bilayers. The $\pi-\pi^*$ absorption of the (*E*)-azobenzene moieties was often at about 340 nm (18) and the $\pi-\pi^*$ absorption of the double bonds conjugated with the phenyl group of the cinnamoyl group was at about 290 nm (19). The films contained these two kinds of groups, so the absorption spectra displayed one broad band centre at 320 nm . The absorbance increased linearly with the number of PDPA/PCAzo pair-layers. The adsorption occurred essentially uniformly, the same amount

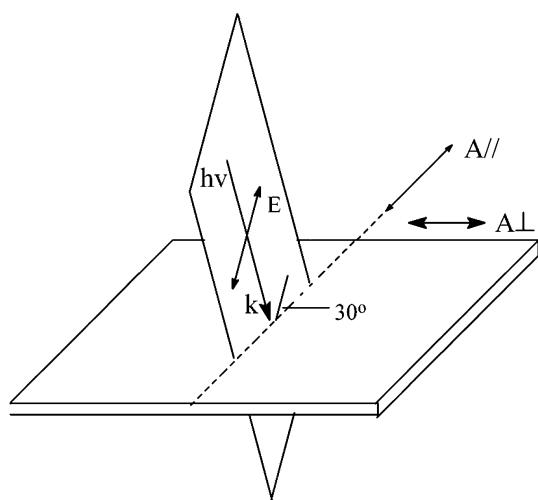


Figure 3. Schematic illustration of oblique photoirradiation with LPUVL.

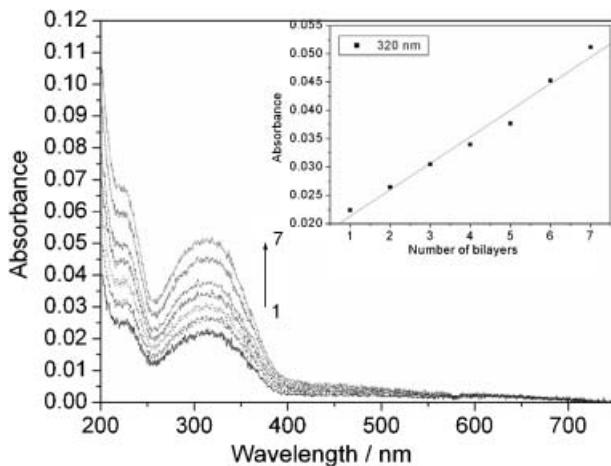


Figure 4. UV-visible absorption spectra of PDDA/PCAz film on quartz wafer as a function of the number of bilayers. The inset diagram shows the increase of absorbance at 320 nm with the number of bilayers.

being deposited on each cycle. The linear increase of the band with the number of the bilayers clearly indicated the regular growth of the PDDA/PCAz film. Moreover, the absorption maximum of PCAz solution (0.005 mg ml^{-1}) occurs at 310 nm. Thus, the LBL absorbance was red-shifted 10 nm compared to PCAz solution.

The aggregation of the polycation in an ordered structure with corresponding dipoles resulted in a splitting of the excitation energy levels. The shifts in the absorption spectra are dependent on the mutual orientation of the interaction dipole moments (20, 21). When the dipole moments were parallel, a blue shift occurred (H band). If the transition dipoles were in-line, the spectra exhibited a red shift and the aggregates were termed J-aggregates (J band). The red-shift behaviour for PCAz suggested the formation of J-aggregates where the orientation of the aggregates could be described as tilted. In contrast to the solution, the moieties were not independent from each other in the films. Comparison of the λ_{\max} centred at about 320 nm with increasing number of layers revealed a small shift in λ_{\max} position occurring intermittently. This implied that the degree of aggregation changed with thickness.

Photochemical reaction in the LBL multilayer film

In order to investigate the photoreaction procedure in the LBL multilayer films in detail, the LBL multilayer films of PDDA/PCAz having dual photoreaction moieties per chemical repeat unit in the side chains in the polyanions were obliquely irradiated by LPUVL with an incident angle of 30° (as shown in Figure 3). The photoreaction procedure was examined by UV-visible spectroscopy and FTIR spectroscopy.

Figure 5 shows the linearly polarised UV-visible absorption spectra of a seven-bilayer PDDA/PCAz film irradiated with LPUVL for 8 min. The polarised absorbance A_\perp was measured with the polarised probing UV-visible light with polarisation perpendicular to the incident plane of the LPUVL (Figure 3). Then the substrate was rotated 90° , and the polarised absorbance A_\parallel was measured. Prior to LPUVL irradiation, the absorption was isotropic ($A_0 = A_\perp = A_\parallel$). After the irradiation, both the $\pi-\pi^*$ transition of the azobenzene group ($\lambda = 340 \text{ nm}$) and of the cinnamoyl group ($\lambda = 290 \text{ nm}$) decreased concurrently with the irradiation of LPUVL, and a new absorption band appeared at 400 nm, which might be due to E-Z isomerisation of the azobenzene groups.

A huge variation in the absorbance was observed between A_\perp and A_\parallel . This result implies that the photoreactions of the dual photoreactive groups jointly participated in the generation of azimuthal anisotropy of the film: (1) E-Z isomerisation of the azobenzene groups (2); (2) the direction-selective [2+2] photodimerisation or E-Z isomerisation of the cinnamoyl groups (5). As reported by Chigrinov and coworkers, when the dual photoreactive groups are optically pumped by a polarised light, the energy absorbed for the transformation is non-uniform and has an angular dependence, which is proportional to $(\cos \theta)^2$, where θ is the angle between the transition dipole moment of the molecules and the direction of the polarisation of the incident light (22, 23). The dual photoreactive groups parallel to the polarisation direction of the LPUVL were consumed more rapidly than those positioned perpendicular. The direction-selective photoreactions generated the anisotropy of the PDDA/PCAz film. The LPUVL oblique

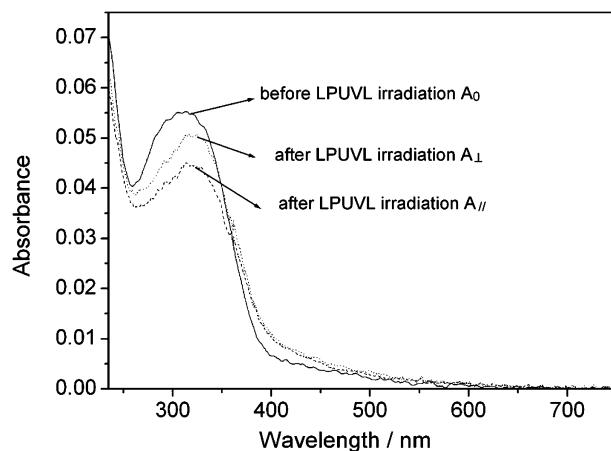


Figure 5. Polarised UV-visible absorption spectra of a seven-bilayer PDDA/PCAz film irradiated with LPUVL for 8 min. The plot shows the spectra before and after LPUVL irradiation. The LPUVL intensity was 0.58 mW cm^{-2} .

irradiation induced an asymmetric potential field. With the oblique LPUVL irradiation, the photo-crosslinking of the cinnamoyl groups, the isomerisation of the azobenzene and aligning symmetries had to be changed. LC alignment might not occur perpendicularly to **E** as before (perpendicular LPUVL irradiation) (5) but within the plane defined by **E** and **k** (3). From Figure 5, we also found that the irradiation of the films with LPUVL caused a redshift of the λ_{\max} to 327 nm, which implies that the photoreorientation took place after LPUVL oblique irradiation. LPUVL oblique irradiation changed the aggregate states, and an efficient photoinduced orientation took place.

The photoreactions of the PDDA/PCAzO were further investigated by FTIR spectroscopy. Figures 6a and 6b show the FTIR spectra of the PDDA/PCAzO film before and after irradiation with LPUVL. The unexposed film has vibrational absorption bands at 1740, 1635, 1600 and 1506 cm⁻¹. The band at 1740 cm⁻¹ is attributed to the conjugated C=O stretching vibration. The band at 1635 cm⁻¹ corresponds to the vinylene C=C of the cinnamoyl group stretching vibration. Additional bands at 1600 and 1506 cm⁻¹ result from the vibrational modes of the benzene ring in the side chain. For the LPUVL-irradiated film, the IR bands of the vinylene linkage (1635 cm⁻¹) decreased. The intensity of the band at 1740 cm⁻¹ due to the conjugated C=O stretching vibration decreased and a new band appeared at higher wavenumbers. These intensity drops of the conjugated C=C and C=O stretching bands, as well as the appearance of a new band could be due to two possible factors: the loss of π -conjugation due to photodimerisation of the cinnamoyl chromophores and photoisomerisation of the cinnamoyl

chromophores. According to the report of Chakrabartik *et al.*, the position shift of the conjugated C=O stretching band corresponds to E-Z isomerisation (24). In fact, such a small position shift can not be resolved in the present study because of the extensive overlap with the new band, which presumably can be attributed to the non-conjugated C=O stretching bands. The results support the conjecture that the intensity drops of the conjugated C=C and C=O stretching bands originated principally from the photodimerisation of the cinnamoyl chromophores and possibly in part from the E-Z isomerisation of the cinnamoyl chromophores.

Thus, UV absorption and FTIR spectroscopic results lead to the conclusion that the PDDA/PCAzO films underwent both isomerisation of the azobenzene groups and the photocycloaddition of the cinnamoyl groups when the films were irradiated with LPUVL. The photoreactions and photoreorientation of the dual photoreactive groups jointly participated in the generation of azimuthal anisotropy of the film.

The photoinduced optical anisotropy of the film was investigated by measuring UV-visible absorbance at λ_{\max} (320 nm) in parallel (A_{\parallel}) and perpendicular to (A_{\perp}) the incident plane of LPUVL (as shown in Figure 3). The optical anisotropy is expressed here by the UV dichroic ratio [$= (A_{\perp} - A_{\parallel}) / (A_{\perp} + A_{\parallel})$]. The determined dichroic ratios are displayed in Figure 7. As can be seen in the figure, all the measured dichroic ratios are positive over the irradiation time range of ≤ 30 min. With increasing irradiation time, the dichroic ratio increased rapidly to a maximum at 8 min and then levelled off or decreased slightly with further irradiation. These results indicated that the

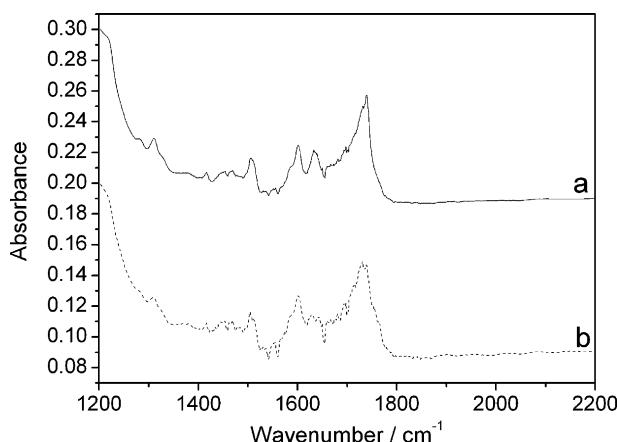


Figure 6. FTIR spectroscopy of a 100-bilayer PDDA/PCAzO film on a CaF₂ substrate (a) before and (b) after LPUVL irradiation. The LPUVL intensity was 0.58 mW cm⁻². Irradiation time: 8 min.

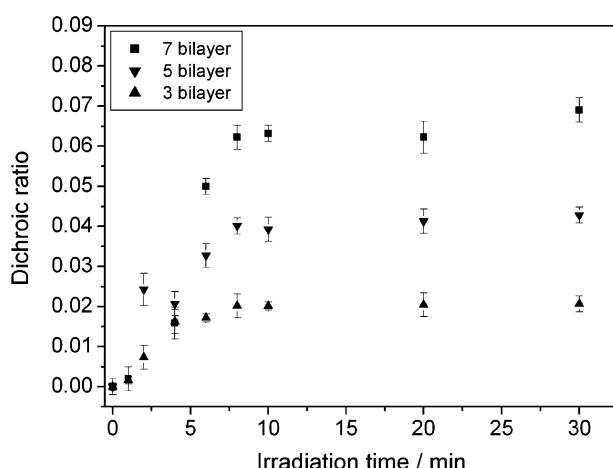


Figure 7. Dichroic ratios measured for PDDA/PCAzO films of different thickness irradiated by LPUVL for various times: three (▲), five (▼) and seven (■) bilayers. The LPUVL intensity was 0.58 mW cm⁻².

dual photoreactive groups parallel to the polarisation direction of the LPUVL were consumed more rapidly than those positioned perpendicular. The direction-selective photoreaction of the dual photoreactive groups in the film induced the structural anisotropy of the multilayer film. The anisotropic film would give rise to the anisotropic interactions with the LC molecules, which might possibly generate the LC homogeneous alignment. From Figure 7, we also found that the thicker films had the larger dichroic ratio after LPUVL irradiation. Thickness dependence on photoreaction has been reported previously for LBL films, where the extent of the photoreactive group aggregation and layer ordering played an important role (13, 25). Thicker films always had a larger photoreaction degree for the same irradiation time. The photoreaction primarily induced the anisotropy of the film. Hence, the thicker film would have the larger dichroic ratio after the LPUVL irradiation.

AFM images of the LBL multilayer films

Images of the morphology of the PDDA/PCAzO films with different numbers of layers were obtained by atomic force microscopy (AFM) (Figure 8). The morphology was comprised of many round-shaped domains. Clearly, the surface topography showed a non-smooth but homogeneous film with round-shaped domains varying in size with increasing number of bilayers. The films were amorphous and suggested an isotropic growth showing no preferred orientation. In general, the roughness increased with increasing number of bilayers, but the degree of change was slight. The difference was largely due to the presence of larger and more irregular patches with thicker films. When LPUVL irradiation was applied to the film, there was no visible morphological change as observed by AFM. This indicated that there was no clear morphological anisotropy on the exposed PDDA/PCAzO films. This phenomenon was in contrast to previously reported photoalignment behaviour in azobenzene dye LBL photoalignment film for which the roughness increased after irradiation (25).

Alignment of LCs on the irradiated LBL multilayer film

A uniform homogeneous alignment of the LC molecules was obtained in the antiparallel cell modified by the irradiated LBL multilayer films. Figure 9 shows POM micrographs of an antiparallel LC cell with three-bilayer LBL film irradiated for 8 min by LPUVL. Figure 9a shows the dark state

when one of the crossed polarisers was parallel to the optical axis of the sample; Figure 9b shows the bright state when the two crossed polarisers were kept at 45°C to the optical axis of the sample. Both of them contained few defects and disclinations, indicating that excellent homogenous alignment was obtained.

The transmittance intensity of visible light (400–700 nm) through the LC cell between crossed polarisers was monitored as a function of the rotation angle of the cell in the plane under a polarising microscope. Figure 10 shows the angular transmittance intensity of LC cells with three-, five- and seven-bilayer multilayer films. The maximum transmittance increased with increasing number of bilayers. In previous studies, we found that the photoalignment behaviour of LBL multilayer film was influenced by the thickness of the sample, i.e. the dichroic ratios were larger for the thicker samples after the same time irradiation. Hence, the alignment property of the LC molecules could be influenced by the thickness of PDDA/PCAzO film. This indicated that LCs reorientation might not simply be influenced by the contact photoreaction molecule, but might be controlled by the overall thickness and ordering of the film. This was in contrast to previously reported photoalignment behaviours in LBL film which was independent of thickness (26, 27).

The pretilt angle of the LCs in the cells was measured by the crystal rotation method. The pretilt angle varied in the range 0.5–2.3°, depending on the LPUVL irradiation time. As shown in Figure 11, the pretilt angle initially increased with increasing irradiation time, becoming almost saturated at 10 min. The pretilt angle was larger than that of cinnamate LBL ultrathin films (12). According to Sekkat *et al.*, the azobenzenes molecules were subjected to angular-selective isomerisation, followed by angular redistribution and rotational diffusion to minimise light absorption through the reversible E/Z photoisomerisation (28). Two kinds of orientation modes were possible by irradiation of LPUVL: the uniaxial in-plane orientation of the azobenzene and the out-of-plane orientation (11). From these results, it could be reasonably concluded that the isomerisation of the azobenzene chromophores was an important factor for pretilt angle generation. The isomerisation of the azobenzene chromophores might lead to spatial reorientation. The pretilt angles of the LCs were not obviously changed with increasing number of bilayers.

The LCs cell was left for three months under ambient conditions, and the pretilt angle was monitored. A slight decrease was observed. The

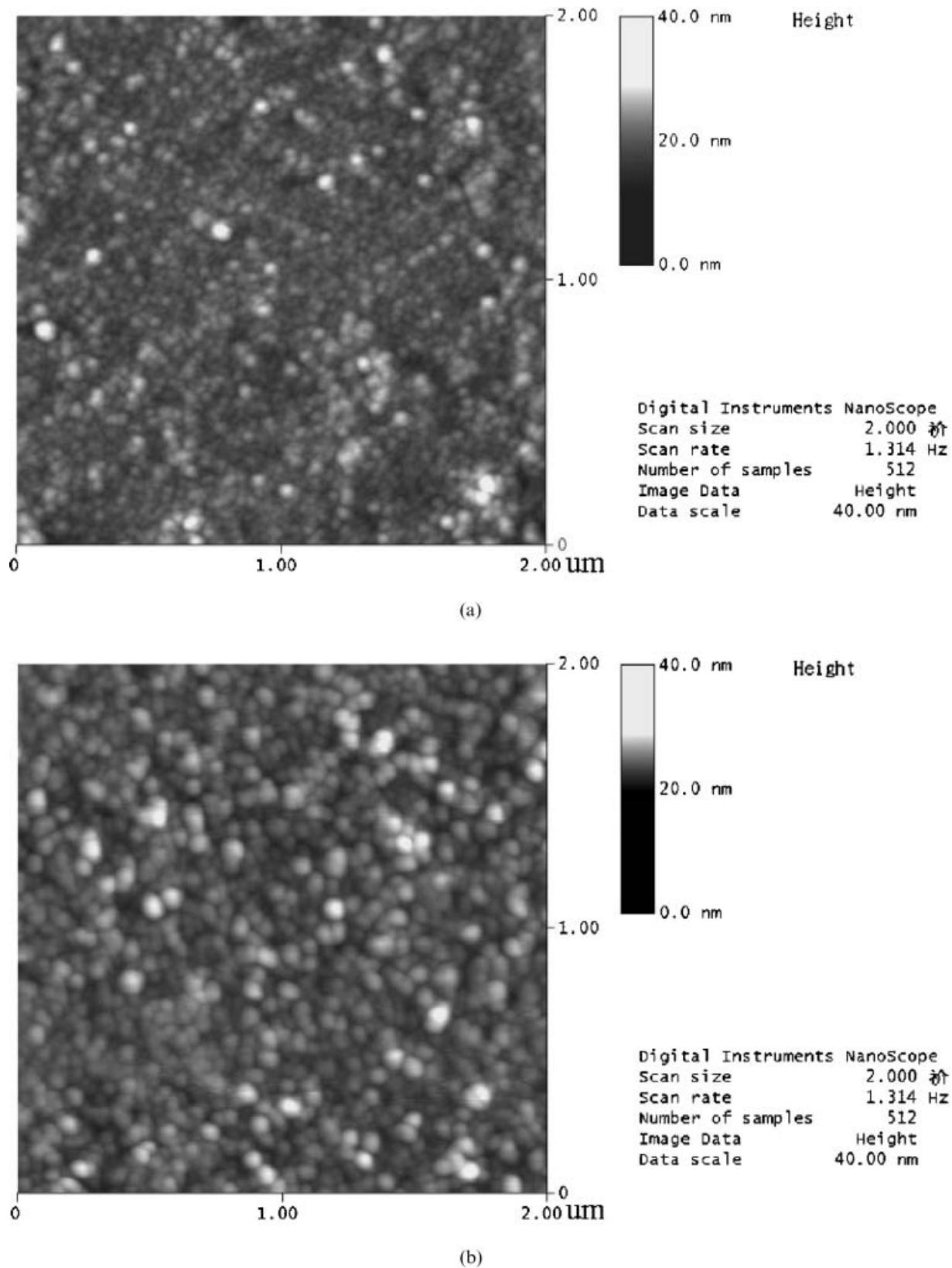


Figure 8. Topographic AFM images of films of different thickness: (a) five bilayers (2.098 nm rms); (b) ten bilayers (2.690 nm rms).

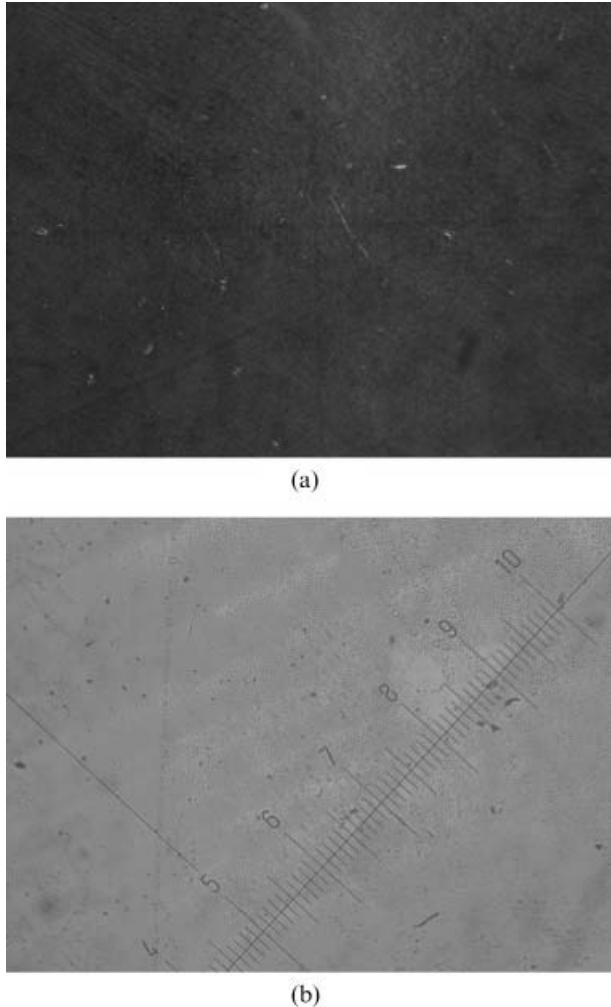


Figure 9. Polarising microscopy texture for a homogeneously aligned nematic LC cell prepared using the three-bilayer LBL multilayer film irradiated for 8 min by LPUVL: (a) dark state; (b) bright state. The LPUVL intensity was 0.58 mW cm^{-2} .

stability of the LCs cell was also examined against heat treatment. The cell was injected at 71°C and heated to 75°C for 10 min, and then cooled to room temperature naturally. The LCs in the cell maintained good alignment, and the pretilt angle was not decreased. Then the cells were sequentially heated at a temperature 5°C higher than the preceding heating step and cooled as before. We discovered that even when the temperature reached 90°C , the cells could maintain good homogeneous alignment and the pretilt angle as before. The good stability might be ascribed to photodimerisation of the cinnamoyl groups.

4. Conclusions

In this work, a photosensitive PDDA/PCAzO layer-by-layer (LBL) ultrathin film was used to induce LC

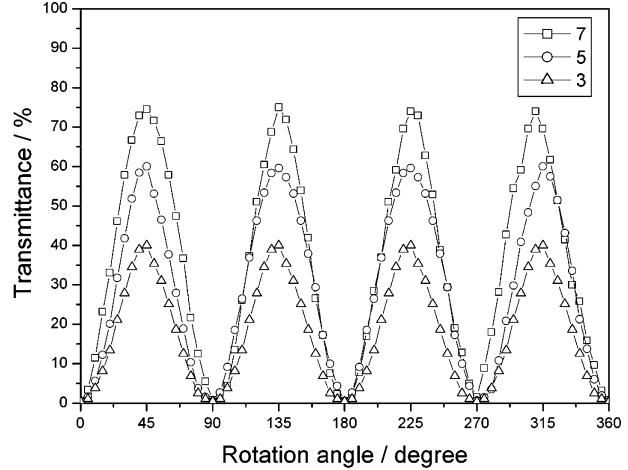


Figure 10. Angular transmittance intensity of the LC cell under crossed polarizers with different number of bilayers: three (Δ), five (\circ) and seven (\square) bilayers.

alignment. The LBL multilayer film was prepared from polycation PDDA and a photosensitive poly-anion PCAzo. Its deposition procedure was uniform and suitable for photoalignment film, which was proved from UV-visible spectra. After irradiation under LPUVL, the LBL film became anisotropic. The UV absorption and FTIR spectroscopic results indicated that the photoreactions of the dual photo-reactive groups jointly participated in the generation of azimuthal anisotropy of the film. The irradiated LBL photoalignment film could align nematic LCs homogeneously. There was no visible morphological change of the irradiated films as observed by AFM. The alignment of the LCs came from the anisotropic interactions with the films. It was also found that the alignment performance of the multilayer film depended largely on the number of bilayers. A thicker

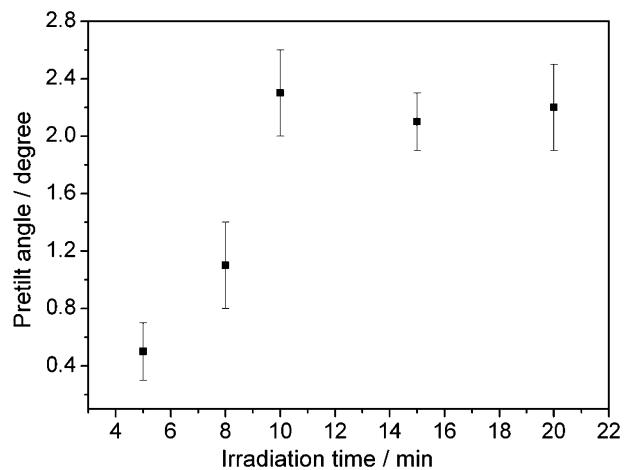


Figure 11. Pretilt angle variations of LCs measured in LC cells with different LPUVL irradiation time. The LPUVL intensity was 0.58 mW cm^{-2} .

film had a larger dichroic ratio after LPUVL irradiation. These results were correlated with the LC homogeneous alignment behaviour in the LC cell. The reorientation behaviour of the LC molecules was found to be associated with the LBL film thickness. The stability of film was good. A pretilt angle of up to 2.3° was achievable, which is larger than that of common cinnamate LBL ultrathin films. Hence, LBL ultrathin films with dual photoreaction moieties are a promising film-preparation method for LC photoalignment.

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