# Photoalignment of liquid crystals using a covalently attached self-assembled ultrathin film fabricated from diazoresin and cinnamate polyelectrolyte

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Layer-by-layer films have been fabricated from diazoresin (DR) and poly[4-sulfonyl phenoxy(4acryloyloxy)cinnamate, sodium salt] (PACSS) in aqueous solution via electrostatic attraction. The ionic bonds between the diazonium ions and sulfonate ions in the film were converted into covalent bonds by irradiation with 365 nm UV light. It was also confirmed that the vinylene units of the cinnamovl group in PACSS did not change in this process. Covalently attached selfassembled ultrathin films containing photosensitive cinnamoyl groups could align liquid crystals (LC) uniformly with good stability after irradiation with linearly polarized ultraviolet light (LPUVL). In this work, polarized UV-vis spectroscopy was utilized to investigate the photochemical process of the covalent film. It was found that cinnamoyl moieties parallel to the polarization direction of the LPUVL were consumed by the photoreaction faster than those perpendicular to the polarization direction. It can be concluded that the selective photoreaction induced the anisotropy of the films. Experimental results revealed that the degree of photoreaction and the dichroic ratio of the films depended on the number of adsorbed layers and the irradiation time. These results were correlated with the LC homogeneous alignment behavior in the parallel LC cell. The reorientation behavior of the LC molecules was found to be associated with the covalent film thickness and irradiation time.

## Introduction

The liquid crystal (LC) alignment layer is one of the most important technologies in forming high-performance LC devices, as it can directly affect the contrast ratio in display applications.<sup>1</sup> Till now, the contact method based on surface rubbing has dominated the mainstream of the LC cell preparation process. Drawbacks to the contact method include unstable static electricity, residual stress, and dust pollution. These drawbacks result in poor yield and reliability in the micro-fabrication of small panel applications.<sup>2,3</sup> Thus, developing a non-contact technology has been a viable solution to overcome the drawbacks of the rubbing method.

In the 1970s, the reorientation of a mesophase using photoresponsive molecules was reported by Sackmann and Haas *et al.*<sup>4,5</sup> Ichimura *et al.* revolutionized this approach by attaching a chromophore to a surface for LC alignment in 1988.<sup>6</sup> Since then, the photoalignment technique of LC has gained great attention as a non-contact alignment method. Numerous investigations on the photoalignment of LC have confirmed that the macroscopic orientation of LC molecules can be controlled by photoinduced microscopic changes in structure as well as orientation of photoreaction moieties, including azobenzenes,<sup>6,7</sup> cinnamates<sup>8</sup> and polyimides.<sup>9</sup>

are most suitable for durable LC photoalignment films because of the irreversible [2 + 2] photodimerization of cinnamoyl groups.<sup>8</sup> However, the photoreaction ratio of cinnamate materials is low and the thermal stability of the photoalignment film is not strong enough; both will limit the application of the photoalignment technique in industry. Our previous investigations showed that ordered cinnamate layer-by-layer (LBL) ultrathin films as photoalignment films can readily overcome these obstacles.<sup>10,11</sup> LBL assembly of oppositely charged polyelectrolytes is a simple and powerful method for the construction of self-assembled planar ordered composites on the nanometer scale.<sup>12,13</sup> Since the photosensitive cinnamates are oriented in the LBL films, the [2 + 2] photoreaction can proceed easily. The coulombic interaction between layers also enhances the film stability compared to the van der Waals force in spin-coated films. The main advantage of these cinnamate films over those prepared by spin coating is that the concentration and layer sequence of aggregates can be well characterized.14

However, the force between layers in such films is based on coulombic interactions, which may be insufficient to stabilize the films in certain cases. Cao and co-workers prepared a family of stable ultrathin multilayer films from conventional polymers. They reported the conversion of the ionic linkage nature of the films from ionic bonds to covalent bonds under ultraviolet irradiation.<sup>15,16</sup>

In this investigation, new covalently attached multilayer ultrathin films were prepared for photoalignment studies. The ultrathin films were fabricated using diazoresin (DR) as polycation and poly[4-sulfonate phenoxy(4-acryloyloxy)cinnamate, sodium salt] (PACSS) as polyanion (the chemical

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Fig. 1 Chemical structures of diazoresin (DR) and poly[4-sulfonate phenoxy(4-acryloyloxy)cinnamate, sodium salt] (PACSS).

structures are shown in Fig. 1), by a self-assembly technique. First, the self-assembled films were irradiated with 365 nm UV light, which changed the linkage between the layers of the films from ionic to covalent. Then, the covalent self-assembled films were irradiated with 297 nm linearly polarized UV light (LPUVL) to form anisotropic surfaces because of the axially selective photoreaction of cinnamates in the films. The product films showed excellent LC alignment performance. The stabilities of the films were also enhanced by the linkage conversion of the DR/PACSS layers from ionic to covalent bonds. The films were also thermally stable to 180 °C, which was 80 °C higher than conventional LBL photoalignment films.

#### Experimental

#### Synthesis

Diazoresin (DR) was synthesized from diphenylamine-diazonium salt and formaldehyde in concentrated sulfuric acid,  $M_n \approx 2000 \text{ g mol}^{-1}$ ,  $\eta_{sp}/c = 0.12 \text{ g dL}^{-1.17}$  4-Hydroxycinnamic acid and 4-hydroxybenzenesulfonic acid sodium salt were supplied by Aldrich and used without further purification. The typical procedure to prepare poly[4-sulfonate phenoxy(4-acryloyloxy)cinnamate, sodium salt] (PACSS) is shown in Fig. 2.

**4-Acryloyloxycinnamic acid (1).** To a well stirred mixture solution of 4-hydroxycinnamic acid (13.12 g, 80 mmol) and NaOH (6.4 g, 160 mmol) in 40 mL of water and 40 mL dioxane, acryloyl chloride (9.8 mL, density = 1.11, 120 mmol) was added dropwise at 5–10 °C. After stirring at room temperature for 4 h, the reaction mixture was neutralized with dilute aqueous HCl. The solid 4-acryloyloxycinnamic acid precipitate was filtered off, washed with warm water, dilute HCl and water, successively. The crude product was purified *via* column chromatography (silica gel, THF) to give a white solid product (11.3 g, 52 mmol, 65% yield). Mp 186 °C. <sup>13</sup>C NMR (DMSO-d<sub>6</sub>):  $\delta$  120.27, 123.12, 128.38, 130.34, 131.26,



Fig. 2 Synthetic route to poly[4-sulfonate phenoxy(4-acryloyloxy) cinnamate, sodium salt].

134.72, 143.74, 152.38, 168.34, 171.62. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ 6.17 (d, 1H, CH<sub>2</sub>=CH), 6.43 (m, 1H, CH=CH<sub>2</sub>), 6.52 (d, 1H, CH<sub>2</sub>=CH), 6.6 (d, 1H, CH=CH), 7.23 (d, 2H, ArH), 7.6 (d, 1H, CH=CH), 7.78 (d, 2H, ArH). IR (KBr powder): 979 (=CH), 1169 (C–O), 1688 (C=O), 1743 (C–O) cm<sup>-1</sup>. *m*/*z* (ESI) 217 ([M – H]<sup>-</sup>, 100%), 173.1 (17), 119.2 (66) and 71.0 (8).  $\lambda_{max}$ (ethanol)/nm 282 ( $\varepsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 25320), 217 (19080). Elemental analysis, Calculated for C<sub>12</sub>H<sub>10</sub>O<sub>4</sub>: C, 66.06; H, 4.59. Found: C, 65.96; H, 4.37%.

4-Sulfonate phenoxy(4-acryloyloxy)cinnamate sodium salt (2). 4-Acryloyloxycinnamic acid (1) (8.72 g, 40 mmol) 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 needle-like crystals of 4-acryloyloxycinnamic acid chloride were produced. After filtering, the crude product was recrystallized using dry toluene. In a 250 mL flask, 4-hydroxybenzenesulfonic acid sodium salt (1.96 g, 10 mmol) and NaOH (0.8 g, 20 mmol) were dissolved in 100 mL of water and 50 mL THF, and cooled to 0-5 °C. Then, 4-acryloyloxycinnamic acid chloride (4.73 g, 20 mmol) in 20 mL of THF was added dropwise with stirring at the same temperature. After stirring at room temperature for 24 h, some of the solvent was removed by vacuum distillation. The precipitated was filtered off, washed with water and recrystallized from THF (1.58 g, 4 mmol, 10% yield). Mp 243 °C. <sup>13</sup>C NMR (DMSO-d<sub>6</sub>):  $\delta$ 118.02, 121.88, 127.75, 129.55, 130.92, 131.65, 132.71, 146.22,

146.67, 153.01, 165.01. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ 6.18 (d, 1H, CH<sub>2</sub>=CH), 6.46 (m, 1H, CH=CH<sub>2</sub>), 6.54 (d, 1H, CH<sub>2</sub>=CH), 6.6 (d, 1H, CH=CH), 7.16 (d, 2H, ArH), 7.23 (d, 2H, ArH), 7.3 (d, 2H, ArH), 7.61 (d, 1H, CH=CH), 7.77 (d, 2H, ArH). IR (KBr powder): 1050 (S=O), 1688(C=O), 1739 (C-O) cm<sup>-1</sup>. *m*/*z* (ESI) 373.1 ([M - Na]<sup>-</sup>, 100%), 293 (69), 226.9 (23), 172.1 (96) and 147.2 (28).  $\lambda_{max}$  (ethanol)/nm 302 (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 26640), 220 (18980). Elemental analysis, calculated for C<sub>18</sub>H<sub>13</sub>O<sub>7</sub>SNa: C, 54.5; H, 3.28. Found: C, 54.92; H, 3.68%.

**Poly[4-sulfonate phenoxy(4-acryloyloxy)cinnamate, sodium salt] (PACSS) (3).** The compound **2** (1 g) was polymerized in 20 mL DMF with 0.01 g AIBN as the initiator at 65 °C under nitrogen atmosphere. The polymers were isolated after polymerization for 12 h by adding the reaction solution to an excess of methanol, purified by reprecipitation from DMF solution to methanol, and dried under vacuum (56% yield). The GPC analysis gave  $M_n$  = 1317 and  $M_w$  = 1558. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ 1.10 (d, 2H, CH<sub>2</sub>–CH), 2.65 (m, 1H, CH–CH<sub>2</sub>), 6.6 (d, 1H, CH=CH), 7.23 (d, 2H, ArH), 7.58 (d, 1H, CH=CH), 7.61 (d, 2H, ArH), 7.73 (d, 2H, ArH), 7.89 (d, 2H, ArH).  $\lambda_{max}$  (ethanol)/nm 302 (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 28200), 220 (17410).

#### Preparation of covalently attached films

The self-assembled film were constructed on quartz slides for UV-vis measurement, on silicon wafers for ellipsometry, on CaF<sub>2</sub> wafers for Fourier-transform (FT) IR spectroscopy and on indium tin oxide (ITO) glass for the assembly of LC cells. Before the film construction, the quartz wafers and the silicon wafers were treated in fresh piranha solution (v/v = 1 : 3, 30% $H_2O_2$ : 98%  $H_2SO_4$ ) for 1 h, washed carefully with deionized water and dried. The CaF2 wafers and ITO glass slides were cleaned by washing with deionized water. The concentrations of DR and PACSS in deionized water for dip coating were all  $0.1 \text{ mg mL}^{-1}$ . In all cases, DR was the first layer, and PACSS was the last layer (outermost layer). For  $(DR/PACSS)_n$ multilayer films, the deposition time for each layer was 10 min, followed by washing with deionized water and nitrogen gas blow drying. All fabrication processes were performed in darkness. DR solution and films were also kept in the dark before the irradiation. The quantity of material deposited at each step was deduced from its absorption spectrum, which was determined on a Shimadzu UV-3101PC spectrophotometer. The thickness of the multilayer film on a silicon wafer was determined with a Jobin Yvon UVISEL ellipsometer (240-830 nm, 70° incident angle).

The well fabricated films were exposed to 365 nm UV light (irradiation intensity: 0.23 mW cm<sup>-2</sup> at 365 nm) which was obtained from a 300 W high pressure Hg–Xe lamp with glass band-pass filters (365 nm  $\pm$  5 nm) for a given time to ensure the photoreaction proceeded to completion.

#### Photoalignment characterization of covalently attached films

The covalent films were irradiated using a high pressure Hg–Xe lamp system (300 W) with glass band-pass filters (297 nm  $\pm$  5 nm) and a Glan-Talor lens to induce anisotropy used for LC alignment. The intensity of LPUVL on the surface

of the film was 0.58 mW cm<sup>-2</sup> (at 297 nm). Linearly polarized UV-vis absorption spectra were recorded on a Shimadzu UV-3101PC spectrophotometer equipped with special polarizing accessories and used to monitor the photoreaction process of the films. IR spectra were collected on a Bio-Rad FTS3000 spectrophotometer. The surface morphology of the films was obtained by using a Nanoscope III atomic force microscope (AFM) (Dimention 3100 s, Digital Instrument Co.). All measurements were performed in contact mode using triangular Si<sub>3</sub>N<sub>4</sub> cantilevers in air under ambient conditions.

#### Liquid crystal cells

A pair of substrates with photoirradiated covalently attached films were assembled together in the parallel direction of LPUVL irradiation by using 20  $\mu$ m thick spacers. A commercial LC material TEB30A (Slichem Co., China) was injected into the cell at 71 °C, which is slightly higher than the nematic-to-isotropic transition temperature ( $T_{\rm NI} = 61.2$  °C) of this LC. Then the LC cell was cooled to room temperature slowly, to remove any flow-induced memory. Polarizing microscopy (FOIC-2, China) with a digital camera was used to evaluate the alignment quality of the LC and measure the transmittance. The polarization directions of the two polarizers were crossed.

#### **Results and discussion**

#### Covalently attached self-assembled film formation

The layer-by-layer deposition of the DR/PACSS selfassembled multilayer film was investigated by UV-vis absorption spectroscopic measurement (Fig. 3). The characteristic peaks at 380 nm and 296 nm belong to the diazonium group of the diazoresin<sup>18</sup> and the  $\pi$ - $\pi$ \* transition of the double bond conjugated with the phenyl group of the cinnamoyl group in PACSS,<sup>19</sup> respectively. The linear increase of the two peaks with the number of bilayers clearly indicates the regular growth of the DR/PACSS layers. The LBL film absorbance was red-shifted 11 nm compared to the 1 mg mL<sup>-1</sup> PACSS



Fig. 3 UV-vis absorption spectra of DR/PACSS film on quartz substrate with increasing number of bilayers. The inset diagram shows the increase of absorbance at 296 and 380 nm with the number of bilayers.



Fig. 4 The change in thickness as obtained by ellipsometry.

solution ( $\lambda_{max}$  = 285 nm) indicating aggregates in the film. The red-shift behavior for DR/PACSS shows the formation of J-aggregates in each layer where the orientation of the cinnamoyl groups could be described as end-to-end.20,21 Comparison of the  $\lambda_{max}$  centred at about 296 nm values with increasing number of layers revealed a small shift in  $\lambda_{max}$ position occurring intermittently. This implies that the degree of aggregation changes with thickness. The reorganization of the aggregates with increasing layer thickness is consistent with a self-healing capacity for these types of films.<sup>22,23</sup> Ellipsometric measurement was carried out to provide information about the film thickness. The average thickness was 2.3 nm bilayer<sup>-1</sup> when the concentration of DR (PACSS) was  $0.1 \text{ mg mL}^{-1}$ . Fig. 4 shows that the film thickness increased linearly with the number of bilayers. In summary, the fact that the linear absorbance and thickness increase was observed for each deposition cycle indicated a quantified adsorption of polyelectrolyte.

The polycation diazoresin and cinnamate polyanion were linked by electrostatic interaction between the cationic diazonium group  $(-N_2^+)$  and the anionic  $-SO_3^-$  to form a layer-by-layer ultrathin film. The diazoresin was a photosensitive polymer and decomposed readily by UV irradiation;<sup>24</sup> the ionic bond between  $-N_2^+$  and  $O^-$  could be easily transformed into a covalent bond under UV light (as shown in



**Fig. 6** UV-vis absorption spectra of an 8 bilayer DR/PACSS film under 365 nm UV irradiation for different times. Irradiation time (s) (from top to bottom): 0, 10, 30, 60, 120, 240, 600, 900 and 1200. Irradiation intensity (at 365 nm):  $0.23 \text{ mW cm}^{-2}$ . The inset plot shows the decrease of absorbance at 380 nm with the irradiation time.

Fig. 5), which improved the stability of the film. Fig. 6 shows the changes by means of UV-vis spectra of the films after 365 nm UV irradiation. As indicated in the figure, under 365 nm UV irradiation, the diazonium groups decomposed gradually as indicated by the decrease of the absorbance at 380 nm and concomitant increase of the absorbance at 300 nm. An isosbestic point at 340 nm appeared in accordance with the results from previous investigations with DR as a component in planar films.<sup>15,25</sup> The decomposition was complete within 5 min. In order to further confirm this reaction, films of 100 bilayers of DR/PACSS were constructed on CaF2 plates, and the IR spectra were recorded before and after irradiation as shown in Fig. 7. As seen in Fig. 7, the asymmetric stretching vibration of the  $-N_2^+$  at 2169 cm<sup>-1</sup> in the DR/PACSS film disappeared completely after 365 nm UV irradiation for 5 min, indicating the complete decomposition of the diazonium group.<sup>15</sup> At the same time, the absorbance at 1580 cm<sup>-1</sup> corresponding to the vibration of the benzene ring conjugated with an unsaturated group in the DR/PACSS film shifted to



Fig. 5 Fabrication of self-assembled DR/PACSS multilayer films and conversion of the interlayer linkage from ionic to covalent under UV irradiation.



Fig. 7 IR spectra of a 100 bilayer DR/PACSS film on a  $CaF_2$  substrate (a) before and (b) after UV irradiation. Irradiation intensity (at 365 nm): 0.23 mW cm<sup>-2</sup>. Irradiation time: 5 min.

 $1600 \text{ cm}^{-1}$ , which is the normal absorption of the benzene ring.<sup>26</sup> The band at  $1633 \text{ cm}^{-1}$  due to the vinylene C=C of the cinnamoyl group stretching vibration had no obvious change.<sup>27</sup> Thus the ionic bond between the diazonium and the sulfonate group converted to a covalent bond by the first irradiation, whereas the photosensitive double bond in the PACSS did not change. Thus, covalently attached self-assembled films containing photosensitive cinnamoyl groups have been fabricated.

#### Polarized photoreaction of the covalently attached films

The covalent self-assembled films having one cinnamoyl moiety per chemical repeat unit in the side chains in the polyanion were then irradiated by 297 nm LPUVL to induce anisotropy. The photoreaction procedure in the film was examined by UV-vis spectroscopy.

Fig. 8 shows the linearly polarized UV-vis absorption spectra of 3 bilayers DR/PACSS covalently attached film irradiated with 297 nm LPUVL for 10 min. The polarized absorbance  $A_{\perp}$  ( $A_{\parallel}$ ) was measured with a probing UV-vis light linearly polarized perpendicular (parallel) to the polarization



**Fig. 8** Polarized UV-vis absorption spectra of a 3 bilayer covalent film of DR/PACSS irradiated with 297 nm LPUVL. The plot shows the spectra before 297 nm LPUVL irradiation, and after irradiation perpendicular  $(A_{\perp})$  and parallel  $(A_{ll})$  to the polarization direction of the LPUVL.

direction of the LPUVL. Prior to 297 nm LPUVL irradiation, the absorption was isotropic  $(A_0 = A_{\perp} = A_{\parallel})$ . After the irradiation, the intensity of the band at 296 nm decreased with the irradiation of LPUVL, and a huge variance in the absorbance was observed between  $A_{\perp}$  and  $A_{\parallel}$ . The result indicated that the cinnamoyl groups with vinylene units positioned parallel to the polarization direction of the LPUVL  $(A_{ll})$  were consumed by photoreaction faster than those perpendicular to the polarization direction  $(A_{\perp})$  during LPUVL irradiation. As a result of the direction selective photoreaction, the vinylene C=C bonds of unreacted cinnamovl groups aligned perpendicular to the polarization direction of the LPUVL were left in a greater number relative to those aligned parallel to the polarization direction. Therefore, the structural anisotropy of the multilayer film was generated from the selective photoreaction of the cinnamoyl group in the film. The LPUVL-induced anisotropic film would give rise to anisotropic interactions with the LC molecules, which might possibly generate LC homogeneous alignment.

In order to verify the photoreaction process of the films, the absorbance at 296 nm was plotted as a function of LPUVL irradiation time. Fig. 9 shows the changes in absorbance at 296 nm of DR/PACSS films with respect to LPUVL irradiation.  $A_0$  and  $A_t$  are the absorbance before (0 min) and after 297 nm LPUVL irradiation (t min) at 296 nm. As shown in Fig. 9, the intensity of the absorbance at 296 nm decreased rapidly with the increase of the irradiation time. However, the change in slope was greater for thicker film. Clearly, there was a significant effect of the bilayer number on the photoreaction characteristics. The phenomena could be explained thus: thicker films have a larger total amount of cinnamoyl groups and should have more aggregated domains. As mentioned above, the degree of aggregation changed with the thickness of the film. The efficiencies of photoreaction were affected by the micro-environmental properties including polarity, free volume, molecule-to-molecule interactions, etc. So photoalignment became a function of the total film thickness, where each laver contributed a finite number of photoalignment domains. Thickness dependence on photoreaction of LBL films has also been reported previously for azobenzene materials.<sup>14,28</sup> Like photochromic layers, we believe that the differences of



Fig. 9 Changes in absorbance at 296 nm of different thickness of DR/PACSS films as a function of LPUVL irradiation time: 3 ( $\Box$ ), 5 ( $\bullet$ ) and 7 ( $\triangle$ ) bilayers.



**Fig. 10** Dichroic ratios measured from different thick DR/PACSS films irradiated by LPUVL with various time:  $3 (\Box)$ ,  $5 (\bullet)$  and  $7 (\triangle)$  bilayers.

photoreaction with different thicknesses of these self-assembled films are due to matrix effects.<sup>7</sup>

Photoinduced optical anisotropy of the film was investigated by measuring the absorbance at 296 nm parallel  $(A_{II})$  and perpendicular  $(A_{\perp})$  to the electric vector of LPUVL. The optical anisotropy is expressed here by the UV dichroic ratio  $[(A_{\perp} - A_{ll})/(A_{\perp} + A_{ll})]$ . The results are shown in Fig. 10. As seen in the figure, all the measured dichroic ratios were positive over the irradiation time range of ≤65 min. The dichroic ratio reached 0.1, which is larger than that of spin-coated photoalignment films.<sup>29,30</sup> With increasing irradiation time, the dichroic ratio increased rapidly to a maximum at 10 min and then decreased. This could be reasonably explained by assuming a possible mechanism, the preferred depletion of cinnamic acid side chains parallel to the LPUVL.8 At the beginning of linear photodimerization, those cinnamoyl chromophores in the cinnamic acid side chains started to be cross-linked which were parallel to the polarization direction of LPUVL. The chromophores with off-axis transition moments would at first be hardly affected. This led to the observed initial increase of the dichroic ratio. With the irradiation time increasing, the chromophore depletion parallel to the LPUVL saturated and the probability that chromophore pairs with off-axis orientation would undergo crosslinking increased. Thus further irradiation would lead to the gradual reduction of the dichroic ratio. From Fig. 10, we also found that the thicker films had the larger dichroic ratio after the LPUVL irradiation. This result is consistent with the photoreaction efficiencies for films with different thicknesses. As mentioned above, thicker films always have a larger photoreaction degree for the same irradiation time. It was already known that the photoreaction primarily induced the anisotropy of the film. So the thicker film would have the larger dichroic ratio after the LPUVL irradiation.

#### AFM images

Fig. 11 showed micrographs of the DR/PACSS films at different thicknesses. The morphology was comprised of corrugated features with many round-shaped domains. Clearly the surface topography showed a non-smooth but



**Fig. 11** Topographic AFM images of films of different thicknesses: (a) 5 bilayers (3.3 nm rms); (b) 10 bilayers (4.5 nm rms).

homogeneous film with the round-shaped domains varying in size with thicker layers. The films were amorphous and suggested an isotropic growth showing no preferred orientation. In general, the roughness increased with increasing thickness. Roughness was determined from the histogram as rms 2-3 nm for thinner films (5 bilayer) and 4-5 nm for thicker films (10 bilayer). The difference was largely due to the presence of larger and more irregular patches with thicker layers broadening the size histogram. It is not clear whether the aggregates within the domains exhibit anisotropic orientation. However, it was confirmed that the aggregation behaviour correlated with some of the photoreaction behaviour observed and the fact that the  $\lambda_{max}$  centred at about 296 nm shifted with different thicknesses. There was no visible morphological change after LPUVL irradiation as observed by AFM. This result is in accord with spin-coated photoalignment polymer films.31

#### LC alignment properties studies

A uniform homogeneous alignment of the LC molecules could be obtained in a parallel cell modified by the irradiated covalent self-assembled films. The transmittance intensity of visible light (400–700 nm) through the LC cell between crossed polarizers was monitored as a function of the rotation angle of the cell in the plane under a polarizing microscope.

Fig. 12 shows the evolution of transmittance with irradiation time as monitored through the cell. For a 7 bilayer DR/ PACSS film cell, the first few minutes did not produce significant changes in the transmittance-angle dependence. However, at 5 min birefringence began to be observed. The maximum of transmittance was reached at 70% at 10 min. The transmittance began to decrease with further irradiation. This result suggests that the LPUVL irradiation time of 10 min was



Fig. 12 Angular transmittance intensity of LC cell under crossed polarizers with 7 bilayer DR/PACSS covalent films with different LPUVL irradiation times: 1 min ( $\triangle$ ), 5 min ( $\bigcirc$ ), 10 min ( $\square$ ) and 15 min ( $\bigcirc$ ).

sufficient to induce preferential reorientation of LC molecules, which is consistent with the conclusion drawn from the dichroic ratio measurements presented above. Similar results were obtained for a 3 bilayer DR/PACSS film cell (data not shown). However, the maximum transmittance of the 3 bilayer cell was about 50% after 10 min, which means that the birefringence of LC in the 3 bilayer cell is smaller than that in a 7 bilayer DR/PACSS cell. Since the homogenous alignment of LC molecules is controlled by the photo-orientation of cinnamates in the DR/PACSS films, it is clear that the alignment of LC molecules could be influenced by the properties of the DR/PACSS film. In previous studies, we found that the photoalignment behavior of a covalent selfassembled film was influenced by the thickness of the sample, i.e., the dichroic ratios were larger for the thicker samples after the same irradiation time. Hence, the alignment properties of the LC molecules could be influenced by the thickness of the DR/PACSS film. This indicates that LC reorientation might not simply be influenced by the contact photoreaction molecule, but might be controlled by the overall thickness and ordering of the film. It is well known that dipole force, polarity, surface energy and topological factors influence the surface anchoring energy of LC molecules.<sup>32</sup> The differences in the orientation and aggregation of cinnamates in the covalently self-assembled films must influence these photoalignment properties of the film. Thus, the alignment of LC is associated with the thickness of the DR/PACSS film. This is in contrast to previously reported photoalignment behaviors in LB which were thickness independent.33,34

The stability of the LC 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 LC in the cell maintained good alignment. Then the cells were sequentially heated at a temperature 5 °C higher than the preceding heating step and cool as before. We discovered that even when the temperature reached 180 °C the cells could maintain good homogeneous alignment as before. These results indicated that the covalent films maintained their LC alignment properties up to at least 180 °C, which was approximately 80 °C higher than the conventional LBL

photoalignment film's thermal stability.<sup>11</sup> Also the LC cell was left for 1 month under ambient conditions, and the transmittance was monitored. A slight decrease in intensity was observed. These results clearly showed the stabilities of the covalent photoalignment films were enhanced. This higher stability was ascribed to the linkage conversion of the DR/PACSS layers from ionic bond to covalent bond.

#### Conclusions

In this paper, the polyanion containing cinnamoyl group was self-assembled with diazoresin to form a kind of stable covalent ultrathin film upon exposure to 365 nm UV irradiation. As LC alignment films, the photoalignment properties of DR/PACSS covalent films were investigated. The covalent films were found to have high anisotropy after irradiation with linearly polarized UV light. It was also obvious in our experimental results that the photoreaction properties were largely dependent on the irradiation time and thickness of the film: the dichroic ratio of the film increased rapidly to a maximum at 10 min and then decreased; and the thicker film had the larger dichroic ratio after the LPUVL irradiation. A uniform homogeneous alignment of the LC molecules could be obtained in the parallel cell modified by the irradiated covalent self-assembled film. The reorientation behaviors of the LC molecules were also found to be associated with the film irradiation time and thickness. Most importantly, the thermal stability of the film is enhanced, reaching 180 °C. This is sufficient for commercial requirements. Thus, the incorporation of the cinnamoyl moiety using the new covalent LBL film is a promising technique for LC photoalignment studies.

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