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Photoalignment of liquid crystals in a hydrogen-bonding-directed layer-by-layer ultrathin film

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In this paper, a new type of hydrogen-bonding-directed layer-by-layer (LBL) ultrathin film with photosensitive cinnamoyl chromophores was prepared. It could induce uniform alignment of liquid crystals (LCs) after being irradiated by linearly polarised ultraviolet light (LPUVL). The hydrogen-bonding-directed formation of a photochromic multilayer film was achieved on the basis of an alternating assembly of poly(4-vinylpyridine) (PVPy) and poly(4-acryloyloxy)cinnamic acid (PCA). The assembly process was followed by UV–visible spectroscopy. The nature of the interaction between the two polymers was identified as a hydrogen bond through Fourier transform infrared spectroscopy. When the film was irradiated by LPUVL, the cinnamoyl units in the film underwent [2+2] cycloaddition along the electric vector direction of the LPUVL. The polarised UV–visible spectra proved that the film was anisotropic, and then the film could induce homogeneous alignment of nematic LCs. With the number increment of the bilayers, the alignment effect of the multilayer film was enhanced, and the contrast ratio became higher. The orientation direction of the LCs was always perpendicular to the electric vector of the irradiating LPUVL.

Keywords: photoalignment; layer-by-layer ultrathin film; hydrogen bond; liquid crystal

1. Introduction

The orientation of liquid crystals (LCs) on a polymer surface irradiated with linearly polarised ultraviolet light (LPUVL) was observed at the beginning of 1990s and this technique promised wide applications in liquid crystal displays (LCDs) (*1, 2*). The photo-aligning technique is a non-contact alignment method which avoids the shortcomings of rubbing, such as unstable static electricity, residual stress and dust pollution. This method is very promising for the fabrication of the LCDs with no size limitation and can be effectively used for the alignment of LCs in tiny telecommunication devices with complicated structures.

Numerous investigations on the photoalignment of LCs have confirmed that the macroscopic orientation of LC molecules can be controlled by photo-induced microscopic changes in structure as well as the orientation of photoreaction moieties, including azobenzenes (*3, 4*), cinnamates (*5*) and polyimides (*6*). Among various photoreactive polymers, cinnamate materials are most suitable for durable LC photo-alignment films because of the irreversible [2+2] photodimerisation of cinnamoyl groups (*5*). There were many methods for the fabrication of a ‘command surface’: the spin-coating method (*5*), Langmuir–Blodgett (LB) method (*7*) and self-assembled monolayers and multilayers (*4, 8*). The first two methods have been widely studied, but few investigations for photoalignment films have been undertaken for the self-assembled film method. The self-assembled film is a system of supramolecular hierarchical organisation, which is more stable than the LB film and more ordered than the spin-coating film (*9*). Multilayers directed by the layer-by-layer (LBL) self-assembled deposition are very simple, easy to automate and could be more adapted to large-scale applications than the monolayers. So they have attracted increasing attention from many researchers (*10, 11*). The driving forces for the multilayers are primarily electrostatic and covalent bonds. Very recently, new approaches for the fabrication of an alternating multilayer film on the basis of hydrogen bonds were reported by Zhang et al. (*12*) and Rubner (*13*) at almost the same time. Unlike electrostatically formed polyelectrolyte multilayers constructed in aqueous solutions, however, one of the advantages of the multilayers based on hydrogen bonding is that the formation of the LBL films can also be obtained in organic solvents, which opened a way for preparing multilayer structures using non-ionic and water-insoluble polymers instead of water-soluble polyelectrolytes. Now the polyelectrolyte LBL photoalignment film has been studied widely and the effect of the photoalignment is excellent (*14–16*). However, the LBL photoalignment films directed by hydrogen bonds have rarely been investigated.

In this article, a new type of hydrogen-bonding-directed LBL film with cinnamoyl units is prepared

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for photoalignment studies. A photosensitive hydrogen donor containing cinnamoyl side groups was synthesised, and then a hydrogen-bonding-directed LBL multilayer film was constructed by alternating deposition of poly(4-vinylpyridine) (PVPy, hydrogen acceptor) and poly(4-acryloyloxy)cinnamic acid (PCA, hydrogen donor); the chemical structures are shown in Figure 1. The assembling process and the photochromic properties of the film were studied using UV–visible spectroscopy. After irradiation with LPUVL, an anisotropy was generated in the UV–visible absorption measurement. It was found that the anisotropic LBL multilayer film could induce homogeneous alignment of LCs and the mechanisms of the alignment were explored.

2. Experimental details

2.1. *Synthesis*

Poly(4-vinylpyridine) (PVPy, M_w=60,000), poly (ethyleneimine) (PEI, M_w=50,000) and 4-hydroxycinnamic acid were purchased from Aldrich and used without further treatment. The hydrogen donor PCA was synthesised in two steps (Figure 2).

*4-Acryloyloxycinnamic acid (**1**).*

To a well-stirred mixture solution of 4-hydroxycinnamic acid (13.12 g, 80 mmol), NaOH (6.4 g, 160 mmol) in 40 ml of water and 40 ml dioxane, acryloyl chloride (9.8 ml, 120 mmol) was added dropwise at 5–10°C. After stirring at room temperature for 4 h, the reaction mixture was neutralised 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). The yield was 65%, melting point 186°C. Fourier transform infrared (FT-IR) spectroscopy (powder, KBr, cm^{-1}): 979 (=CH, δ), 1169 (C–O, ν), 1628 (C=O, ν), 1688 (C=O, ν), 3025 (=CH, ν).

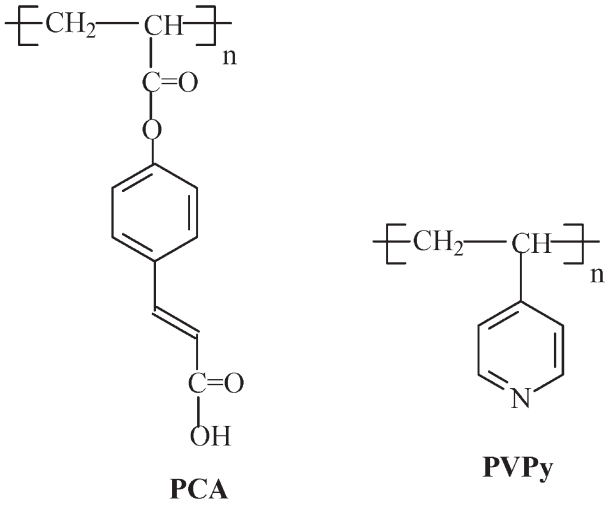

Figure 1. Chemical structures of poly(4-vinylpyridine) (PVPy) and poly(4-acryloyloxy)cinnamic acid (PCA).

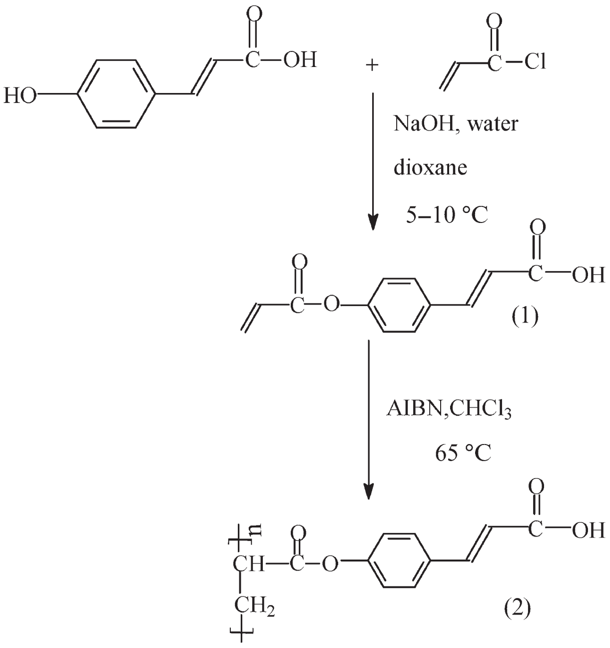

Figure 2. Synthetic route to poly(4-acryloyloxy)cinnamic acid (PCA).

*Poly(4-acryloyloxy)cinnamic acid (PCA) (**2**).*

The compound **1** (1 g) was polymerised in 20 ml chloroform and using 0.01 g AIBN as the initiation at 65°C under a nitrogen atmosphere. The polymers were isolated after 12 h of polymerisation time by adding the reaction solution to an excess of alcohol, purified by reprecipitation from chloroform solution into alcohol. Finally, the product was vacuum dried. The yield was 50%. FT-IR (powder, KBr, cm^{-1}): 1167 (C–O, ν), 1635 (C=C, ν), 1741 (C=O, ν).

2.2. *Film preparation*

The LBL film was assembled on a quartz or a calcium fluoride (CaF_2) plate. The quartz plate was used in UV–visible measurements and the assembly of LC cells, and the CaF_2 plate in Fourier transform infrared (FT-IR) spectroscopy. The quartz and CaF_2 plate need to be modified before LBL deposition. The quartz surface was modified with (4-aminobutyl)-dimethylmethoxysilane, resulting in an NH_2-tailored surface (*17*), and the CaF_2 surface was modified with a precursor layer of PEI. A simplification of the construction of the PVPy/PCA multilayer film is shown in Figure 3. The NH_2-terminated substrate was first immersed in a PVPy ethanol solution for 10 min. In this way, the substrate was covered with a PVPy layer and thus, a surface tailored with hydrogen-bonding acceptors was formed. After being rinsed with pure ethanol and dried under a nitrogen stream, the resulting substrate was transferred into a PCA tetrahydrofuran (THF) solution for 10 min to add a PCA layer. By repetition of the above two steps in a cyclic fashion, the LBL multilayer film was fabricated. The resulting multilayer films can be expressed as $(PVPy/PCA)_n$, where *n* is the number of deposition cycles (namely, the number of bilayers).

2.3. *Instrumentation and measurement*

LPUVL was obtained from a 300 W Hg–Xe lamp system with an optical filter at 300 nm (300 ± 5 nm) (Modef 53370, Oriel Co.) and a Glan–Talor prism. The intensity of LPUVL on the surface of the film was $0.3\,\mathrm{mW\,cm^{-2}}$ (λ=297 nm). UV–visible absorption spectra of the LBL multilayer films were obtained using a Shimadzu UV-3101PC spectrophotometer. Polarised UV–visible absorption spectra were measured by using special polarising accessories. Infrared spectra were recorded with a Bio-Rad FTS3000 spectrophotometer. Polarising microscopy (FOIC-2, China) with a digital camera was used to evaluate the alignment quality of the LC and to measure the transmittance; the polarising directions of the two microscopy polarisers were crossed.

2.4. *Cell fabrication*

A pair of substrates with photoirradiated hydrogen-bonding-directed ultrathin films were assembled together in the parallel direction of LPUVL irradiation by using 20 μm 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_{NI}=61.2°C) of this LC. Then the LC cell was cooled slowly to room temperature to remove any flow-induced memory.

3. Results and discussion

3.1. *LBL multilayer film formation*

The LBL deposition of the PVPy/PCA self-assembled multilayer film was investigated by UV–visible absorption spectroscopic measurement. Figure 4 shows the UV–visible absorption spectra of $(PVPy/PCA)_9$ films on a quartz substrate with increasing number of bilayers. From the UV absorption spectrum of $1\,\mathrm{mg\,ml^{-1}}$ PCA solution, we know the absorption centred at 300 nm is a very broad band

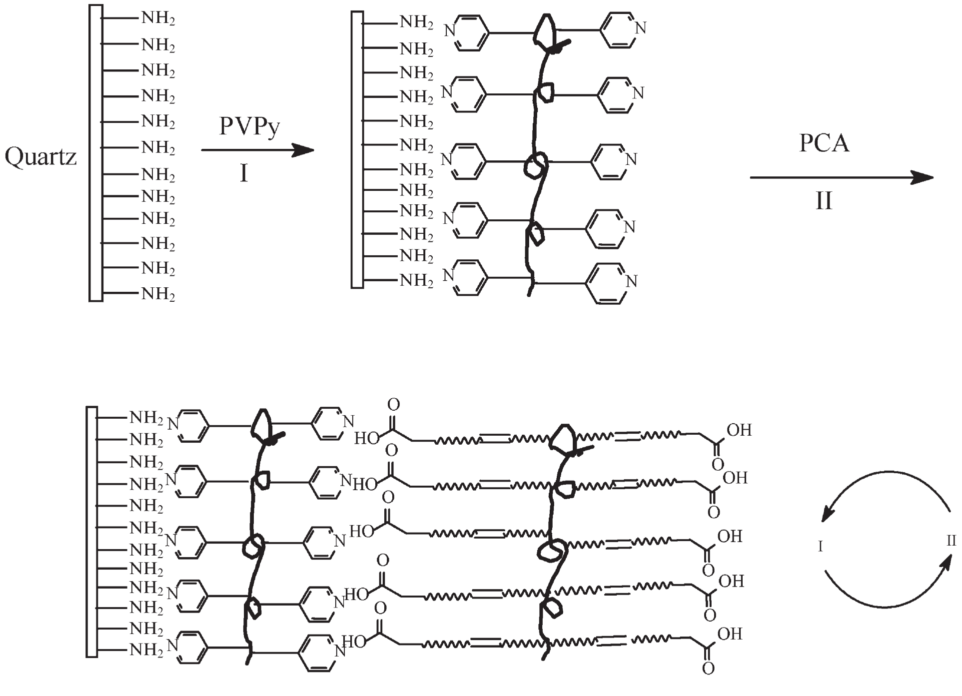

Figure 3. Schematics of the LBL assembly of PVPy and PCA on a quartz substrate based on a hydrogen bond: (I) adsorption of PVPy and (II) adsorption of PCA.

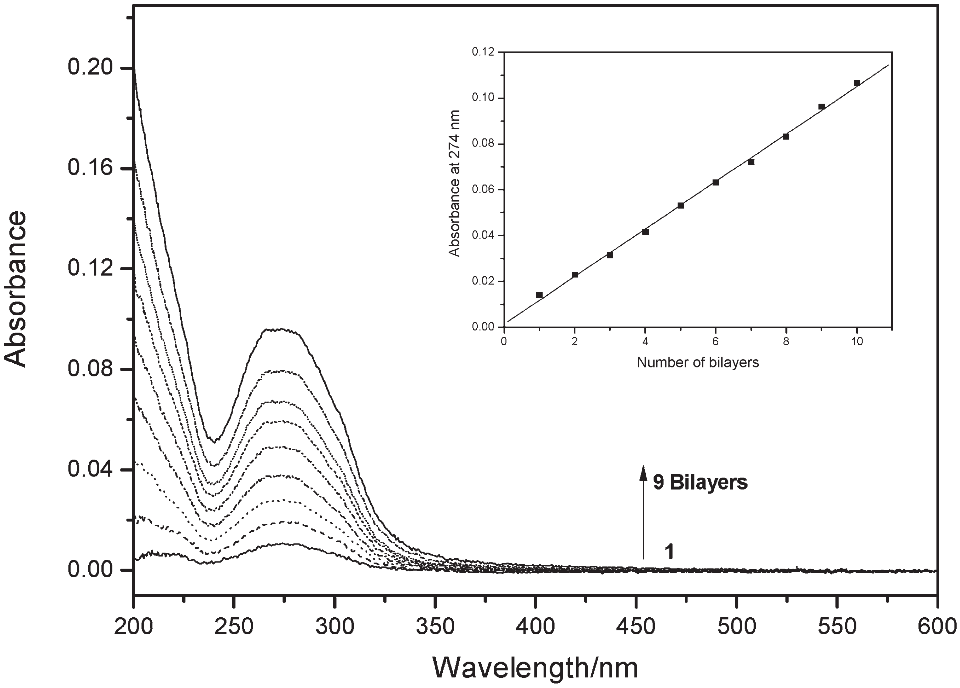

Figure 4. UV–visible absorption spectra of PVPy/PCA film on a quartz substrate with increasing number of bilayers. The inset diagram shows the increase of absorption at 274 nm with the number of bilayers.

and belongs to the π–π^* transition of a double bond conjugated with the phenyl group in PCA. The characteristic peak at 257 nm belongs to the π–π^* transition of the pyridine ring of PVPy. However, we could see from Figure 4 that the absorption spectra displayed only one broad band centred at 274 nm, owing to the interaction of the carboxyl and the pyridyl groups connected through a hydrogen bond. The inset diagram of Figure 4 shows the absorbance of the LBL film at the characteristic wavelength (274 nm) increases in proportion to the number of deposition cycles. The nearly linear growth of the absorption peak at 274 nm indicates that an approximately equal amount of PVPy and PCA is deposited for each adsorption procedure and that the PVPy/PCA LBL films grow uniformly with each deposition cycle. Even when observed with the naked eye, the PVPy/PCA LBL films were clear, transparent and uniform with good optical quality. In summary, the characterisation of the hydrogen-bonding-directed LBL ultrathin film was indicative of the uniform multilayer suitable for photoalignment studies.

3.2. *Photoreaction in the films*

In order to analyse the photoreaction procedure in the LBL multilayer film, UV–visible absorption spectra were measured for different irradiation times. Figure 5 shows the UV–visible spectra of a LPUVL irradiated 10-bilayer film of PVPy/PCA on a quartz substrate with the irradiation time from 0 to 30 min. The intensity of the band at 300 nm decreased rapidly with increasing irradiation time, which indicated that the photosensitive double bonds (the double bond conjugated with the phenyl group in PCA) were consumed. The photoreaction of PCA in the film include a [2+2] photo-crosslinking reaction and photoisomerisation of the cinnamic acid which is similar to the polyester with cinnamate groups, and the hydrogen bond is retained after the photoreaction (*18*). It has been reported that when a solid phase polyester with cinnamate groups was irradiated by UV light, isomerisation produced less than 10% of the photoproducts, but [2+2] photocyclisation took place in most of the nearby chromophores. Thus, photocycloaddtion played the most important role in the reactions in the LBL multilayer films. The products of the photochemical reaction were derivatives of cyclobutane and the photocyclisation occurred along the direction of the polarisation of LPUVL, which generated anisotropy at the interface of the film (*19, 20*). When exposure time exceeded 30 min, the absorbance intensity of the peak would not change a lot which indicated that the photoreaction was basically completed. The inset of Figure 5 illustrated the conversion ratio ($\mathrm{CR}=(A_0-A_t)/A_0$, where A_0 (A_t) is the absorbance of the photosensitive double bond monitored at 0 min (t min)) of the cinnamate moieties in the ultrathin film, the reaction ratio of photosensitive group was about 50% which revealed that the self-assembled films have a high photosensitive efficiency. With the decrease of the absorbance at 300 nm, we can clearly see from Figure 5 that the characteristic peak of PVPy at 257 nm will appear when the reaction of the photosensitive group is completed. Accordingly, the interaction of PVPy and carboxyl will affect the changes of the absorption peak of the photosensitive double bond. So the real conversion ratio of the double bond will be higher than 50%.

The photoreaction of the cinnamic acid side groups proceeds axis-selectively (*5, 21*). Figure 6 shows the polarised UV–visible absorption spectra of a 10-bilayer film of PVPy/PCA irradiated with LPUVL for 10 min. The polarised absorbance $A_{\perp}$ ($A_{//}$) was measured with a probing UV–visible light polarised perpendicular (parallel) to the polarisation direction of the LPUVL. Prior to the LPUVL irradiation, the absorption was isotropic ($A_0=A_{\perp}=A_{//}$). After the irradiation, the intensity of the band at 300 nm decreased with the irradiation of LPUVL, and a variation in the absorbance was observed between $A_{\perp}$ and $A_{//}$. The result indicated that the cinnamoyl groups positioned parallel to the polarisation of the LPUVL ($A_{//}$) were consumed more rapidly by photoreaction than those positioned perpendicular to the polarisation direction of LPUVL ($A_{\perp}$). This selective photoreaction induced the anisotropy of the multilayer film, which might possibly generate the homogeneous alignment of LCs.

The optical anisotropy is expressed here by the UV dichroic ratio [$\mathrm{DR}=(A_{\perp}-A_{//})/(A_{\perp}+A_{//})$]. As shown in Figure 7, the UV dichroic ratio was measured at different irradiation times. With increasing irradiation time, the dichroic ratio increased rapidly to a maximum at 10 min and then decreased. The dichroic ratio reached 0.12, which is larger than that of a spin-coated photoalignment film. This could be reasonably explained by assuming a possible mechanism: the preferred depletion of cinnamic acid side chains parallel to the LPUVL (*5*). At the beginning of the irradiation, those cinnamoyl chromophores in the cinnamic acid side chains which were parallel to the polarisation direction of LPUVL started to be cross-linked. The chromophores with off-axis transition moments would be hardly affected at first. 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 a gradual reduction in the dichroic ratio.

3.3. *Driving force for PVPy/PCA multilayer fabrication*

FT-IR was employed to characterise the interaction between two neighbouring polymers in the LBL film. Figure 8 shows the FT-IR spectra of the 50-bilayer

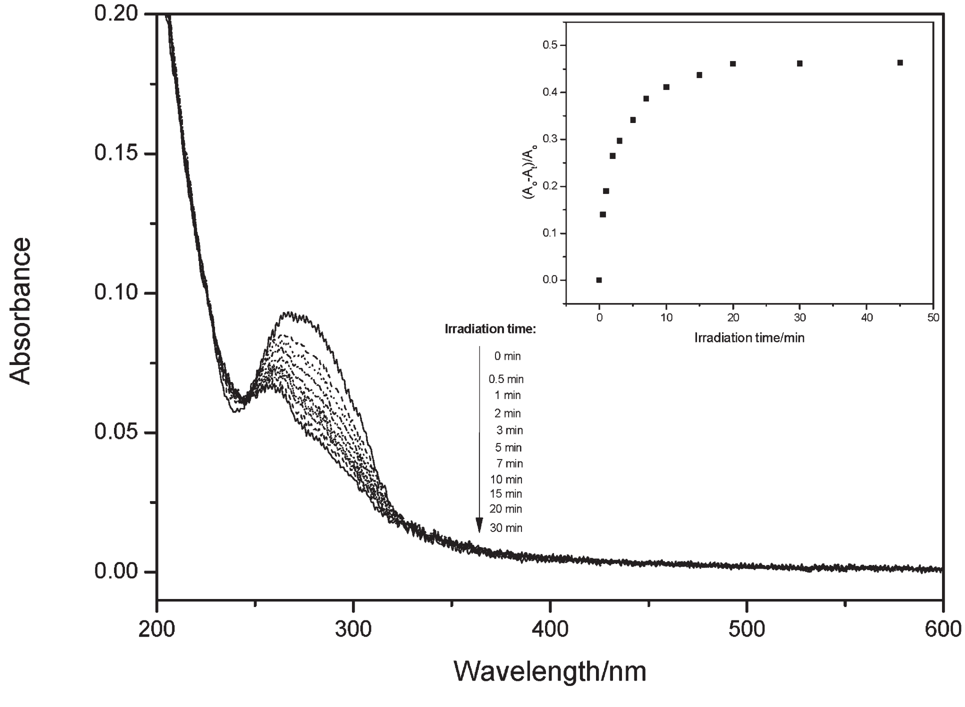

Figure 5. UV–visible spectra of a 10-bilayer PVPy/PCA film irradiated with LPUVL.

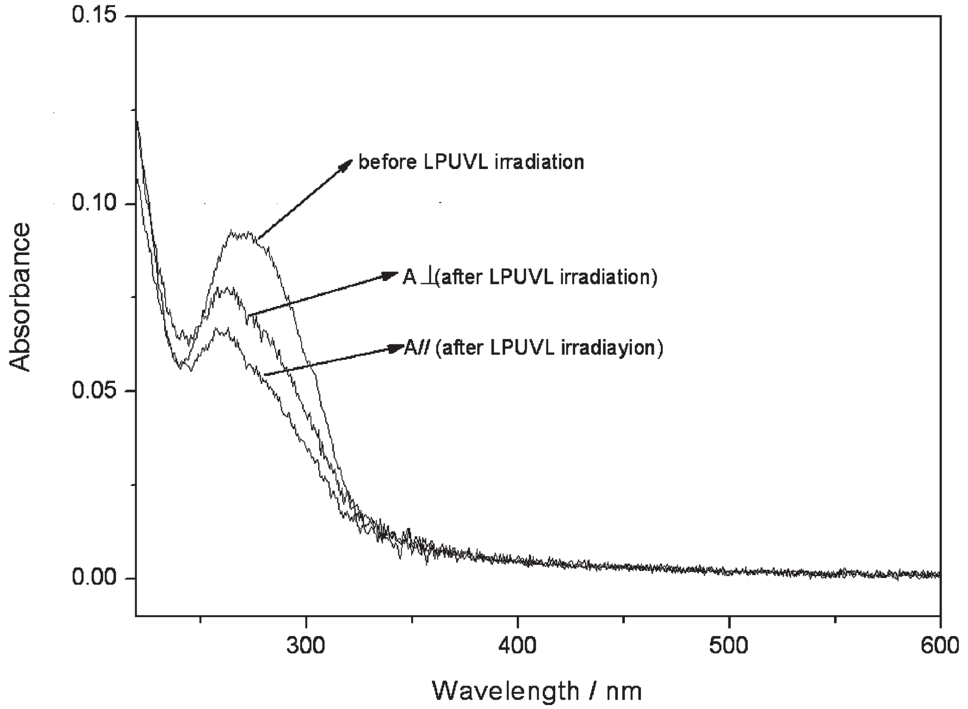

Figure 6. Polarised UV–visible absorption spectra of 10-bilayer film of PVPy/PCA irradiated with LPUVL for 10 min.

PVPy/PCA film recorded at room temperature. In Figure 8, we can clearly find that an O–H stretching vibration appears at 2530 and 1945 cm^{-1}, indicating a strong hydrogen-bonding between the carboxylic acid of PCA and the pyridine groups of PVPy (*22, 23*). Furthermore, in the region from 1660 to 1110 cm^{-1} in the FT-IR spectrum of the PVPy/PCA multilayer film, the absorption peaks could be assigned to the ring vibration of PVPy and PCA, no change in position was observed in comparison with pure PVPy and pure PCA. These results provide further evidence that the multilayer film is assembled via hydrogen bond.

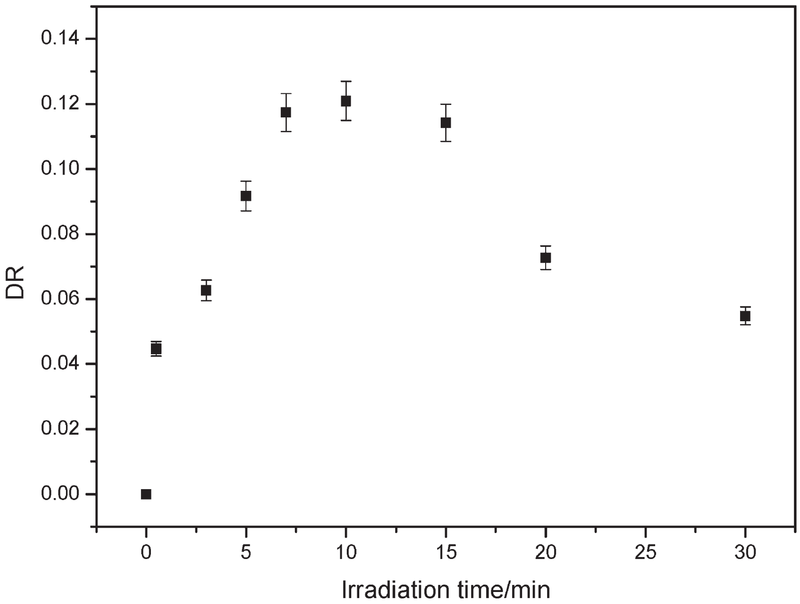

Figure 7. Changes in dichroic ratio (DR) at 300 nm of a 10-bilayer LBL multilayer film irradiated with LPUVL as a function of the irradiation time.

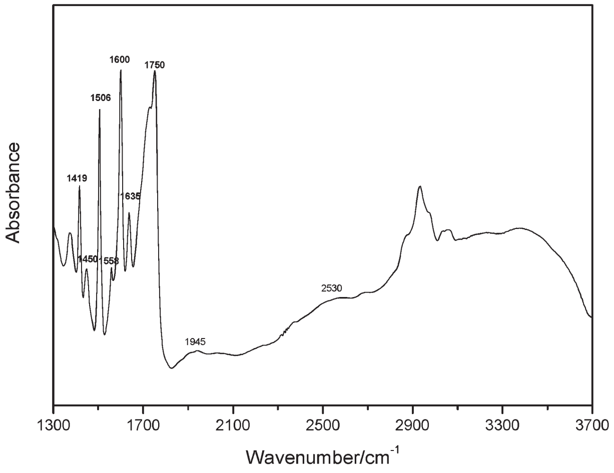

Figure 8. FT-IR spectrum of a 50-bilayer PCA/PVPy film on a PEI-modified CaF_2 plate.

3.4. Photoalignment properties of the LBL multilayer film

A uniform homogeneous alignment of the LC molecules in the parallel cell modified by the irradiated hydrogen-directed ultrathin film could be obtained under optimised cell fabrication conditions. Figure 9(a) and (b) shows the micrographs of a parallel LC cell with the 6-bilayer LBL multilayer film irradiated for 10 min by LPUVL. Figure 9(a) is the dark state when one of the crossed polarisers was parallel to the optical axis of the sample; Figure 9(b) is the bright state when the two crossed polarisers are kept at 45° to the optical axis of the sample. The micrographs of the dark and bright states contained few defects, 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 angular transmittance intensity of the LC cell under polarising microscopy with four-, six- and eight-bilayer multilayer films. The contrast ratio (T_{max}/T_{min}) increased with increasing number of bilayers. The reason for this is as follows: when the number of the bilayers increased, the assembled polymer molecular covered underlying defects, and made the film more homogenous (*8*). Therefore, with the number of bilayers increasing, the alignment performance of multilayer film became uniform, and the contrast ratio increased. As we have proved when the number of the multilayer film reaches 20 (*16*), the alignment effect of LC cell was good, few defects could be found. After this, there was not obviously of improvement in the alignment effect with an increasing number of bilayers.

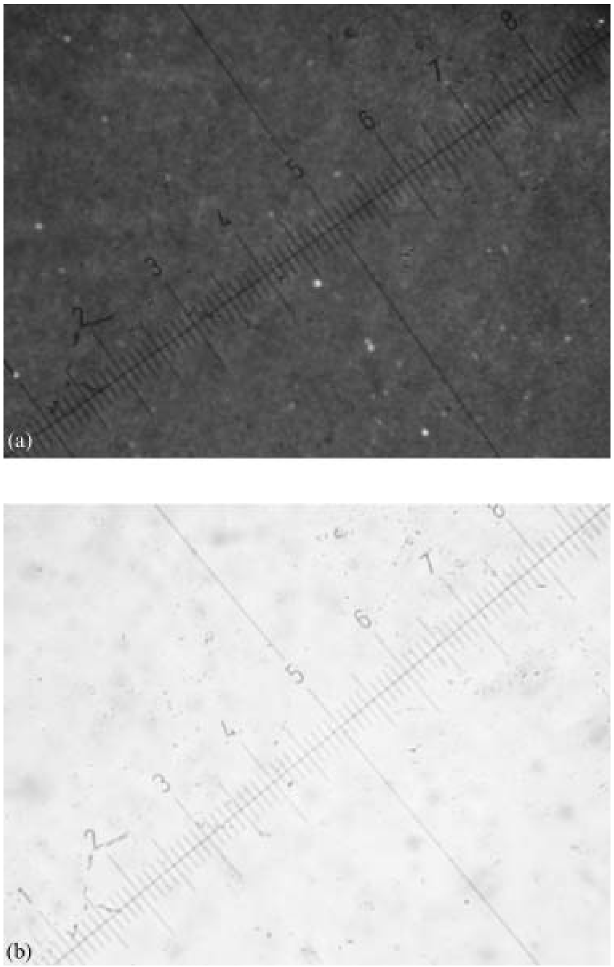

Figure 9. Photograph of (a) dark and (b) bright states of a LC cell under polarised microscopy.

The LC alignment direction can be determined by polarised FT-IR spectroscopy. An IR polariser and LC 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 2231 cm^{-1} was clearly located and the IR vibration direction of the nitrile group is the same as the alignment direction of 5CB. Figure 11 illustrates the angular absorption intensity of the 2231 cm^{-1} peak by the hydrogen-bonding-directed ultrathin alignment film. The arrow in Figure 11 indicates the polarised direction of LPUVL. It indicates that the alignment direction of LC molecules is perpendicular to polarised direction of the LPUVL.

Thermal stability is another important factor for LCDs, and was measured as follows: the LC 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 cooled as before.

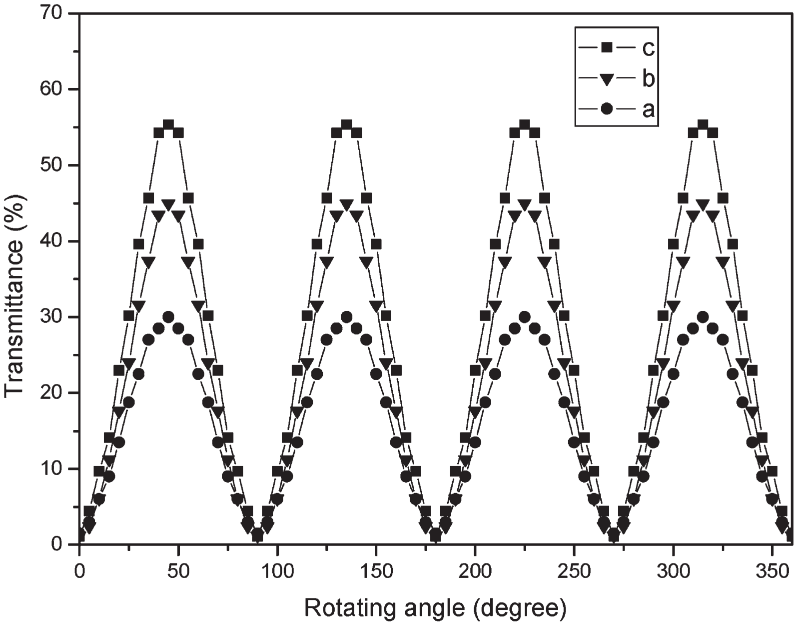

Figure 10. Angular transmittance intensity of a LC cell under crossed polarisers with different numbers of bilayers: (a) four bilayers; (b) six bilayers; and (c) eight bilayers.

We discovered that even when the temperature reached 100°C, the cells could maintain good homogeneous alignment as before.

4. Conclusion

In this paper, the photosensitive hydrogen donor containing cinnamoyl group (PCA) was self-assembled with a hydrogen accepter (PVPy) in an organic solvent to form a new type of hydrogen-bonding-directed ultrathin photoalignment film. Its deposition procedure was uniform and suitable for a photoalignment film, which was proved by UV–visible spectra. After irradiation under LPUVL, the LBL film became anisotropic. The DR of the film increased in the early stages of LPUVL irradiation, then decreased over a long time. Under optimal irradiation conditions, the LBL photoalignment film could align nematic LCs homogeneously. It was also found that the alignment performances of the multilayer film were affected by the number of bilayers. With the increment of bilayers the alignment performance of the multilayer film was enhanced, and the contrast ratio became higher. The hydrogen-bonding-directed formation of a photochromic multilayer films opened the way to prepare photoalignment layers using non-ionic and water-insoluble polymers instead of water-soluble polyelectrolytes, and are a very promising photoalignment technique.

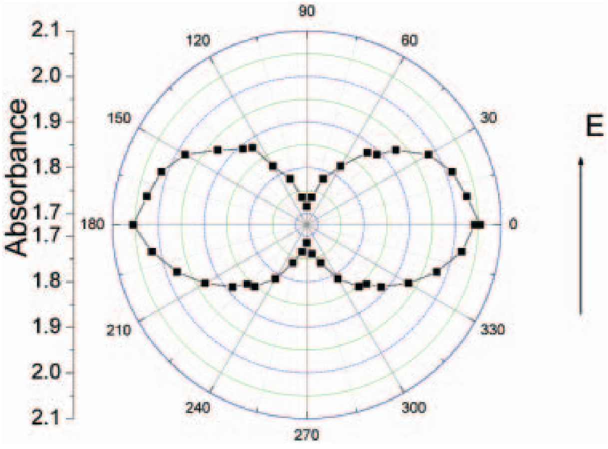

Figure 11. Polar diagrams of the infrared polarised absorption by a LC cell fabricated by a hydrogen bond, as a function of the angle of rotation of the LC cell. (the arrow line is the polarised direction of the LPUVL).

Acknowledgments

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References

(1) Gibbons W.; Shannon P.; Sun S.T.; Swetlin B. *Nature* **1991**, *351*, 49.

(2) Dyadyusha A.G.; Marusii T.Y.; Reznikov Y.A.; Reshetnyak V.Y.; Khizhnyak A.I. *JETP Lett.* **1992**, *56*, 17.

(3) Ichimura K.; Suzuki Y.; Seki T.; Hosoki A.; Aoki K. *Langmuir* **1988**, *4*, 1214.
(4) Ichimura K. *Chem. Rev.* **2000**, *100*, 1847.
(5) Schadt M.; Schmitt K.; Kozinkov V.; Chigrinov V. *Japan. J. Appl. Phys.* **1992**, *31*, 2155.
(6) Wang Y.H.; Xu C.Y.; Kanazawa A.; Shiono T.; Ikeda T.; Matsuki Y.; Takeuchi Y. *J. Appl. Phys.* **1998**, *84*, 181.
(7) Seki T.; Ichimura K.; Fukuda R.I.; Tanigaki T.; Tamaki T. *Macromolecules* **1996**, *29*, 892.
(8) Decher G. *Science* **1997**, *277*, 1232.
(9) Ulman A. *Chem. Rev.* **1996**, *96*, 1533.
(10) Bertrand P.; Jonas A.; Laschewsky A.; Legras R. *Macromol. Rapid Commun.* **2000**, *21*, 319.
(11) Decher G.; Hong J.D.; Schmidt J. *Thin Solid Films* **1992**, *210–211*, 831.
(12) Wang L.Y.; Wang Z.Q.; Zhang X. *Macromol. Rapid Commun.* **1997**, *18*, 509.
(13) Stockton W.B.; Rubner M.F. *Macromolecules* **1997**, *30*, 2717.
(14) Park M.K.; Advincula R.C. *Langmuir* **2002**, *18*, 4532.
(15) Peng Z.H.; Xuan L. *Liq. Cryst.* **2005**, *32*, 239.
(16) Zhang L.L.; Peng Z.H.; Yao L.S.; Fei C.H.; Lv F.Z.; Xuan L. *Appl. Surf. Sci.* **2007**, *253*, 3372.
(17) Haller I. *J. Am. Chem. Soc.* **1978**, *100*, 8050.
(18) Uchida E.; Kawatsuki N. *Macromolecules* **2006**, *39*, 9357.
(19) Egerton P.L.; Pitts E.; Reisner A. *Macromolecules* **1981**, *14*, 95.
(20) Mao G.; Tsao Y.; Tirrell M.; Davis H.T.; Hessel V.; Ringsdorf H. *Langmuir* **1993**, *9*, 3461.
(21) Kawatsuki N.; Ono H.; Takatsuka H.; Yamamoto T.; Sangen O. *Macromolecules* **1997**, *30*, 6680.
(22) Katim T.; Kihara H.; Uryu T.; Fujishims A.; Frechet J.M.J. *Macromolecules* **1992**, *25*, 6838.
(23) Kumar U.; Kato T.; Frechet J.M.J. *J. Am. Chem. Soc.* **1992**, *114*, 6630.