

Photoalignment of liquid crystals by cinnamate polyelectrolyte layer-by-layer ultrathin film

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Abstract

In this paper, a new layer-by-layer (LBL) ultrathin film with photosensitive cinnamoyl chromophores was prepared. It could induce uniform alignment of liquid crystals (LC) after irradiated by linearly polarized ultraviolet (LPUV) light. First, a photosensitive polycation containing cinnamoyl side groups was synthesized. Then a layer-by-layer ultrathin film was prepared in an aqueous solution of the polycations and poly (sodium 4-styrenesulphonate). The spectra of UV–vis absorption and ellipsometric measurement showed that the LBL film was uniform and suitable for the photoalignment of LC. When the film was irradiated by LPUV light, the cinnamoyl units in the film underwent [2 + 2] cycloaddition along the electric vector direction of the LPUV light. The polarized UV–vis spectra also proved that the film was anisotropic, and then the film could induce the homogeneous alignment of nematic LC. With the number of bilayers increasing, the alignment effect of multilayer film became better, and the contrast ratio became higher.

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1. Introduction

In recent years, the photoalignment technique of liquid crystals (LC) has gained great attention as a non-contact alignment method that overcame the shortcomings of the rubbing method, such as dust generation, electrostatic problems, and failures of thin-film transistors [1–3]. It was found in 1988 by Ichimura et al. that photoinduced nematic LC orientation between perpendicular and parallel states was made for the first time by a monolayer on quartz. In this way, the molecular and polymeric films, with the capability to control the orientation of LC, were referred to as “command surface” [4]. Since then, more studies have been carried out on the “command surface” focused on two different aspects: photoreaction materials and fabrication technique.

During the past 20 years, a lot of work has been done on different photoreaction materials, which could be reorientation in a proper direction by linearly polarized ultraviolet (LPUV) light exposure. The materials commonly belonged to three major categories. The first involved azobenzenes [4] and stilbenes, which could undergo *e/z* photoisomerization. Materials of the second category underwent [2 + 2] photocyclization, for example cinnamates [5] and coumarins [2]. The third category was polyimides [6], which could be degraded by LPUV light. Among these materials, the photocyclization materials were more suitable for the permanent alignment of liquid crystal displays due to their thermal and optical stability [1]. There were many ways for the fabrication of “command surface”, spin-coating method [5], Langmuir–Blodgett (LB) method [7] and self assembled monolayers (SAMs) [4]. In conventional photoalignment technology, spin-coating method was adopted to prepare “command surface” because of practical reasons. In this way, the photoreaction molecules were isotropic in the film. So the photoreaction ratio of the

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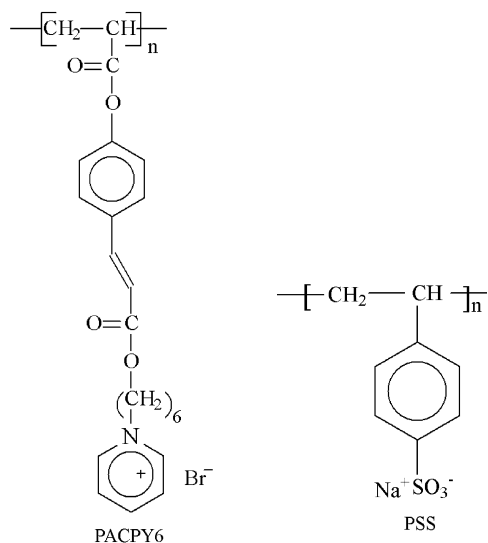


Fig. 1. Chemical structures of poly{4-acryloyloxycinnamic acid (6-pyridinium-*N*-ylundecyl-ester) bromide} (PACPY6) and poly (sodium 4-styrenesulphonate) (PSS).

photosensitive units was very low. However, LB film and SAMs, all could form an ordered reorganizing film, in which the molecules were oriented and the photoreaction could perform easily, it benefited for the alignment of LC. But the depositions of these two methods were tedious and were not adaptable for large-scale application. Also, the orientation parameters in LB films suppressed selective photoalignment. In the early 1990s, the fabrication of ultrathin molecular film by alternate electrostatic adsorption or layer-by-layer (LBL)

deposition of oppositely charged polyelectrolyte from solution has been reported by Decher et al. [8,9]. The LBL ultrathin film was also an ordered reorganizing system, and fabrication of LBL film was very simple, easy to automate and could be adapted to large-scale application. So it has attracted more and more attentions of many researchers [8,10,11]. In 2002, Park and Advincula prepared photochromic azobenzene polymer ultrathin films using the LBL approach and first used the LBL polyelectrolyte films for in-plane photoalignment of LC [12]. The photoalignment effect was excellent. However, the photoalignment of LBL ultrathin film with cinnamoyl groups have rarely been investigated.

In this work, a new LBL polyelectrolyte film with cinnamoyl units was prepared for photoalignment studies. A photosensitive polycation (PACPY6) containing cinnamoyl side groups was synthesized, and then a LBL self-assembled deposition multilayer film was prepared in aqueous solution of PACPY6 and poly (sodium 4-styrenesulphonate) (PSS) (Fig. 1). After irradiation with LPUV light, anisotropy was generated, this was proved by the UV–vis absorption measurement. It was found that the anisotropic LBL film could induce homogeneous alignment of LC.

2. Experimental

2.1. Synthesis

PSS ($M_w \approx 70,000$, 30 wt% aq.) was purchased from Aldrich Co. It was used without further purification. The polycation PACPY6 was synthesized in six steps (Fig. 2).

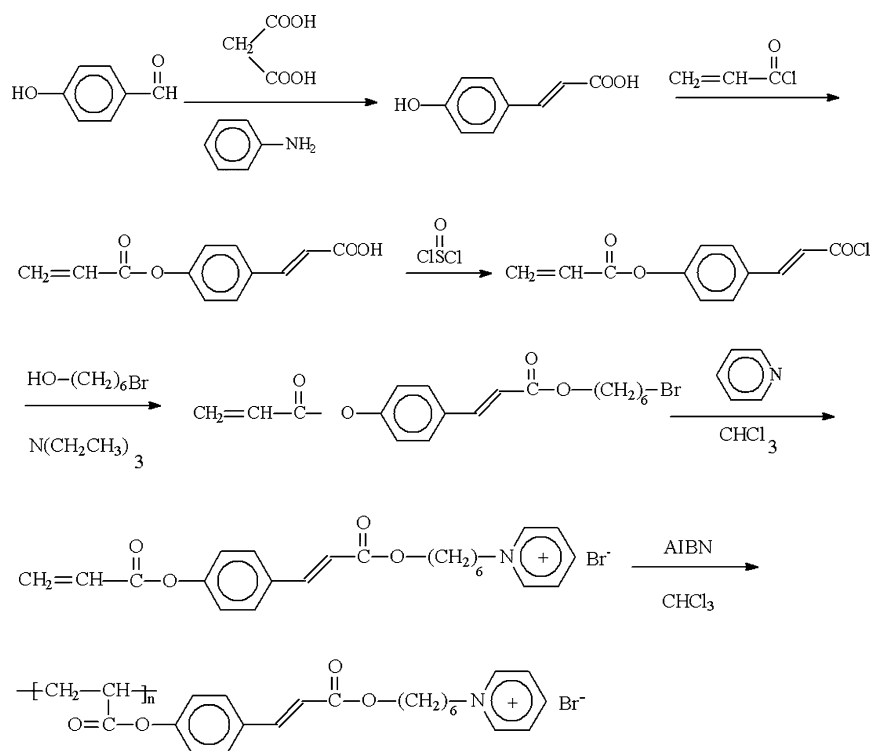


Fig. 2. Synthesis of the polycation (PACPY6).

2.1.1. 4-Hydroxycinnamic acid (I)

4-Hydroxybenzaldehyde (12.2 g, 0.1 mol) and malonic acid (10.4 g, 0.1 mol) were dissolved in pyridine (20 mL); aniline (1 mL) was added as catalyst. The solution was stirred at 90 °C, and carbon dioxide was generated as a by-product. When solution stopped producing gas, it was poured into 250 mL 1 M hydrochloric acid. A large quantity of yellow precipitate was generated; the product I was obtained by filtration. The crude product was recrystallized in the mixed solution of alcohol and water. Yield: 70%, mp: 214 °C. FTIR (powder, KBr, cm^{-1}): 979(=CH, δ), 1605(C=C, ν), 1674(C=O, ν), 3025(=CH, ν), 3383(O-H, ν).

2.1.2. 4-Acryloyloxycinnamic acid (II)

To a well-stirred solution of compound I (13.12 g, 0.08 mol) and NaOH (6.4 g, 0.16 mol) in 40 mL of water and 40 mL dioxane was added dropwise 0.12 mol of acryloyl chloride at 10–15 °C. After stirring at room temperature for 4 h, the reaction mixture was neutralized with dilute HCl aq. The solid 4-acryloyloxycinnamic acid thus precipitated was filtered, washed with warm water, dilute HCl and water, successively. The crude product was purified via column chromatography. THF was used as the solvent. Yield: 65%, mp: 186 °C. FTIR (powder, KBr, cm^{-1}): 979(=CH, δ), 1169(C–O, ν), 1628(C=O, ν), 1688(C=O, ν), 3025(=CH, ν).

2.1.3. 4-Acryloyloxycinnamic acid chloride (III)

Compound II (10.9 g, 0.05 mol) was refluxed with 50 mL of thionylchloride (freshly distilled) in presence of a trace amount of dimethylformamide for 6 h. And then the excess of thionylchloride was removed by vacuum distillation. The product was recrystallized from CH_2Cl_2 . Yield: 60%, mp: 156 °C. FTIR (powder, KBr, cm^{-1}): 975(=CH, δ), 1145(C–O, ν), 1628(C=C, ν), 1741(C=O, ν), 3023(=CH, ν).

2.1.4. 4-Acryloyloxycinnamic acid (6-bromoundecyl ester) (IV)

In a 250 mL flask, 6-bromo-1-octanol (3.62 g, 0.02 mol) and triethylamine (2.222 g, 0.022 mol) were dissolved in 100 mL of THF, and the contents were cooled to 0–5 °C. Then, the compound III (5.2 g, 0.022 mol) in 80 mL THF was added dropwise with stirring at the same temperature. After stirring at room temperature for 3 h, the precipitated triethylamine-hydrochloride was filtered off. The solvent of the organic solution was removed by vacuum distillation, and the crude product was purified via flash chromatography. The mixture of chloroform and petroleum ether was used as the solvent. Yield: 30%, mp: 131 °C. FTIR (powder, KBr, cm^{-1}): 645(C–Br, ν), 986(=CH, δ), 1144(C–O, ν), 1741(C=O, ν), 2928(CH_2 , ν), 3042(CH_2 , ν).

2.1.5. 4-Acryloyloxycinnamic acid (6-pyridinium-N-ylundecyl-ester) bromide (V) (ACPYP6)

The ester (IV) (1.5 g) and pyridine (3 mL) were stirred in 30 mL chloroform at 60 °C for 48 h. The mixture then was poured into 300 mL of dry ether. The light yellow product (V) was filtered off and recrystallized in dry ether. Yield: 70%, mp:

267 °C. FTIR (powder, KBr, cm^{-1}): 991(=CH, δ), 1143(C–O, ν), 1634(C=C, ν), 1723(C=O, ν), 2920(CH_2 , ν), 3063(CH_2 , ν).

2.1.6. Poly(4-acryloyloxycinnamic acid (6-pyridinium-N-ylundecyl-ester) bromide) (VI) (PACPYP6)

The compound V (1 g) was polymerized in 20 mL chloroform and using 0.01 g AIBN as the initiation at 65 °C under nitrogen atmosphere. The polymers were isolated after 12 h of polymerization time by adding the reaction solution to excess of alcohol, purified by reprecipitation from chloroform solution into alcohol. Finally, the product was vacuum dried. Yield: 50%. T_g : 107 °C. FTIR (powder, KBr, cm^{-1}): 1167(C–O, ν), 1741(C=O, ν), 2927(CH_2 , ν), 3071(CH_2 , ν).

2.2. Film fabrication

Clean quartz substrates were immersed in piranha solution ($\nu/\nu = 1:3$. 30% H_2O_2 :98% H_2SO_4) for 1 h, then carefully washed with deionized water and dried, after that treated them with a solution of aminopropyltriethoxysilane (Aldrich Co.) in xylene, and rinsed successively with toluene, ethanol and deionized water. Last, the substrates were soaked in 0.1 M HCl solution to render a positively charged surface. The electrostatic LBL deposition on substrates was done using well-reported procedures [9]. The substrates were immersed in aqueous solution of PSS (1.0 mg/mL) and PACPY6 (1.0 mg/mL) for 20 min alternately, with deionized water rinsing and nitrogen gas blown drying for each time. The last deposition was always done with PACPY6.

2.3. Cell fabrication

First the polyelectrolyte deposited substrates were illuminated by LPUV light, with perpendicular to the incident light path. Then parallel LC cell was fabricated and the cell gap was 20 μm . The commercial liquid crystal material TEB30A (Slichem Co., China, $T_c = 61$ °C) was injected into the cell at 70 °C and then the cell was cooled to the room temperature slowly, to remove any flow-induced memory that have been induced by the LC injection process.

2.4. Instrumentation and measurement

LPUV light was obtained from a 300 W Hg–Xe lamp system with an optical filter at 300 nm (Model 53370, Oriel Co.) and a Glan-Talor lens. The intensity of LPUV light on the surface of the film was 0.95 mW/cm^2 ($\lambda = 297$ nm). UV–vis absorption spectra of the LBL multilayer films were obtained using Shimadzu UV-3101PC spectrophotometer. Polarized UV–vis absorption spectra were measured by using special polarizing accessories. The ellipsometric measurements were carried out with Jobin Yvon's UVISEL ellipsometer (240–830 nm, 70° incidence angle). IR spectra were recorded with a Bio-Rad FTS3000 spectrophotometer equipped. Polarizing microscopy (FOIC-2, China) with a digital camera was used to evaluate the alignment quality of the liquid crystal and to measure the transmittance, the polarizing directions of the two microscopy polarizers were crossed.

3. Results and discussion

3.1. LBL Multilayer Film Formation

The layer-by-layer deposition of the polyelectrolyte pair layers was investigated by UV–vis absorption spectroscopic and ellipsometric measurements. Fig. 3 shows the UV–vis absorption spectra of PSS/PACPY6 films on quartz substrate with increasing number of bilayers. The absorption spectra displayed two broad bands centered at 293 and 225 nm. The band at 293 nm was due to the π – π^* transition of double bond conjugated with the phenyl group in PACPY6. The band at 225 nm arose from the absorption of the phenyl group in PSS [11]. The linear increase of the two bands with the number of bilayers clearly indicated the regular growth of the PSS/PACPY6 layers. Ellipsometric measurement was carried out to provide information of film thickness. The average thickness was 1.5 nm/bilayer when the concentration of PSS/PACPY6 was 1 mg/mL. Fig. 4 shows that the film thickness increased in portion to the number of bilayers. The fact that the linear absorbance and thickness increase were observed for each deposition cycle indicated a quantified adsorption of polyelectrolyte. And seen by the naked eye, the PSS/PACPY6 LBL films were clear, transparent and uniform, with good optical quality. In summary, the characterization of the LBL ultrathin film indicated the uniform multilayer suitable for photoalignment studies.

3.2. Photoreaction in the films

The LBL multilayer film that has one cinnamoyl moiety per chemical repeat unit in the side chains in the polycation was exposed to LPUV light and then examined by UV–vis spectroscopy in order to analyze the photoreaction procedure in the film in detail.

Fig. 5 shows the UV–vis spectra of a LPUV light irradiated 50-layer film of PSS/PACPY6 on a quartz substrate with the

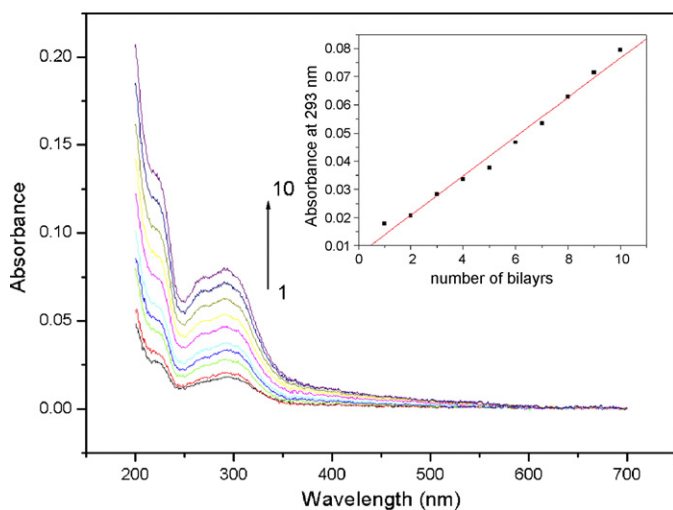


Fig. 3. UV–vis absorption spectra of PSS/PACPY6 films on quartz substrate with increasing number of bilayers. The inset diagram showed the increase of absorbance at 293 nm with the number of bilayers.

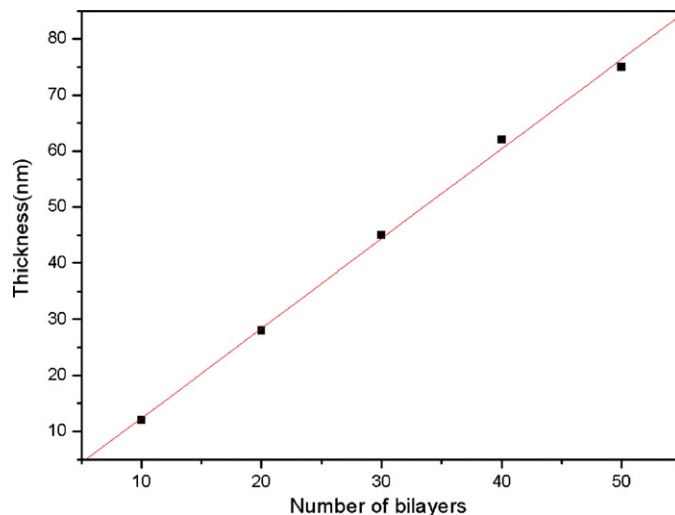


Fig. 4. The film thickness depended on the number of bilayers.

irradiation time from 0 to 100 min. The intensity of the band at 293 nm decreased rapidly with increasing irradiation time, which indicated that the photosensitive double bonds (the double bond conjugated with the phenyl group in PACPY6) were consumed. The band intensity decreased abruptly at the forefront of photoreaction. There was an isobestic point at 249 nm in Fig. 5 with increasing irradiation time. Further irradiation of LPUV light brought about spectral changes with gradual decrease in absorbance at 293 nm, accompanied by deviation from the isobestic point. The former research indicated that two photoreaction pathways were available for cinnamate groups when irradiated by LPUV light: photocyclization and photoisomerization [13]. The product distribution of cinnamate moieties could be estimated from the absorption spectral changes [14,15]. The inset of Fig. 5 illustrated the chemical distribution of cinnamate moieties in the ultrathin film. The photocyclized formation took place

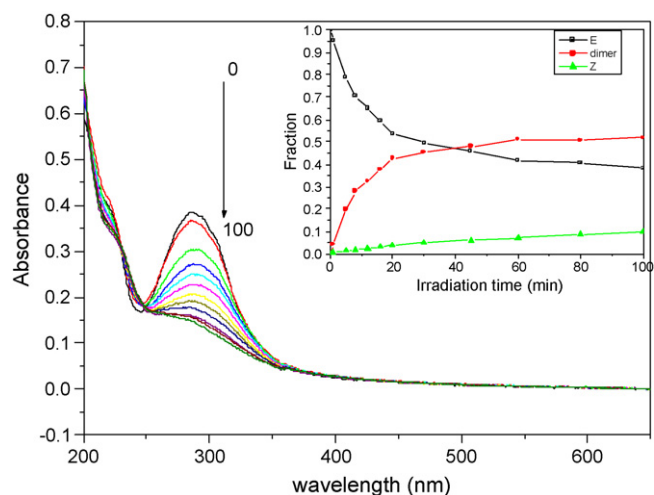


Fig. 5. UV–vis spectra of a 50-bilayers PSS/PACPY6 film irradiated with LPUV light. The inset also showed changes of fractions of E (\square) and Z (\triangle) and photodimers (\bullet) of cinnamates as the function of the LPUV light irradiation time of the 50-bilayers PSS/PACPY6 film.

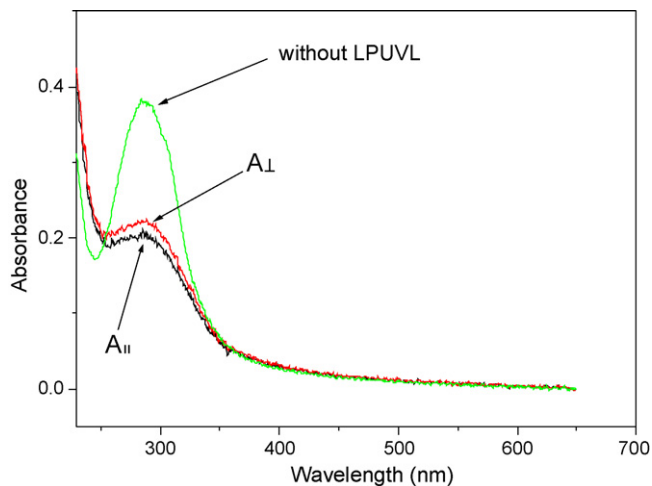


Fig. 6. Polarized UV-vis absorption spectra of 50-bilayer film of PSS/PACPY6 irradiated with LPUV light for 20 min.

predominantly at the forefront of photoreaction, whereas the photoisomerization only reached 2% with the 10 min irradiation. When exposure time reached 100 min, there were 53% of the photocyclization and 10% of the photoisomerization. So it would lead to the photoisomerization prolonged LPUV light irradiation. However, the photocyclization also played the most important role in the reaction in the LBL multilayer films. When irradiated with LPUV light, the photocyclization occurred along the direction of the polarization of LPUV light, which generated anisotropy at the interface of the film.

Fig. 6 shows polarized UV-vis absorption spectra of 50-bilayer film of PSS/PACPY6 irradiated with LPUV light for 20 min. The polarized absorbance A_{\perp} (A_{\parallel}) was measured with the polarized UV-vis spectra light polarized perpendicular (parallel) to the polarization direction of the LPUV light. After the irradiation, a difference in the absorbance was observed between A_{\perp} (A_{\parallel}). The result indicated that the cinnamoyl groups positioned parallel to the polarization of the LPUV light

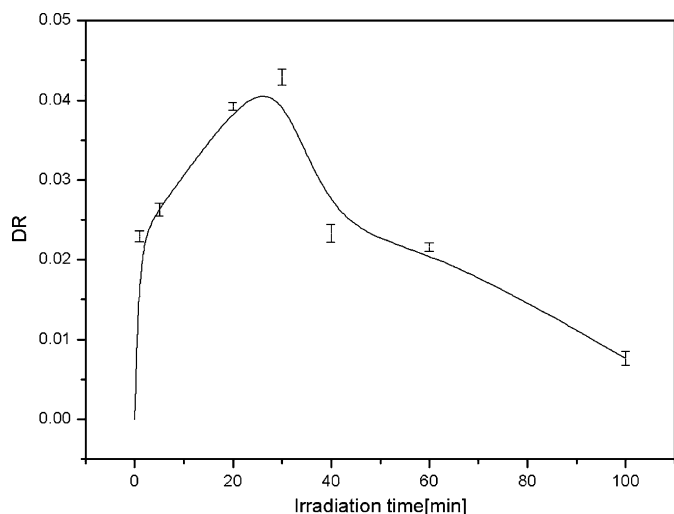


Fig. 7. Change in dichroic ratio (DR) at 293 nm of a 10 bilayer LBL multilayer film irradiated with LPUV light as a function of the irradiation time.

(A_{\parallel}) were consumed more rapidly by photoreaction than those positioned perpendicular to the polarization direction of LPUV light (A_{\perp}). This selective photoreaction induced the anisotropy of the multilayer film, which might possibly generate the homogeneous alignment of LC.

As shown in Fig. 7, the UV dichroic ratio [DR = $(A_{\perp} - A_{\parallel}) / (A_{\perp} + A_{\parallel})$] was a function of irradiation time (the polarized absorbance A_{\perp} (A_{\parallel}) was monitored at 293 nm). The DR value of the LBL multilayer film first increased rapidly and then decreased. The phenomenon could be explained by assuming a single mechanism. At the beginning of irradiation, those cinnamoyl chromophores of the parallel direction in the film were cross-linked. This process led to the observed initial increase of DR. But a competing mechanism would cause DR to decrease with irradiation time, which was the photodecomposition of cyclobutene derivatives. In the first, the velocity of photocyclization was greater than photodecomposition, so the DR increased. However, with increasing of the irradiation time, the quantity of cyclobutene derivatives increased. While the velocity of photodecomposition exceeded the rate of photocyclization, the DR decreased. Peng and Xuan also have reported the similar result [16]. From Fig. 7, it was found that

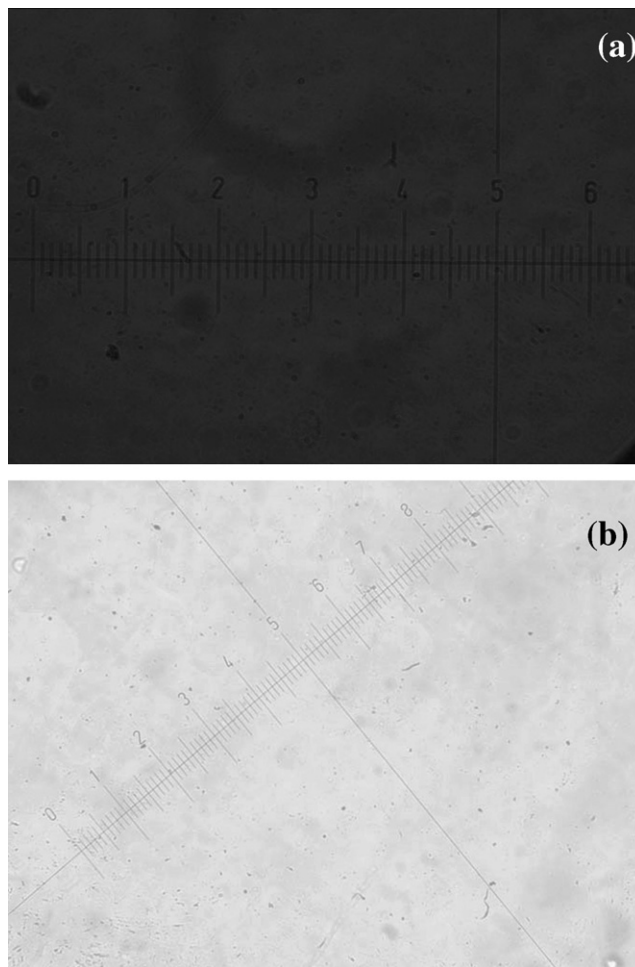


Fig. 8. Polarizing microscopy texture for a homogeneously aligned nematic LC cell prepared by the 8-bilayers LBL photoalignment film. The time of irradiation was 25 min: (a) dark state and (b) bright state.

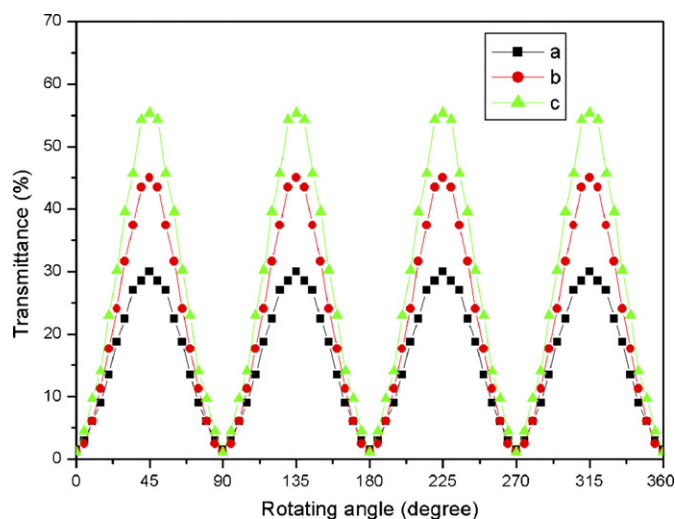


Fig. 9. Angular transmittance intensity of a LC cell under crossed polarizers with different number of bilayers: (a) 6 bilayers, (b) 8 bilayers and (c) 10 bilayers.

the largest DR could be achieved at 25 min irradiation. So an irradiation time of 25 min was selected for photoalignment film fabrications.

3.3. The photoalignment properties of the LBL multilayer film

A uniform homogeneous alignment of the LC molecules in the parallel cell modified by the irradiated LBL multilayer film could be obtained under optimized cell fabrication conditions. Fig. 8(a and b) shows the micrographs of a parallel LC cell with the 8-bilayer LBL multilayer film irradiated for 25 min by LPUV light. Fig. 8(a) was the dark state when one of the crossed polarizers was parallel to the optical axis of the sample; Fig. 8(b) was the bright state when the two crossed polarizers were kept at 45 °C to the optical axis of the sample. The micrographs of the dark and bright states contained few defects and disclinations, indicating that excellent homogenous alignment was obtained.

Fig. 9 shows angular transmittance intensity of a LC cell under polarizing microscopy with 6, 8, 10-bilayer multilayer films. The contrast ratio (T_{\max}/T_{\min}) increased with increasing number of bilayers. The reason was described as follow, when the bilayer number increased, the polyelectrolyte covered underlying defects, and made the film more homogenous [9]. Therefore, with the number of bilayers increasing, the alignment performance of multilayer film became uniform, and the contrast ratio increased. When the number of the multilayer film reaches 20, the alignment effect of LC cell was good, defects hardly could be found. And after that, there were not evident improvement of the alignment effect with increasing of the number of bilayers.

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 100 °C the cells could maintain good homogeneous alignment as before.

4. Conclusion

In this work, a photosensitive PACPY6/PSS self-assemble multilayer film was used for inducing LC alignment. The LBL multilayer film was prepared from a photosensitive polycation PACPY6 and polyanion PSS. Its deposition procedure was uniform and suitable for photoalignment film, which was proved by UV–vis spectra and ellipsometric measurement. After irradiation under LPUV light, the LBL film became anisotropic. And the DR of the film increased in the early stages of LPUV irradiation, then decreased upon long time. In optimal irradiation conditions, the LBL photoalignment film could align nematic LC homogeneously. It was also found that the number of bilayers affected the alignment performance of the multilayer film. With the number of bilayers increasing, the alignment performance of multilayer film became better, and the contrast ratio became higher.

Acknowledgements

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