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A novel liquid crystals photoalignment layer-by-layer self-assembled film fabricated with long side-chain cinnamate polyelectrolyte

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A novel photoalignment film for liquid crystals (LC) was prepared based on layer-by-layer self-assembly of photosensitive long side-chain cinnamate polyelectrolyte. A series of self-assembled films with different methylene spacer groups was prepared and used as alignment film. The film became anisotropic, and could induce uniform alignment of LC after irradiation by linearly polarised ultraviolet light (LPUVL). The effects of spacer chain lengths of the cinnamoyl polycations on the structure and photoalignment properties of the self-assembled film were studied. The polycation films with longer spacer chain obtained a larger dichroic ratio after LPUVL irradiation. The contrast ratio ($T_{\text{max}}/T_{\text{min}}$) of the LC cell increased with spacer chain length increase. However, it was found that the thermal stability of PSS/PACPY\textit{n} films decreased with increasing chain length of polycation.

**Keywords:** LBL ultrathin film; liquid crystal; photoalignment; polycation

1. Introduction

The photoalignment technique of liquid crystals (LC) has gained great attention as a non-contact alignment method that overcomes the shortcomings of the rubbing method, such as sample contamination, static charge generation, and scratches [1–4]. In conventional photoalignment technology, spin-coated films of cinnamate materials, whose photoaligning mechanism was first described by Schadt \textit{et al.} [2, 4] and differed fundamentally from the azo-photo-alignment process of Ichimura \textit{et al.} [1], have been widely used to fabricate film for investigating alignment properties, which are most suitable for the durable LC photoalignment film because of the irreversible [2+2] photodimerisation of cinnamoyl groups [4–6]. In this film system, the cinnamate polymers are isotropic, which affects the photoreaction of cinnamate and makes the photoreaction ratio lower. Recently, many researchers have focused on the fabrication of ultrathin films by alternate layer-by-layer (LBL) adsorption of polyelectrolytes [7–9]. This is a simple technique, easy to automate and can be adapted to large-scale applications. A large variety of water-soluble polycations can be used. The most important advantage of the LBL method over spin-coated systems is that the concentration and the layer order of the polyelectrolytes in the LBL film can be well characterised, an advantage in optical studies.

In this work, a series of photosensitive cinnamoyl polycations (PACPY\textit{n}) with different methylene spacer groups was synthesised, and the LBL ultrathin films of the polyanion (PSS)/polycation (PACPY\textit{n}) (chemical structures as illustrated in Figure 1) were then prepared for photoalignment studies. The influences of spacer chain lengths of the polycation on the film structure and the photoreaction of the cinnamate have been investigated. We have focused our attention on the changes after linearly polarised ultraviolet light (LPUVL) irradiation and the photoalignment effect of the films.

2. Experimental details

2.1 Materials and synthesis

PSS ($M_w \approx 70000$, 30 wt% aq.), 4-hydroxycinnamic acid, 2-bromo-alcohol, 6-bromo-1-hexanol and 11-bromo-1-undecanol were purchased from Aldrich Co. They were used without further purification. The polycations (PACPY\textit{n}) were synthesised according to the reaction scheme in Figure 2. All reagents were obtained from Shanghai Chemical inc. and used directly. Dry solvents were freshly distilled under anhydrous conditions.

2.1.1 4-acryloyloxycinnamic acid (n-bromoalkyl ester) (ACAE)

4-acryloyloxycinnamic acid (ACA) (shown in Figure 2) was synthesised according to the literature method [10]. ACA (10.9 g, 50 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 N,N-dimethylformamide (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 recrystallised using dry toluene. In a 250 ml flask, 2-bromo-alcohol (20 mmol) and triethylamine (2.222 g, 22 mmol) were dissolved in 100 ml of THF, and cooled to 0–5°C. Then, 4-acryloyloxycinnamic acid chloride (5.2 g, 22 mmol) in 40 ml of 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. A mixture of chloroform and petroleum ether was used as the solvent. Yield: 35%. FTIR (powder, KBr, cm⁻¹): 645(C-Br, v), 740(C-H, δ), 982(=CH, δ), 1163(C-O-C, v), 1212 (C-O-C, v), 1738(C=O, v), 2930 (CH₂, v).

4-acryloyloxycinnamic acid (6-bromohexyl ester): Yield: 30%. FTIR (powder, KBr, cm⁻¹): 645(C-Br, v), 722(C-H, δ), 986(=CH, δ), 1167(C-O-C, v), 1204(C-O-C, v), 1726(C=O, v), 2928(CH₂, v).

4-acryloyloxycinnamic acid (11-bromoundecyl ester): Yield: 32%. FTIR (powder, KBr, cm⁻¹): 645(C-Br, v), 740(C-H, δ), 986(=CH, δ), 1167(C-O-C, v), 1204(C-O-C, v), 1726(C=O, v), 2928(CH₂, v).

2.1.2 Synthesis of 4-acryloyloxycinnamic acid (n-pyridinium-N-ylalkyl-ester) bromide (ACPYN)
The ester (0.004 mol) 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 product (ACPYN) was filtered off and recrystallised in dry ether.
4-acryloyloxy-cinnamic acid (2-pyridinium-N-yethyl-ester) bromide: Yield: 76%. FTIR (powder, KBr, cm\(^{-1}\)): 986(=CH, \(\delta\)), 1166(C-O-C, v), 1716(C=O, v), 2923(CH\(_2\), v).

4-acryloyloxy-cinnamic acid (6-pyridinium-N-yhexyl-ester) bromide: Yield: 70%. FTIR (powder, KBr, cm\(^{-1}\)): 987(=CH, \(\delta\)), 1167(C-O-C, v), 1734(C=O, v), 2923(CH\(_2\), v).

4-acryloyloxy-cinnamic acid (11-pyridinium-N-yundecyl-ester) bromide: Yield: 50%. FTIR (powder, KBr, cm\(^{-1}\)): 987(=CH, \(\delta\)), 1163(C-O-C, v), 1726(C=O, v), 2928(CH\(_2\), v).

2.1.3 Synthesis of poly (4-acryloyloxy-cinnamic acid (n-pyridinium-N-ylalkyl-ester) bromide) (PACPYN)
The compound ACPy\(_n\) (0.002 mol) was polymerised in 20 ml chloroform using 0.01 g AIBN as the initiation at 65\(^\circ\)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, and purified by reprecipitation from chloroform solution into alcohol. Finally the product was vacuum dried.

2.2 LBL deposition
Quartz slides (10 mm \(\times\) 20 mm \(\times\) 1 mm) were used as substrates for the UV-Vis spectroscopy. Indium tin oxide (ITO) glass was used for photoalignment studies. The clean substrates were immersed in piranha solution (v/v = 1:3. 30%H\(_2\)O\(_2\): 98%H\(_2\)SO\(_4\)) for 1 h, then carefully washed with deionised water and dried, then treated with a solution of aminopropyltriethoxysilane (Aldrich Co.) in xylene, and rinsed successively with toluene, ethanol and deionised water. Finally, the substrates were soaked in 0.1 M HCl solution to render a positively charged surface. The prepared substrates were then alternately immersed in aqueous solution of PSS (Aldrich Co.) (1.0 mg/ml) and PACPY2 (1.0 mg/ml) for 20 min each, with rinsing with deionised water and blow drying with nitrogen gas between each deposition, according to well-reported procedures [7]. The final deposition was always done with PACPY2. The PSS/PACPY2 ultrathin film was thus fabricated. The fabrication process for PSS/PACPY6 film and PSS/PACPY11 film was the same.

2.3 Cell fabrication
The polyelectrolyte deposited substrates were illuminated by LPUVL, perpendicular to the incident light path. The anti-parallel LC cell was then fabricated, and the cell gap was 20 \(\mu\)m. The resulting vacant cell was filled with a nematic LC TEB30A (\(T_c = 61^\circ\)C) by capillary action at a temperature above 61\(^\circ\)C, and the cell was then cooled slowly to room temperature, to remove any flow-induced memory that may have been induced by the LC injection process.

2.4 Instrumentation and measurement
The UV exposure system consists of a 300 W Hg-Xe lamp, an optical filter at 300 nm (Model 53370, Oriel Co.) and a Glan-Talor lens. The intensity of LPUVL 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 with a dichroic polariser. FTIR spectra were performed on a Bio-Rad FT3000 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.

3. Results and discussion
3.1 LBL deposition
The LBL deposition of the polyelectrolyte pair layers was investigated by UV-Vis absorption spectroscopy. Figure 3 shows the UV-Vis spectra of the self-assembled 6-bilayer PSS/PACPY\(_n\) (\(n = 2, 6, 11\)) film on the substrates, respectively.

The maximum absorbance was observed at 297 nm for the PSS/PACPY2 film, which belonged to the \(\pi-\pi^*\) transition of the double bond conjugated with the phenyl group of the cinnamoyl group in PACPY2. By extending the spacer chain lengths from...
2 to 6 and 11 carbons, the maximum absorbance was blue-shifted to 293 nm and 287 nm for PSS/PACPY6 and PSS/PACPY11 films, respectively. It should be noted that the extension of the spacer chain length from 2 to 11 carbons caused the change of the aggregate state of cinnamoyl polycation. This may be due to the changed aggregate state of cinnamate that took place from the realignment of the spacer chains in the multilayer assemblies on a solid substrate. To clarify the reason, the fabrication processes of the self-assembled films were investigated. Figure 4 shows the maximum $\pi-\pi^*$ absorbance of cinnamoyl polycation at 297 nm (PACPY2), 293 nm (PACPY6), 287 nm (PACPY11) as a function of the number of bilayers deposited. The linear increase of the absorbance with the number of bilayers clearly indicates the regular growth of the PSS/PACPYn layers. It was also confirmed that the adsorption occurred uniformly, the same amount being deposited on each cycle. Interestingly, it could be more clearly seen that the adsorbed quantity of polyelectrolyte was drastically increased with spacer chain length increase of polycation in the UV-Vis absorbance spectra. As seen in the UV-Vis spectra of self-assembled films, increasing the spacer chain length affected the formation of the aggregate states that seemed to cause the increased adsorption of polycation on the oppositely charged surface. It was seen that the polycation with longer spacer chain formed densely packed monolayers.

### 3.2 Photoreaction in the films

The LBL multilayer film with one cinnamoyl moiety per chemical repeat unit in the side chains in the polycation was exposed to LPUVL and then examined by UV-Vis spectroscopy in order to analyse the photoreaction procedure in the film in detail.

Figure 5 shows the linearly polarised UV-Vis absorption spectra of a 50-bilayer PSS/PACPY6 film irradiated by LPUVL for 20 min. The polarised absorbance $A_{//}$ ($A_{\perp}$) was measured with a probing linearly polarised light parallel (perpendicular) to the electric vector of LPUVL. Prior to LPUVL irradiation, the absorption was isotropic. After irradiation, the intensity of the band at 293 nm decreased, and a huge variance in the absorbance was observed between $A_{//}$ and $A_{\perp}$. The result indicated that the cinnamoyl groups with vinylene units positioned parallel to the polarisation direction of 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 may possibly generate the homogeneous LC alignment.

Photoinduced optical anisotropy of these self-assembled films with different spacer chain lengths was investigated by measuring the maximum absorbance in spectra in parallel with ($A_{//}$) and perpendicular to ($A_{\perp}$) the electric vector of LPUVL. The optical anisotropy was expressed here by the UV dichroic ratio (DR) \[ DR = \left( A_{\perp} - A_{//} \right) / \left( A_{\perp} + A_{//} \right) \]. As seen in Figure 6, all measured DRs were positive over the irradiation time range of $\leq 80$ min. Clearly, there was an effect of the spacer chain length on the optical anisotropy of the films. The polycation films with longer spacer chains obtained larger DR.

Natansohn et al. reported that the level of optical anisotropy was seen to be directly proportional to

![Figure 4](image-url)  
**Figure 4.** The maximum absorbance of cinnamoyl polycation at 297 nm (PACPY2), 293 nm (PACPY6), 287 nm (PACPY11) as a function of the number of bilayers deposited.

![Figure 5](image-url)  
**Figure 5.** Polarised UV-Vis absorption spectra of 50-bilayer PSS/PACPY6 film irradiated with LPUVL for 20 min.
the number of photons involved in the irradiation process [11]. It has been also shown that structural factors played a significant role in control over the levels of the induced birefringence [12]. The polycation with longer spacer chain could undergo [2+2] photodimerisation of cinnamoyl groups more easily, because the flexible spacer resulted in less restricted movement. Also, the polycation with a longer spacer chain has a large quantity deposited, and formed densely packed monolayers. These could affect the photoreaction of the films. We believe that the differences in photoreactive properties with different spacer chain lengths of these self-assembled films were due to matrix effects.

3.3 LC alignment properties studies

The alignment of LC on these irradiated PSS/PACPy\(n\) (\(n = 2, 6, 11\)) films was studied using crossed polarised optical microscopy. The uniform homogenous alignment of LC molecules could be obtained in a parallel cell modified by the irradiated film. Figure 7 shows the micrographs of a parallel LC cell with the 6-bilayer PSS/PACPy6 film irradiated for 25 min by LPUVL. Figure 7(a) shows the dark state when one of the crossed polarisers was parallel to the optical axis of the sample; Figure 7(b) shows the bright state when the two crossed polarisers were kept at 45° to the optical axis of the sample. All micrographs of the dark and bright states contained few defects and disclinations, indicating that excellent homogenous alignment was obtained.

It is clear that the alignment of LC molecules could be influenced by the property of the alignment films. Hence, the spacer chain length of polycation could affect the alignment properties of LC molecules. Figure 8 illustrates the angular transmittance intensity of the LC cell under polarising microscopy with PSS/PACPy2, PSS/PACPy6 and PSS/PACPy11, respectively. Obviously, the contrast ratio (\(T_{\text{max}}/T_{\text{min}}\)) increased with the spacer chain length increase. The polycation films with longer spacer chains obtained a larger DR. Thus the contrast ratio (\(T_{\text{max}}/T_{\text{min}}\)) of the LC cell with the longer chain length was larger. However, the difference between PSS/PACPy6 film and PSS/PACPy11 was small.

The thermal stability of the photoalignment films of PSS/PACPy\(n\) was also examined. The alignment was maintained even after heating at 120°C for 10 min when substrate surfaces were coated with PSS/PACPy2 films. Under the same conditions, the LC cells coated with PSS/PACPy6 films and PSS/PACPy11 films have lower aligning stability and held their contrast ratio to 110°C and 90°C, respectively. The thermal stability of PSS/PACPy\(n\)
Figure 8. Angular transmittance intensity of LC cell under crossed polarisers with different layer-by-layer films.

films decreased with increase in polycation chain length.

4. Conclusion

In this work, PSS/PACPYn self-assembled films could induce LC homogeneous alignment after LPUVL irradiation. The side-chain length of the cinnamoyl polycation affected the structure of the LBL films, as well as the photoalignment properties of the films. Increasing the spacer chain length affected the formation of the aggregate states that seem to cause the increased adsorption of polycation on the oppositely charged surface. The polycation films with longer spacer chain obtained larger DR after LPUVL irradiation. In addition, the contrast ratio ($T_{\text{max}}/T_{\text{min}}$) of the LC cell increased with the increase in spacer chain length. However, it was found that the thermal stability of PSS/PACPYn films decreased with increasing polycation chain length.

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References