Fabrication and structural characterization of the Langmuir–Blodgett films from a new chitosan derivative containing cinnamate chromophores

Yusong Wu *, Kenji Hisada, Shiro Maeda, Takashi Sasaki, Kensuke Sakurai

Department of Materials Science and Engineering, Faculty of Engineering, University of Fukui, Fukui 910-8507, Japan

Abstract

A new amphiphilic chitosan derivative, octanoylchitosan cinnamate (OCC) was synthesized through regioselective modifications of chitosan. A solution of OCC was spread to water to form a stable monolayer at the air/water interface. The surface pressure (π)–area (A) isotherm indicated that the polymer had a limiting area of about 100 Å^2 per repeat unit. YZ-type multilayers were deposited onto hydrophobic substrates through Langmuir–Blodgett (LB) technique. The structural features of the LB films were investigated by UV absorption, circular dichroism (CD) and linear dichroism (LD) spectroscopy. The results showed that the intrinsic chirality originating from the helical order of the OCC backbones was maintained in the LB films. Besides, the polymer backbones were uni-axially oriented in the LB film. The ordered structures of OCC assembled in a dilute solution and in a cast film were also investigated and the results were compared with that of the LB film.
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1. Introduction

Polymeric amphiphiles have been the subject of extensive investigation due to their specific structures and functions based on self-assembly. A variety of amphiphilic polysaccharides have been transferred to solid substrates through Langmuir–Blodgett (LB) technique. Among them, of particular interest are those containing optical, photosensitive chromophores, in view of not only the fundamental importance for studying the energy and electron transfer in the system, but also the potential applications as microelectronic components (Henry, Armand, Araspin, Bourgoin, & Wegner, 1999; Mao & Ritcey, 1996; Tedeschi et al., 1998; Tsujii, Itoh, Kukuda, & Miyamoto, 1992; Wiegand, Jaworek, Wegner, & Sackmann, 1997).

Chitosan is a hydrophilic polymer obtained by deacetylation of chitin, a naturally occurring polysaccharide found in the exoskeletons of crustaceans. The multifunctional groups (two hydroxyl groups and an amino group in its structural repeat unit) of chitosan provide the sites for numerous chemical modifications, among which acylation reactions have been intensively investigated because they provide facile ways to incorporate hydrophobic moieties to the chitosan backbones and thus may confer the chitosan derivatives with amphiphilic properties. Besides, taking advantages of the different reactivity of the amine and hydroxyl groups, it is possible to obtain elaborately designed chitosan derivatives through controlled acylations of chitosan.

The present paper concerns the fabrication of LB films by a novel amphiphilic *N,O*-acyl chitosan derivative having both aromatic and aliphatic side groups, i.e., octanoylchitosan cinnamate (denoted as OCC), prepared by means of regio-selective acylation of chitosan. This research was

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also prompted to study the molecular orientation in the LB films. Since chitosan is known to be a chiral molecule, it is of great interest and importance to understand whether such chiral ordered structure can be maintained or what kind of ordered structure can be formed due to the forced monolayer organization at air/water interface and subsequent transfer to a substrate, from the point of view of designing membrane materials with high performance. The OCC was expected to be an ideal system for our study in that the long aliphatic side chains may be conducive to formation of a stable LB monolayer at air/water interface; while the appended cinnamate chromophore may serve as a reporter group for optical measurements in order to study the molecule orientation.

Here, we will present some initial results on formation of the LB multilayer from an OCC/chloroform solution and the studies of the structural features of the LB films through optical techniques, including UV absorption, linear dichroism (LD), and circular dichroism (CD) spectroscopy. For the purpose of comparison, the ordered structures formed in a dilute solution of OCC/chloroform and a film cast from the solution are also described.

2. Experimental

2.1. Material

Chitosan from Katakura Chikkarin, which has a degree of deacetylation of 96% and an average molecular weight of (M_V) 1,090,000 g/mol, was used. Octanoyl chloride, cinnamoyl chloride, and all the other reagents are commercially available, and were used without further purification.

2.2. Synthesis of octanoylchitosan cinnamate (OCC)

OCC was synthesized through a strategy of two-step reactions as follows:

A precursor, *O*-octanoylchitosan, was synthesized according to method reported previously (Wu et al., 2005). In brief, to 10 mL of methane sulfonic acid was added 1.0 g of chitosan. Then, to the above homogeneous solution was added octanoyl chloride (5 equivalent of amine group of chitosan) under cooling with ice water. The reaction mixture was stirred for 3 h at room temperature (20 °C), and then kept in a freezer (−27 °C) overnight. To isolate the product, ice water was poured and the precipitate was collected. After washing with distilled-deionized water, the precipitate was neutralized by ammonium hydroxide (1.4%, w/w). The product was purified by re-precipitation from pyridine solution in ether and dried under vacuum (60 °C). The degree of substitution (DS) of octanoyl groups per glucosidic unit was 2.2 as determined by ^{1}H NMR, suggesting that a small amount of the amine groups (about 20% of total number) were also substituted. Spectral data are given as follows: FTIR (KBr, cm^{-1}): 3447, 2966, 2940, 2883, 1742, 1639, 1557, 1470, 1173, and 1071. ^{1}H NMR (DMSO-d_6, ppm, 100 °C): δ 0.8–1.6

(m, $-(CH_2)_5-CH_3$), 2.04 (s, NH_2), 2.28 (s, $-CH_2(\alpha)$), 2.9–5.0 (m, H-1,2,3,4,5,6,6′), 7.33 (s, amide N$-$H).

To obtain the *N,O*-acyl chitosan, i.e,. OCC, the *O*-octanol chitosan obtained above was dispersed to 20 mL of *N,N*-dimethylacetamide (DMAc) and 20 mL of pyridine. To this mixture was added slowly a solution of cinnamoyl chloride (3.0 g) in 20 mL of DMAc under cooling with ice water in 30 min. The mixture was then stirred at 80 °C for 24 h under N_2 atmosphere. The product was cooled to room temperature and then poured into 600 mL methanol/water (1:1 v/v) to precipitate the product. The precipitate was collected, washed with methanol, and finally dried under vacuum at 60 °C. The DS of cinnamate groups per glucosidic unit was about 0.8 as determined by ^{1}H NMR. Spectral data are given as follows: FTIR (KBr, cm^{-1}): 3426, 3027, 2959, 2935, 2873, 1734, 1670, 1632, 1521, 1171, 1060, 871, 764, 728, and 687. ^{1}H NMR (CDCl$_3$, ppm, 30 °C): δ 0.67–1.46 (m, $-(CH_2)_5CH_3$), 2.18 (s, $-CH_2(\alpha)$), 3.5–5.0 (m, H-1,2,3,4,5,6,6′ of GlcN unit) 5.7–6.8 (br m, $-OC(=O)-C\underline{H}=CH-$ and amide N$-$H), 7.28–7.51 (m, phenyl and $-C\underline{H}=CH$-phenyl).

2.3. Fabrication of LB films

Prior to deposition of the LB films, the commercial rectangular quartz plates (35 mm × 15 mm) were undergone a process of ultrasonic washing and a treatment by oxygen plasma. The plates were then treated with a 10 v/v% 1,1,1,3,3,3-haxamethyl disilazane (HMDS)/toluene solution and rinsed in toluene for 3 times to obtain hydrophobic substrates for deposition.

During the balance experiment, 200 μL of the OCC/chloroform solution (0.1 mg/mL) was spread to the water surface using a LB trough (NIWA Type 312D). The monolayer was then compressed and the pressure-area (π–A) isotherm was recorded at the temperature of the water subphase at 20 °C. Monolayer was transferred onto the quartz substrates by a vertical lifting method with a dipping speed of 10 mm/min for both down and up processes under a constant surface pressure of 10 mN/m. The transferred layers were undergone stabilization for 20 s in water and 60 s in the air during every dipping cycle.

2.4. Spectroscopy

Infrared spectra were recorded on a Nicolet Magna 560 FTIR spectrometer by KBr method. ^{1}H NMR spectra were obtained on a JEOL LA-500 spectrometer operating at a frequency of 500 MHz for [1]H. Electronic absorbance spectra (UV spectra) were recorded on a Hitachi U-3000 spectrometer using a 1.0-cm quartz cell at ambient temperature. CD experiments were conducted by a Jasco J-500A spectropolarimeter at ambient temperature. The solution samples were measured using a 0.5-cm water-jacketed quartz cell. The quartz plates supporting the films were mounted perpendicular to the light path, and allowed rotation around the light path, which was controlled by an

angle-ration device. The rotation angle is defined as the angle between the dipping direction of the quartz plate and the vertical polarized light. LD spectra were recorded by an expanded set of the CD instrument used in this study.

3. Results and discussion

3.1. Controlled N,O-acylation of chitosan

Since the amino group is more active than the two hydroxyl groups, a protection is often necessary in order to prepare N,O-acyl chitosan with refined substitution pattern. Nishimura et al. (1993) reported the preparation of amphiphilic N,O-palmitoyl chitosans by using an N-phthaloyl chitosan as a intermediate. However, this method needs several steps for the protection and deprotection of the amine groups. In addition, as pointed out (Sashiwa et al., 2002), it is difficult to maintain ester linkage during a hydrazine treatment in the deprotection process. Seo, Ikeda, Torada, Nakata, and Shimomura (2001) also reported a heterogeneous method to prepare N,O-acyl chitosan by using N-acyl chitosan as a precursor. However, the resultant N,O-acyl chitosans had lower DS and showed poor dissolvability in organic solvents.

At the same time, a new method for selective O-acylation of chitosan in methanesulfonic acid (MSA) was proposed (Seo et al., 2001), although similar method has been previously employed in acylations of chitin (Somorin, Nishi, Tokura, & Noguchi, 1979). This method is based on the idea that the amine groups are protonated through formation of a salt with MSA, which is disadvantageous for a nucleophilic displacement reaction. As a result, the substitution occurs preferentially on the hydroxyl groups of chitosan. The O-acyl chitosans synthesized via an MSA protection method generally dissolve in N,N-dimethylacetamide (DMAc). Therefore, further N-acylations could be conducted on the O-acyl chitosans in homogeneous systems using DMAc as solvent. The N,O-acyl chitosans obtained by this method were demonstrated to have higher DS and better solubility in organic solvents. Following a similar strategy by using the O-octanoyl chitosan as a precursor for further N-acylation, we obtained a new amphiphilic chitosan derivatives with dualistic acyl groups

(aromatic and aliphatic) in the N and O positions, i.e., OCC (Scheme 1). The OCC is readily dissolved in common organic solvents especially in a volatile solvent of chloroform, which is essential for spreading to form a monomolecular layer by LB method.

3.2. Monolayer behavior and deposition of LB films

There has been a little work concerning the studies of monolayer behavior of amphiphilic chitosan derivatives. Nishimura et al. (1993) first reported that two amphiphilic chitosan derivatives bearing tripalmitoyl groups could form monomolecular films with high collapse pressures ($\geqslant 65$ mN/m) and a slight increase in molecular diameter (with molecular areas of approximately 60 Å^2/monomer). Shin (1996) studied the monolayer behavior of three N,O-acyl chitosans with long fatty chains (C_{10}, C_{12} and C_{16}) and found that the limiting area per glucosamine unit for the condensed monolayers were 48, 53 and 70 Å^2 for the acyl chitosans having fatty chains of C_{10}, C_{12} and C_{16}, respectively. Li, Xin, and Miyashita (2002) achieved the preparation of LB film by a N,N-dilauryl chitosan oligomer (pentamer). The occupied area per glucosamine were calculated from the π–A isotherms to be around 50–60 Å^2 in the temperature range of 5–37 °C. Tong, Wang, Xu, Chua, and He (2005) studied the amphiphilic behavior of an O-dipalmitoyl chitosan. From an extrapolation of the π–A isotherm, a molecular area of approximately 55 Å^2 per glucosamine unit was estimated and the formation of a monolayer with highly condensed packing was concluded.

The surface pressure–area isotherm of the OCC monolayer recorded at 20 °C is shown in Fig. 1. It is indicated from the isotherm that the monolayer collapses under a surface pressure less than 25 mN m^{-1}. The limiting occupied area of OCC per repeat unit can also be estimated to be about 100 Å^2 by extrapolating the isotherm to zeroth surface pressure from the steepest region. Notice that the collapsing pressure for the OCC is a little lower, and the limiting area per repeat unit is much larger than those reported for chitosan derivatives containing only two or three flexible alkyl side groups (Shin, 1996; Tong et al., 2005). The value of limiting area per monomer unit of OCC is nearly two times of an idealized glucosidic unit
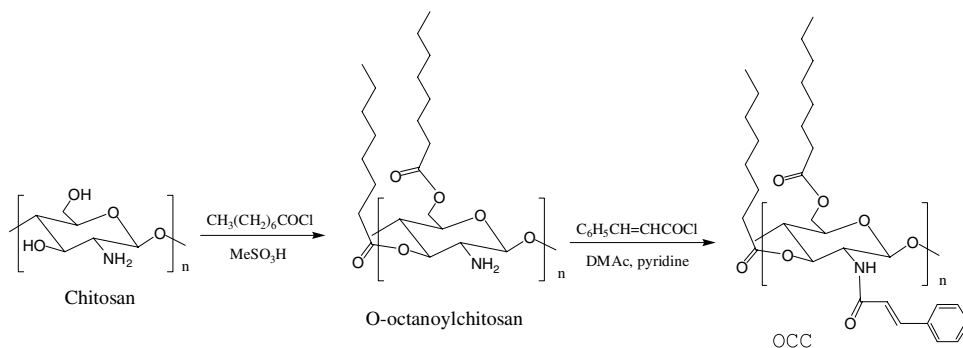
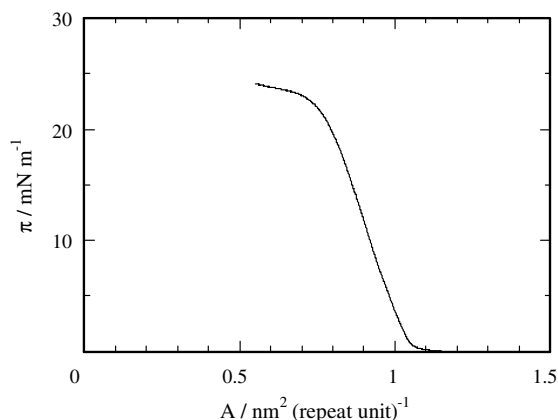Scheme 1. Synthesis and structure of OCC.

Fig. 1. Surface pressure (π)–area (A) isotherm measured at 20 °C.

Fig. 2. Deposition profile of a 20-layer LB film of OCC.

(estimated to be about 50 Å^2 (Kawaguchi, Nakahara, & Fukuda, 1985)). These results imply that the OCC monolayer cannot form condensed packing. The reason may be due to the rigid and bulky cinnamate moieties which prevent the polymer backbones from being compressed tightly.

It is worth mentioning that we have also tried preparing some other chitosan derivatives having both aliphatic groups and cinnamate groups, e.g., N-fatty acyl-O-dicinnamoyl chitosan derivatives (Wu et al., 2005). Interestingly, the limiting areas per repeat unit for all of these polymers were found to be in the order of only around 60–70 Å^2. Notice that those chitosan derivatives have denser cinnamate groups (two in each repeat unit) than the OCC (less than one in each repeat unit). The result indicates that the larger limiting area of OCC may not be caused simply by the bulkiness, but the orientation of the cinnamate group. It can be considered that unlike the soft aliphatic groups which may preferentially orient normal to the water surface through rotations of C—C bonds, the sterically hindered cinnamate moieties are conformationally restricted and do not have sufficient mobility. As a result, they could not be preferentially oriented perpendicular to the water surface in the similar way as the flexible alkyl chains when interacted with the air/water interface, but spatially distributed around the backbone as illustrated in Scheme 2.

The OCC monolayer can be transferred onto solid substrates at a constant surface pressure of 10 mN m^{-1}. In Fig. 2, the deposition profile of a LB film with 20 layers is shown. The depositi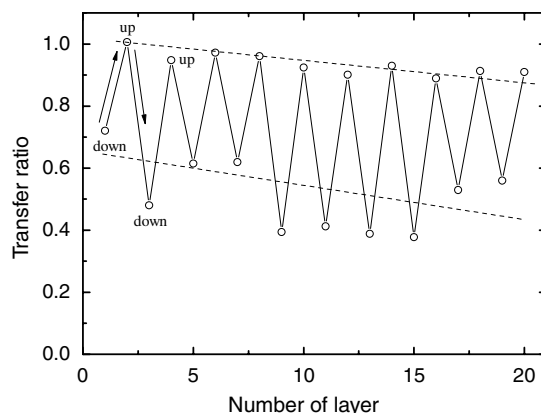on transfer ratios for the lifting processes are larger than those for the descending processes, with average transfer ratios of 94% and 60%, respectively. This indicates that the deposited LB multilayer has a YZ-type structure.

UV absorption was used to monitor the formation of the OCC multilayers, and the results are shown in Fig. 3. The UV spectra of the LB films have nearly the same absorption maximum (at around 278 nm) as that obtained from the dilute solution, suggesting that no aggregation of the cinnamate chromophores happens in the LB film. Although the absorbance at 278 nm increases with increasing number of deposited layer (see inserted plot in Fig. 3), no linear relationship is found between them. The reason may be ascribed to the irregular deposition as suggested from both the fluctuant and gradually decreased average transfer ratio with increasing number of deposited layers as shown in Fig. 2.

3.3. Optical activities of a dilute solution and a cast film

The CD and UV spectra of a dilute solution of OCC/chloroform are shown in Fig. 4. The CD signals in the measuring region are bisignate. The negative and positive "wings" have maxima at around 292 and 264 nm, respectively. The bisignate signals center on 278 nm, which is consistent with the position of the corresponding UV absorption maximum. The splitting CD signals are clearly due to exciton coupling between the cinnamate chormophores. It is known that under certain condition, identical chromophores in a helical orientation will interact in a
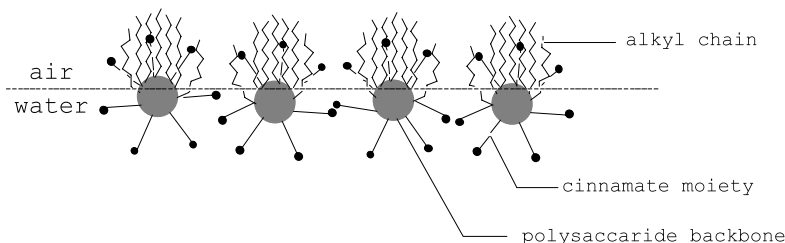
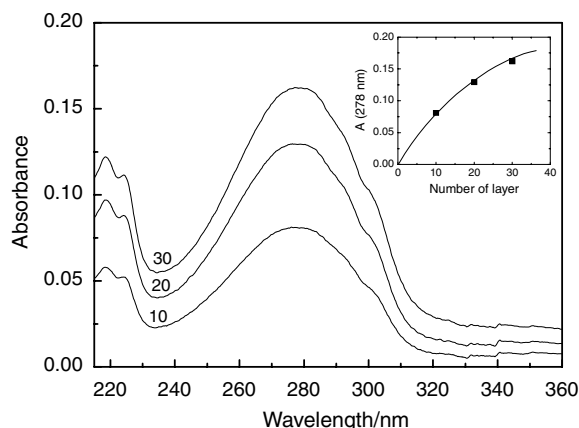Scheme 2. A sketch of the arrangement of the rigid and flexible side groups of OCC at air/water interface.

Fig. 3. UV absorption spectra of the LB films with 10, 20, and 30 deposited layers. Inserted figure is the plot of the intensity of the absorption at 278 nm as a function of the layer number.
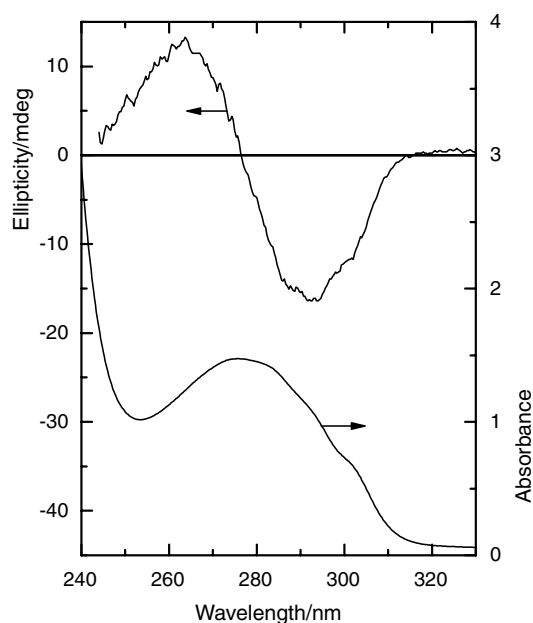

Fig. 4. CD and UV spectra of OCC in dilute solution of chloroform. Concentration: 0.26 mg/mL.

form of exciton coupling, which splits the associated CD band into a biphase couplet. According to the so-called exciton chirality method (Berova, Nakanishi, & Woody, 2000), the negative sign of the bisignate Cotton effect (reading from long to short wavelength of the CD spectrum is negative to positive) as displayed in Fig. 4 is in agreement with an ordered orientation of the cinnamate groups along a left-handed polymer helix.

Fig. 5 shows the CD spectra of the OCC solid film prepared by drop-casting from the dilute OCC/chloroform solution. The spectra were measured at various rotation angles by rotating the sample around the light path. The CD spectra are independent of rotation, indicating that the apparent CD of this sample contains nearly no contribution from linear effect (Indeed, nearly no linear
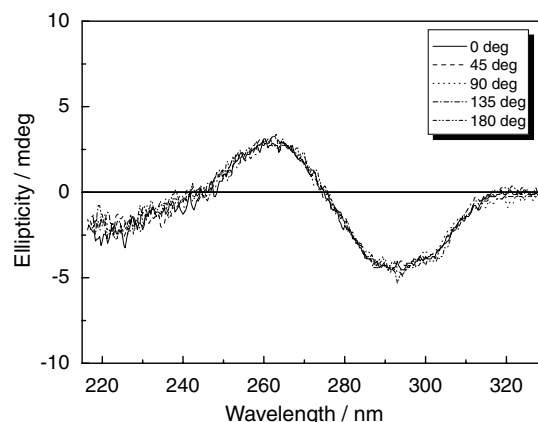

Fig. 5. CD spectra of the OCC casting film measured by orientating the quartz plate around the light path for 0°, 45°, 90°, 135°, and 180°.

dichroism (LD) signal could be recorded for this sample at any rotating angle). Thus, the observed CD signals are induced from the real chirality of the cast film. The CD spectral shapes in Fig. 5 are almost identical to that displayed in Fig. 4, suggesting that the OCC molecules adopt the same helical order in both the cast film and the solution.

3.4. Ordered structures of the LB film

Fig. 6 shows the CD spectra of the LB film with 20 layers measured at various rotation angles. The apparent CD signals strongly depend on rotating the sample. By rotating the sample on the quartz plate around the light path from 0° to 90°, the apparent CD signals within the region of 240–320 nm turns from a negative one to a bisignate couplet, and finally to a positive one. The angle dependence of the CD signals implies that the apparent CD signals are strongly influenced by some linear effects.

It is known that a major problem frequently encountered in the CD measurement of an oriented sample is the artifacts caused by some accidental imitators such as LD and linear birefringence. Thus, a consideration of
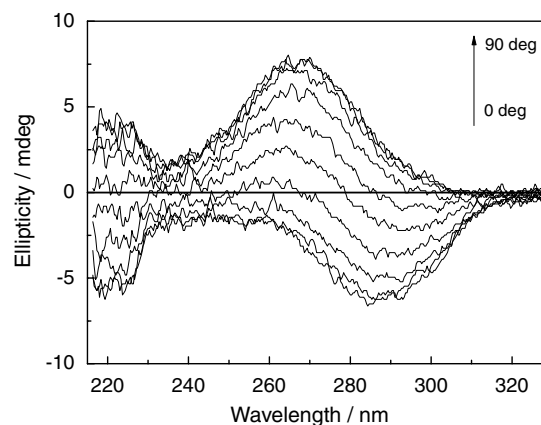

Fig. 6. CD spectra of the LB film of OCC with 20 layers. The sample was analyzed by rotating the quartz plate in steps of 10°.
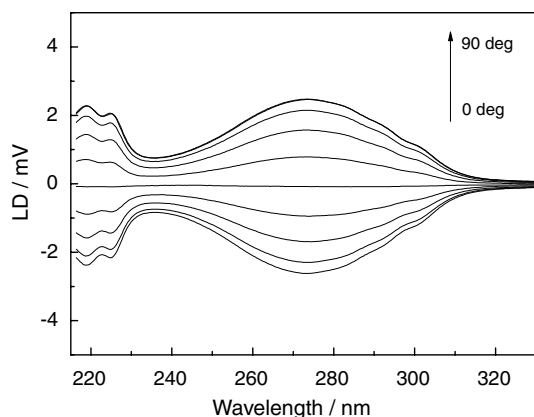
Fig. 7. LD spectra of the LB film of OCC with 20 layers recorded at the same condition as in Fig. 6.

possible parasitic artifacts is generally recommended in data interpretation when dealing with an oriented sample. It has been found that the apparent CD signal (Gillgren et al., 2002) measured by a CD spectrometer equipped with a photoelastic modulator (PEM) can be approximated by the following equation:

$$CD_{app} = CD + 0.02LD \qquad (1)$$

in which CD_{app} is the apparent CD signal, CD and LD stand for the true CD and LD signals, respectively. As LD depends on the orientation of a sample, it varies with the rotation angle of the sample. On the other hand, the intrinsic CD is independent of the rotation of a sample.

In order to distinguish the intrinsic chirality of the LB film of OCC, LD of the sample were measured and the results are given in Fig. 7. It is clearly shown that the LD of our LB film is considerably strong when the sample is placed in a vertical position in the spectrometer. Although both the LD (Fig. 7) and the CD (Fig. 6) are the most intensified when measured at 0° or 90°, and both change from negative to positive during a rotation of the sample from 0° to 90°, the positions of absorption maxima are quite different. The positions of the LD maxima (Fig. 7) are constant (about 278 nm) during the rotation. While, the negative and positive CD maxima shift depending on the rotation angle (Fig. 6). In deed, when rotated the quartz plate by an angle of about 40°, the LD signal became zero, while strong CD signals could be still observed. Thus, the observed CD in this case can be considered as the true CD of the sample according to Eq. (1). Thus, we can suppose that the observed CD spectrum at each ration angle is virtually a combination of an invariable bisignate CD signal (with the negative and the positive wings centering at 292 and 264 nm, respectively) and a variable LD signal (centering at 278 nm) depending on the rotation of the sample. In short, both the intrinsic CD and the linear dichroism contribute to the measured CD of the LB film of OCC.

From the above discussion, it is concluded that intrinsic chirality originating from the helical order of OCC is maintained in the two-dimensionally organized LB film.

It is also interesting to notice that the exciton coupling which happens in the LB film has the same form as that found in the dilute solution. This means that the helical conformations of OCC did not suffer obvious change when interacted with the air/water interface and underwent a forced organization during the deposition process. Again, we can ascribe this result to the effect of the rigid cinnamate groups, which cannot be compressed and oriented in one direction like soft aliphatic chains, but are spatially arranged along the polymer helix of OCC in a helical way. The result confirms an arrangement of the side groups in air/water interface as proposed in Scheme 2.

Although LD is a headachy imitator in measuring intrinsic CD of an oriented sample, it may, on the other hand, give information about macroscopic molecular orientation if the interested transition moments are oriented (Rodger & Nordén, 1997). Since the LB film of OCC induced strong LD signal, we can also draw a conclusion that the polymer chains are uni-axially oriented in the LB film. Such distinct structural feature could not be obtained by a cast film.

4. Conclusions

A novel amphiphilic chitosan derivative containing both octanoyl groups and cinnamate chromophores was first synthesized. A dilute OCC/chloroform solution could be spread onto the water surface to form a monomolecular layer using LB method. A limiting area of about 100 Å^2 was estimated from the π–A isotherm. YZ-type LB films with 10, 20, and 30 layers were deposited onto hydrophobic quartz substrates by a vertical dipping method under a surface pressure of 10 mN m^{-1} with acceptable transfer ratio. The intrinsic chirality originating from the helical backbones of OCC is maintained in the LB film. The helical conformations of OCC do not suffer any obvious change during a casting process or a forced organizing process by LB method. The main chains of OCC in the two dimensional LB films are also preferentially oriented.

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