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Study of Langmuir-Blodgett films of chiral nematic liquid crystals prepared by a templating method

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ABSTRACT

The ordered alignment of liquid crystal molecules plays a critical role in the applications of their optical properties. Langmuir-Blodgett (LB) monolayer films of chiral nematic liquid crystal, 4-cyano-4′-pentylbiphenyl(5CB), doped with a proprietary left-handed chiral additive were prepared using stearic acid (SA) as template. The Langmuir isotherms of the chiral nematic liquid crystal at the $CdCl_2$ interface with SA were studied. In the surface pressure curves, there was one sharp peak at the transition from gas phase to liquid phase. The phenomenon is considered to be the phase-separation of liquid crystals from SA. The chiral nematic liquid crystal multilayers LB films were characterized by ultraviolet-visible spectroscopy, X-ray diffraction, and atomic force microscopy. The results show that the chiral nematic liquid crystals were homogeneously and regularly dispersed in the SA template.

1. Introduction

Chiral nematic liquid crystals represent important class of functional materials having unique optical properties such as selective reflection, high optical rotation power, and circular dichroism [1,2]. It is known that organized molecular assemblies of chiral nematic liquid crystals have a strong effect on their properties. In the course of past studies, various approaches were developed to fabricate structured surfaces that could orient liquid crystals, including mechanical rubbing of polymer-coated substrates, physical vapor deposition of metals, uniaxial stretching of polymer films. However, above methods need an alignment layer materials for orienting liquid crystals [3].

The Langmuir-Blodgett (LB) technique is a sophisticated method that offers a way to obtain well-ordered monolayers and multilayers films [4,5,6]. In the preparation of LB films, the amphiphilic molecules spread at the air–water interface are able to form insoluble Langmuir films [7,8]. The chiral nematic liquid crystal studied herein has a rigid structure without good hydrophilic groups, so the stable monolayers LB films cannot be obtained easily. One method for introducing nonamphiphilic or water-soluble molecules into a LB film is to mix them with amphiphilic molecules such as fatty acids or stearic acid to form a monolayer at air-water interface [9,10,11]. Collins et al. [12] and Reuter et al. [13] have used the above method to obtain liquid crystal LB films.

In this study, we pursued development of a templating method to prepare LB films of a chiral nematic liquid crystal, 4-cyano-4′-pentylbiphenyl(5CB), doped with chiral additive. Successful alignment of standard liquid crystal has been achieved with LB films of SA mixed with the chiral nematic liquid crystal. The LB films were characterized by several techniques, including surface pressure measurements (π-A), UV–vis absorption spectra (UV–vis), X-Ray Diffractometer (XRD), and atomic force microscope (AFM). The molecular intermolecular force of the chiral nematic liquid crystal and SA were discussed.

2. Experimental details

2.1. Materials

Stearic acid (SA), purity > 99%, obtained from Energy Chemical Reagent Company, Shanghai (purity > 99%), was used without further purification. The chiral liquid crystal was prepared by mixing a left-handed chiral additive (S811, a Merk company) with nematic liquid crystal 4-cyano-4′-pentylbiphenyl (5CB) by the mass proportion (S811: 5CB = 2: 98). The nematic liquid crystal 5CB and S811 were provided by (a Merk company). The molecular structures of used materials are showed in Fig. 1. Spectroscopy grade chloroform was used as the solvent of the spreading solution.

2.2. Methods

Langmuir films were prepared at ca 25 ± 1 °C using a KSV5000 (KSV Instruments Ltd., Finland) LB system placed on an antivibration table in

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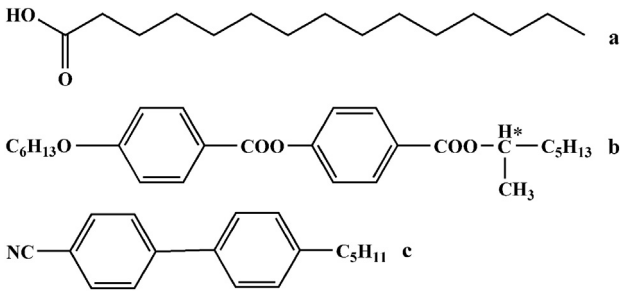

Fig. 1. Chemical structures of used materials: a. SA; b. S811; c. 5CB.

a class 10,000 clean room. Ultrapure water with resistivity 18.2 MΩ cm was supplied by a Milli-RO coupled to a purification system. $CdCl_2$ (1×10^{-5}) was used as the subphase. Stearic acid were dissolved in chloroform obtained a solutions of 1 mg/mL. A stearic acid monolayer was formed by placing an amount of 30 μL at the $CdCl_2$ interface using a microsyringe (Hamilton). Subsequently, a solution of 1 mg/mL of chiral nematic liquid crystal (5CB + S811) in chloroform was added to the surface. The surface pressure-area (π-A) isotherms were recorded after 15 min of the evaporation of the solvent. The monolayers were compressed at a barrier speed of 10 mm/min. Y-type deposition of monolayers films were achieved by slowly withdrawing the substrates vertically at a speed of 5 mm/min under a constant surface pressure. Finally, the substrates were stored at room temperature in an exsiccator for 24 h to dryness.

UV–vis absorption spectra for the LB film of chiral nematic liquid crystal/SA were measured with the use of UV–vis spectrometer (Shimadzu UV-3100). The films were tested by the X-Ray Diffractometer (Shimadzu XRD-6000) which uses Cu-K_α radiation ($\lambda = 1.543$ Å). For the LB films morphology studies, the atomic force microscope (AFM Bruker Multi-Mode 8) was used, working in tapping-mode.

3. Results and discussions

3.1. Isotherm characteristics

The surface pressure isotherms of the chiral nematic liquid crystal with SA were determined using a Langmuir trough system with two movable barriers and a Wilhelmy plate of platinum. The Langmuir film isotherms are the surface pressure (p) as a function of the trough area cm^2 of the compounds. Fig. 2 shows the Langmuir isotherms of chiral nematic liquid crystal (5CB + S811) without SA at the different compression speeds of 10 mm/min, 8 mm/min, 5 mm/min. From the graph, we can find that the collapse pressures are all too low to form uniform

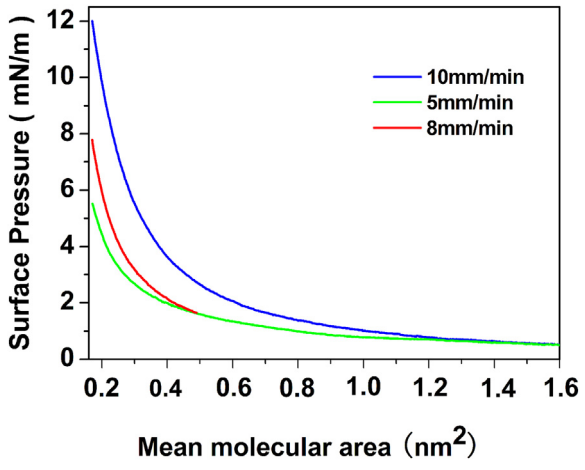

Fig. 2. Surface pressure-area (π–A) isotherms of chiral nematic liquid crystal (5CB + S811) at different compression speeds.

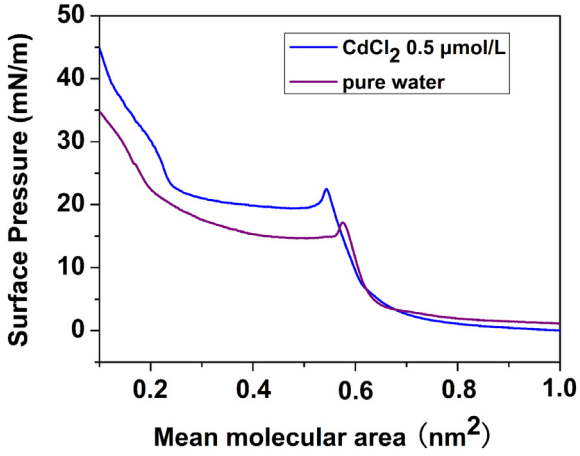

Fig. 3. Surface pressure-area (π–A) isotherms of chiral nematic liquid crystal/SA at different subphases.

films. Therefore, SA is used as a template to prepare the chiral nematic liquid crystal LB films.

Fig. 3 presents the Langmuir isotherm of 5CB/S811 using SA as template. The characteristic of π-A isotherms was carried out on pure water and $CdCl_2$ subphases, respectively. The graphs are similar in the shape. The results show that the collapse pressure of the chiral nematic liquid crystal monolayers LB films on the ion-containing $CdCl_2$ subphase is much higher than the one on the pure water subphase. That is to say, the structures of chiral nematic liquid crystal LB films prepared on the $CdCl_2$ subphase are more condensed than the one developed on the pure water. This indicates the metal ions $CdCl_2$ can pull the amphiphilic acid molecules together at the subphase surface [14].

In the isotherm graphs, there are two steep increase points. The surface pressures rise up at the area of 150 cm^2 and gradually increase with the compression until the surface area near 130 cm^2. These plots exhibit plateau below 5 mN/m which corresponds to the transition state of the monolayers films from the gas phase to the expanded liquid one. Moreover, these plots show a characteristic peak in the region of 125–130 cm^2. The presence of a 'spike' is mentioned as an indication of the instability of the film during compression. Similar 'spikes' in compression isotherms had been reported previously, although their origin remains elusive [15]. For the family of phenyl benzoates in the above linear nematic liquid crystals and chiral dopant S811, the 'spike' are assumed to be related with some undetermined crystallization phenomena [16]. The plateau region of area from 50 to 125 cm^2 indicates a liquid phase state of the mixed LB films. The solid phase regions start at the surface area of 50 cm^2. The collapse of monolayers film occurs at the

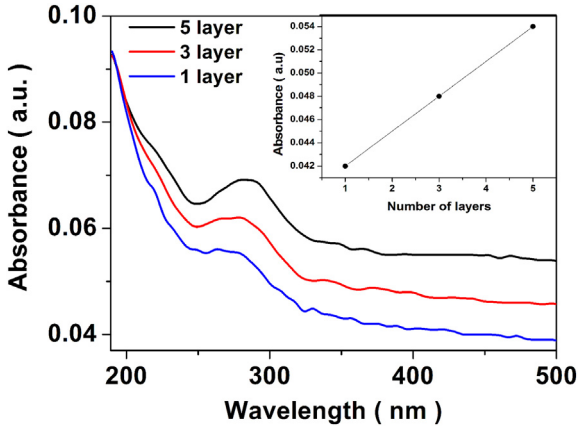

Fig. 4. UV–vis absorption of chiral nematic liquid crystal/SA LB films.