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Molecular Orientation and Structure in LB Films of a Liquid Crystal MPUOPM Investigated by UV-Vis and IR Spectroscopy[†]

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Langmuir monolayers and LB films of 4-((s)-2-methylbutoxy)phenyl-(4'-(10-undecen-1-oyloxy)phenyl) methylenimine (MPUOPM) were investigated by ultraviolet-visible, polarized infrared spectroscopy. π-A isotherms showed well-defined Langmuir monolayers were formed at an air/water interface for the MPUOPM and their mixture with SA. An inflection point at 13 mN/m appeared on the isotherm, which was due to the transition from the monolayer to multilayer. The polarized IR spectra of LB films of MPUOPM had provided new insight into the molecular orientation and structure. In LB films, the tilted angle between the alkyl chain and the normal line of the substrate was 48°, the tilted angle between the dipole moment of C=N and the normal line of the substrate was 51°. The alkyl chains assumed a trans-zigzag conformation but it included a few gauche conformers. The C=N groups were almost in one plane in the LB films.

Key words: Langmuir, π-A isotherm, Polarized IR

I. INTRODUCTION

Liquid crystals (LCs) have attracted much attention because of their applications in high-resolution flat panel display and fast electro-optic devices [1,2]. The physical and electro-optical properties of LCs are strongly dependent on molecular shape and local environment [3], which determines the statistical distribution and equilibrium population of each conformational state of the molecules. But the relationships between them have not yet been clearly elucidated. Therefore, it is very important to investigate the orientation, structure and conformation of LC molecules on a substrate.

The Langmuir-Blodgett (LB) technique is one of powerful methods to fabricate a organic ultrathin film with ideal two-dimensional systems, it can precisely control the thickness and order of a film at the molecular scale [4-6]. Compared with self-assembly technique, the LB technique seems to be more popular to realize molecular architectures with ordered structure because it allows the fabrication of thin film structure by adding a monomolecular layer one after another. It is well known that anisotropic property in smectic phase is one of the basic characters of LCs. Moreover, the structure of multilayer LB films of LCs may be similar to that of LCs in the smectic phase, which is a three-dimensional bulk-layered system [7]. Consequently, LB films pro-

vide a good model for us to investigate the relation between structures and properties of LCs compound at submolecule scale [8-16].

Spectroscopy of LCs in organized thin films can provide important information about molecular orientations and structures, intermolecular interactions, aggregations and the relations among these structural characteristics with the optical and electrochemical properties. Ultraviolet-visible (UV-Vis) spectroscopy may serve as an effective structural probe to investigate chromophore-chromophore interaction in various environments. Polarized IR spectroscopy can provide knowledge about the orientation, conformation, and electronic structure of molecules in the films [17-20]. The combined use of different analytical techniques is powerful for structural characterization of well-ordered monolayer or multilayer films on solid surfaces fabricated by LB technique.

In our previous studies [21-23], we have investigated the structure and orientation of LCs self-assembled films and surface-stabilized films. We have demonstrated that the azimuth of the achiral and chiral chains are opposite each other, and the orientation of the achiral chain is the same direction as the mesogen core and that of the chiral chain is perpendicular to the mesogen part. Their axes are parallel and perpendicular to the average molecular long axis, respectively. The two CH_2 chains (achiral and chiral) are completely ordered with an all-trans zigzag conformer. As a part of our systemic research, in the present study, we have explored the construction of ordered molecular assemblies of LCs using the LB technique.

In this study, structural characterization of Langmuir and LB films of a LCs compound on solid surfaces

have been investigated by use of UV-Vis spectroscopy, polarized IR spectroscopy. The phase transition and the possible molecular aggregation and stacking in pure and mixed Langmuir films are characterized by surface pressure-molecular area (π-A) isotherms and hysteresis curves.

II. EXPERIMENTS

A. Materials

The samples used in this study were synthesized by Kong-zhang Yang group (Department of Chemistry, Shandong University of China): 4-((s)-2-methylbutoxy)phenyl-(4'-(10-undecen-1-oyloxy)phenyl) methylenimine (MPUOPM), whose structure is shown in Fig.1. Stearic acid (SA) was purchased from Wako Pure Chemical Industries (Osaka, Japan). The solvent chloroform was obtained from Tiantai Chemical Ltd (Tianjin, China), without further purification. Distilled deionized water was purified by an ultra-pure water system model Millipore-Q610, its resistance was larger than 18.1 MΩ/cm.
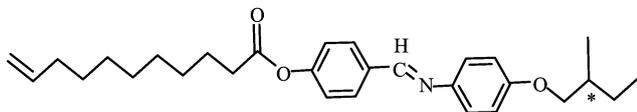
FIG. 1 Structure of 4-((s)- 2-methylbutoxy)phenyl-(4'-(10-undecen-1-oyloxy)phenyl)methylenimine.

B. Preparation of Langmuir and LB Films

A computer-controlled NIMA 622 Langmuir Trough (double trough) with a wihelmy balance was employed for the surface π-A isotherm and LB films study. The temperature of subphase were controlled by water circulating from a water bath with an accuracy of ±0.1 °C. All surface pressure measurements and LB film preparation were carried out at eternal temperature (20 °C). Distilled deionized water was used as the subphase. MPUOPM and its hybrid with SA in molar ratio of 1:1 were dissolved in chloroform. The concentration of MPUOPM in these systems was 1.0 g/L. An 80 μL quantity of chloroform solutions of MPUOPM were spread from the microsyringe to the subphase surface, followed by a 40 min waiting for solvent evaporation. And then the film was compressed at a chosen barrier speed. In hysteresise experiments, the barrier movement was immediately reversed after the pressure reached the desired value. The monolayer was compressed at the constant rate of 20 cm^2/min. At the chosen pressure, the monolayers were allowed to equilibrate for 30 min, then the condensed monolayers were transferred as Y-type deposition mode onto cleaned quartz substrates (for UV-Vis absorption measurement), onto CaF$_2$ substrates (for IR transmission

measurement) with a transfer ratio of 0.9-1.0. In all cases, the dipping speed was set at 6 mm/min. The multiplayer LB films were prepared by successive up-stroke and downstroke accumulation.

C. Instruments

UV-Vis absorption spectra were recorded on a Shimadzu UV-3100 spectrometer and the silt width was set at 2 nm. The bulk spectrum was obtained from a 0.05 g/L solution (diluted from stock) of the MPUOPM in a quartz cell with path length of 1 cm.

Polarized infrared spectra were recorded on a Brusker IFS66V FTIR spectrometer equipped with a liquid-nitrogen-cooled cryogenic MCT detector. A KRS-5 wire grid polarizer was rotated about the axis parallel to the direction of the IR radiation. The angle for the incident light was 0° and 60° from the surface normal of the substrate. A vacuum system was used to eliminate CO_2 and H_2O in the optical sample chamber. The spectra were recorded with a resolution 4 cm^{-1}. To yield the spectra with a high signal-to-noise ration, the spectrum was the accumulation of 1024 scans.

III. RESULTS AND DISCUSSION

A. Langmuir isotherm

Figure 2(a) shows the π-A isotherms of MPUOPM on the subphase of pure water at 20 °C. An inflection region at 13 mN/m appears on the isotherm. And the surface pressure achieves 26 mN/m without observable collapse. The value of the average surface area per molecule is obtained by extrapolating the linear parts of the π-A isotherms to zero pressure. The limiting area is determined to 0.32 and 0.17 nm^2 before and after the inflection region, respectively. The values of the cross-sectional area of the aromatic azo mesogenic unit oriented perpendicular to the air/water surface is
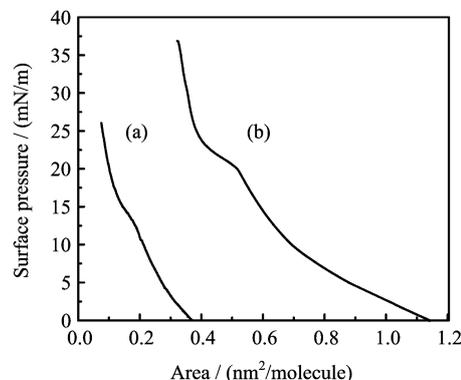
FIG. 2 π-A isotherm of monolayer of MPUOPM on the pure water subphase at 20 °C (a) pure and (b) mixed 1:1 with SA.

0.25 nm^2 [24]. By comparison of them, we imagine that the chains title to the surface of the subphase in the monolayer before the inflection region, and the aggregates or crystallite of MPUOPM molecules appear in the monolayer when the pressure is higher than the inflection point. It can be observed that a large hystersis appears when the reverse pressure exceeds the inflection point [25]. It is due to the formation of aggregates in the monolayer at higher pressure than the inflection pressure, which leads to a higher packing density. This transition is irreversible, so the molecules don't spread to the original state after the pressure release.

Figure 2(b) is the isotherm of the blends of MPUOPM with SA at molar ratio of 1:1. There appears apparently an L-E phase. It is clear that collapse pressure increases notably to about 38 mN/m for the MPUOPM/SA blend, and an inflection region at around 19 mN/m appears on the isotherm. The values of the limiting area (A) before and after the inflection are 0.82 and 0.48 nm^2, respectively. For a completely immiscible or ideally mixed monolayer, the molecular area of the mixture should follow the additivity rule [26] $A_{mixed} = n_1 A_1 + n_2 A_2$, where A_{mixed} refers to the mean molecular area expected in the two-components monolayer, A_m and n_m (m=1, 2) are the molecular area of the pure components and the mole fractions of the components in mixed monolayer, respectively [27]. The molecular area of SA at air/water interface is 0.2 nm^2, so the calculated mean molecular area of the mixed system is around 0.45 nm^2. The A value before the inflection is larger than that calculated, but the A after the inflection is close to the calculated mean molecular are. From this result, we suggest that MPUOPM molecules are distributed uniformly with SA, and the parties do not appear the phase separation. The inflection means that the monolayer undergoes a phase transition. MPUOPM exists as an ordered fluid phase when the pressure is lower than the inflection point. After compressed beyond the inflection point, the molecules arrange in a crystalline stacked pattern, which results to the appearance of the highly imcompressibe solid film. In the inflection region, the chains of molecules become more perpendicular to the subphase surface [28].

B. UV-Vis spectra

UV-Vis spectra are applied to monitor the fabrication process of the multilayer LB films. Figure 3 shows UV-Vis spectra of MPUOPM in chloroform solution (a) and eleven-monolayer films of MPUOPM deposited onto quartz substrates (b). There exist two strong peaks at 270 and 336 nm corresponding to the π-π^* transition and n-π^* transition of the aromatic Schiff base chromophore, respectively [9,29]. The peak is blue shift from 270 nm in the solution to 246 nm, meaning that some H aggregations are formed in LB films [13]. The transition moments of mesogenic units are parallel to each other, arranged perpendicular of slightly tilted
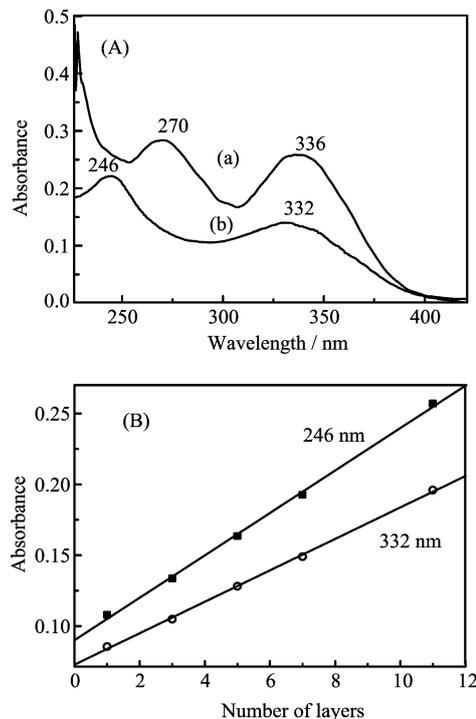

FIG. 3 (A) UV-Vis spectra of MPUOPM in chloroform solution (a) and eleven-monolayer films of MPUOPM deposited onto quartz substrates (b). (B) The integral intensity of the band at 246 and 332 nm in LB films *vs.* the number of layers.

to the stacking direction. The linear increase of absorbance at 246 and 331 nm with the numbers of layers is characteristic of a uniform deposition in each dipping cycle.

C. IR spectra

The frequencies and assignments of major IR band of MPUOPM at room temperature are listed in Table I. The bands are 2921 and 2852 cm^{-1} are assigned to the CH$_2$ asymmetric and symmetric stretching mode of MPUOPM in the LB films, respectively. It is to be noted that due to the presence of CH$_2$ and CH$_3$ groups in two alkyl chains, only averaged information can be obtained from the C−H stretching modes. It is well know that the frequencies of the CH$_2$ stretching modes are sensitive to the conformation of an alkyl chain [30]. The bands appear near 2918 and 2848 cm^{-1}, if the chain is highly ordered (trans-zigzag conformation) [31-34], while the conformational disorder increase, the bands shift upward. Therefore, we suggest that the alkyl chains of MPUOPM LB film have some gauche conformation. In addition, the bands at 1752 cm^{-1} is assigned to the C=O (free) stretching mode, the band at 1626 cm^{-1} is due to C=N stretching mode. The band at 1603 cm^{-1} is originally $a_1 + b_1$ (slight) vibration modes of benzene rings, while the 1508 cm^{-1} band is due to

TABLE I Major infrared band assignments and orientation angles for MPUOPM LB film

Wavenumber/cm^{-1}	Assignments	Orientation angle/($°$)
2920	CH$_2$ asymmetry stretching mode	56.3[a]
2849	CH$_2$ symmetry stretching mode	60.3[a]
1753	C=O stretching mode	26.4
1624	C=N stretching mode	50.6
1603	Phenyl Skeleta ring breathing mode	42.4
1508	Phenyl Skeleta ring breathing mode	38.9
1469	CH$_2$ scissoring mode	63.3

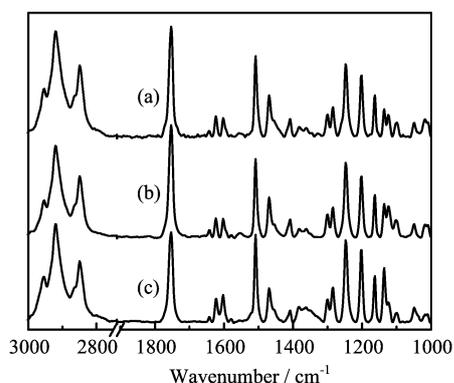[a] The orientation angle is the tilting angle of the hydrocarbon chain with respect to the films surface normal.

FIG. 4 Polarized IR transmission spectra of 11-layer LB films of MPUOPM at different incident angles. (a) A_p ($i=0°$), (b) A_s ($i=0°$), (c) A_p ($i=60°$).

vibration mode a_1 of para-subsituted benzenes. The band of 1469 cm^{-1} is assigned to the CH$_2$ scissoring vibration mode. In addition, a shoulder-peak can be observed at 1463 cm^{-1}. The splitting of the CH$_2$ scissoring vibration is likely to be caused by the crystal field and is characteristic of n-paraffins which crystallize with orthorhombic subcell packing where the hydrocarbon chains are packed alternately. Thus we assume that the crystal structure in mixed LB films is a monoclinic or orthorhombic crystal form, and the hydrocarbon chains are inclined at an angle of about 40° with respect to the surface normal [35-38]. The conclusion is in agreement with those calculative results of the polarized infrared spectra. The CH$_2$ deformation vibration is at 1408 cm^{-1}.

The linearly polarized infrared spectra were used to study the molecular orientation in the LB films. According to the method reported by Vandevyer *et al.* [39], We can character the order of the structure of the LB films. In experiment, the polarized IR beam was introduced the film surface, where electric vector of light is either parallel or perpendicular to the dipping direction. The dichroic ratio $R=A_\parallel(i\neq0)/A_\parallel(i=0)$, where $A_\parallel(i)$ is the band intensity and i denotes the angle between the film normal and the incidence polarized light (under usual condition $i=60°$). The angle ψ transition

dipole moment between the film surface normal and the transition dipole moment is determined by $A_\parallel(i\neq0)$, $A_\parallel(i=0)$ and $A_\perp(i=0)$.

Figure 4 shows the polarized IR spectra of MPUOPM of LB films in 3020-1400 cm^{-1} region. The tilting angle ψ_3 of the hydrocarbon chain with respect to the films surface normal can be obtained from the formula:

$$\cos^2\psi_1 + \cos^2\psi_2 + \cos^2\psi_3 = 1 \qquad (1)$$

where ψ_1 and ψ_2 are defined as the angle ψ of the CH$_2$ asymmetric and symmetric stretching modes, respectively. According to the Vandevyer's equation, we calculate the value of the angle ψ of some bands, which are list in Table I.

IV. CONCLUSION

From the above data and discussions, it is concluded that MPUOPM can form stable monolayer at the air/water interface. The monolayer is apt to be deposited on the substrates in Y type structure by Langmuir-Blodgett technique. An inflection point at 13 mN/m appears on the isotherm, which is due to the transition from the monolayer to multilayer. The mesogenic units of MPUOPM in multilayer LB films are aligned in a side-by-side parallel fashion and packed with the plane of its π system approximately perpendicular to the stacking direction. The polarized IR spectra of LB films of MPUOPM have provided new insight into the molecular orientation and structure. In LB films, the tilted angle between the alkyl chain and the normal line of the substrate is 48°, the tilted angle between the dipole moment of C=N and the normal line of the substrate is 51°. The alkyl chains assume a trans-zigzag conformation but it includes a few gauche conformers. The C=N groups are almost in one plane in the LB films.

V. ACKNOWLEDGMENTS

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