LETTERS

Multilayer Formation of a Series of Chiral Liquid Crystal Molecules at the Air/Water Interface[†]

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A series of liquid crystal molecules, 4-alkoxy-*N*-(2-hydroxy-4-(*s*-2-chloro-3-methylbutanoyloxy)benzylidene)-aniline with $-C_nH_{2n+1}$ as the terminal group (abbreviated as L*n* hereafter, *n* = 2, 4, 6, 8, 10, 12), were spread at the air−water interface and studied by measuring their $\pi-A$ isotherms and surface potential−area isotherms. Films of L*n* at the air−water interface were transferred onto solid substrates and characterized by polarized microscopes, X-ray diffraction, and FTIR spectroscopy. It was found that L12 and L10 formed tetralayer and bilayer, respectively, on water under the compression of the barriers of a Langmuir trough, while L8, L6, L4, and L2 spontaneously formed smectic multilayers of about 25 molecules thick. FTIR studies confirmed that the molecules in the smectic multilayers were oriented with their long molecular axis preferentially perpendicular to the water surface.

1. Introduction

Insoluble monolayers at the air−water interface have long been studied and were reviewed by Gaines in the 1960s.[1] In the 1970s, liquid crystal (LC) molecules were introduced to the air−water interface of a Langmuir trough.[2] The use of LC compounds originates mostly from the idea that they have inherent order in the bulk state, and this order may help them to reorganize on water surface. In the 1990s, Ulman reviewed the amount of work about LC molecules on water surface.[3] All the reported work suggests that the LC inherent order has an impact on the two-dimensional organization of molecules into monolayers[4] or on the organization of monolayers into three-dimensional assemblies.[5] H. Diep-Quang[5] reported the multi-layer formation of two LC molecules with T_{C-N} (T_{C-N} = solid−nematic transition temperature) near 40 °C on water surface, under the compression of the barriers of a Langmuir trough. At water temperatures below T_{C-N}, the monolayer of the LC molecules can develop with compression successively to bilayer, trilayer, and tetralayer. At water temperatures above T_{C-N}, the monolayer of the LC molecules collapsed with compression like ordinary liquids and no multilayer formed. Relatively recently, H. Gruler et al.[6,7] also reported such compression-induced multilayer formation of LC molecules on water. This paper reports both the compression-induced and the spontaneous multilayer formation of a series of LC molecules whose structure is similar to H. Gruler's.

2. Experimental Section

Synthesis of the series of chiral LC molecules, 4-alkoxy-*N*-(2-hydroxy-4-(*s*-2-chloro-3-methylbutanoyloxy)benzylidene)-aniline (L*n*), with *n* = 2, 4, 6, 8, 10, 12 (Scheme 1) has been reported previously.[8] All the L*n* have smectic phase transition temperatures in the range 60−70 °C. With the intramolecular hydrogen bonding between the Schiff's base −CH=N− and
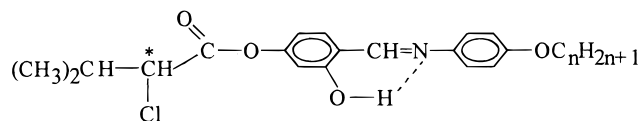
SCHEME 1

L n: n=2, 4, 6, 8, 10, 12

SCHEME 2

L12

A1: | A2: | A3:
water | water | water
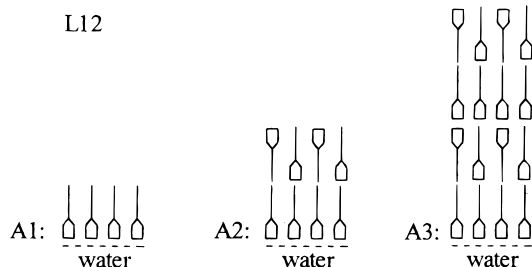
the hydroxyl, the Ln is stable and does not decompose on water. The Ln was dissolved in chloroform and spread onto water (deionized and double distilled) in drops smaller than 1.0 μL. A KSV 5000 Langmuir−Blodgett (LB) trough was used, with the Wilhelmy plate standing at the center and the barriers compressing symmetrically. It was found that unsymmetrical compression gave malformed π−A isotherms. The surface potential (SP) of the films on water was measured with the SP meter provided by KSV Ltd. The noise in the SP measurement was 5 mV, and the SP−area isotherms were well-reproduced. The SP−area isotherms were measured with extremely low compression speed and sufficient stabilization after spreading. The upper electrode was hung in the air, and the lower electrode was immersed under water.

The films at the air−water interface were transferred onto flat substrates using the horizontal lifting method. Throughout this communication, the films were transferred only once, and will be described as "horizontally once-transferred films". The reason we used once-transfer rather than twice-transfer should be clear, since we want to obtain the order information of the films on water. In addition, the molecular area at which the films were transferred was information more important than the surface pressure, and we prefer to describe this information in Table 1.

3. Results

(I) L12. The π−A isotherm of L12 (Figure 1a) shows some typical phase transition points A1 (0.24 nm^2), A2 (0.12 nm^2), and A4 (0.04 nm^2). At the molecular area A1, L12 should form a close-packed monolayer on water. It has been generally known that azobenzene-containing long-chain fatty acids have an area of 0.25 nm^2 when standing vertically on water,[9] and L12 is estimated also to have such a cross-sectional area. The molecular area A2 is half of A1, and the segment from A1 to A2 should reflect a transition from monolayer to bilayer (see Scheme 2). At the area A4, the films were "horizontally once-transferred" onto quartz substrates and observed to show crystalline domains and stripes under a polarized microscope (Zeiss Jena, 80 times). Thus, the film of L12 at A4 should collapse to an undefined state.

However, at the area A3 of Figure 1a, L12 does not collapse, since the film transferred onto quartz at A3 shows no image (appears uniformly dark) under a polarized microscope. In fact, the film once transferred onto silicon substrates has its first X-ray diffraction peak at $2\theta = 1.46°$, corresponding to a period of
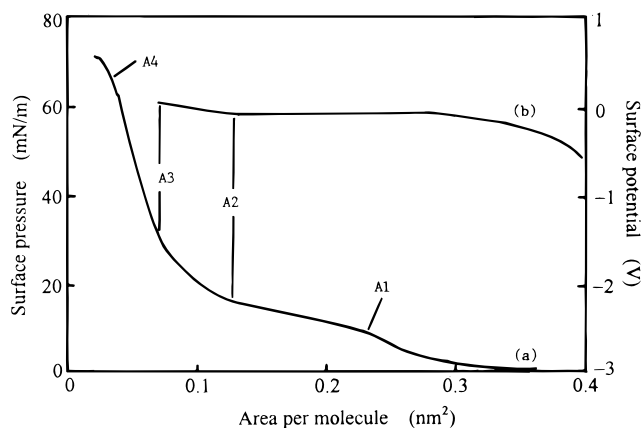

Figure 1. Surface pressure−area isotherm (a) and potential−area isotherm (b) of L12 on water at 20 ± 1 °C.

TABLE 1: d Spacings of Once-Transferred Films of Ln at the Deposition Area (DA) and the Calculated Length (CL)

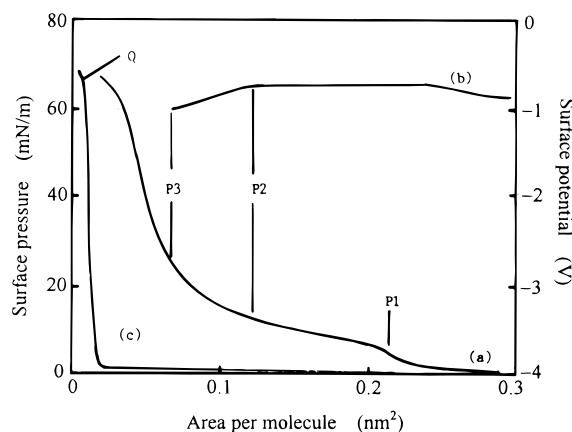| Ln	DA (nm^2)	d_{001} (nm)	d_{002} (nm)	d_{003} (nm)	CL (nm)
L2	0.032	2.14	1.04		2.14
L4	0.020	2.16	1.07	0.712	2.38
L6	0.016	2.35	1.16	0.774	2.64
L8	0.012	2.71	1.32		2.88

Figure 2. Surface pressure−area isotherm of Ll0 (a), potential−area isotherm of L10 (b), and pressure−area isotherm of L6 (c) on water at 20 ± 1 °C.
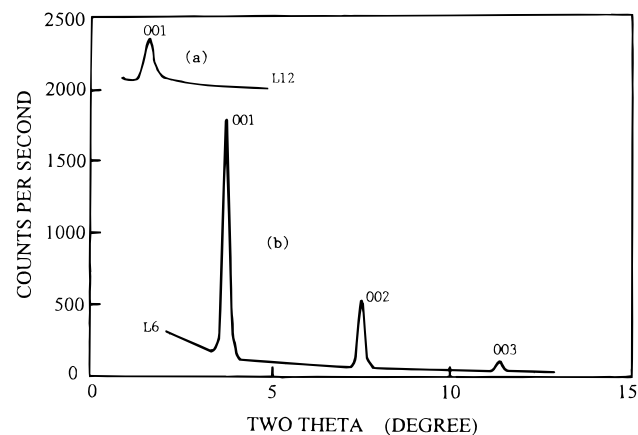

**Figure 3.** X-ray diffraction patterns of once-transferred films on silicon substrates using Cu Kα ($\lambda = 0.154$ nm) irradiation: (a) the film of L12, deposited at the point A3 in Figure 1a; (b) the film of L6, deposited at the point (20 mN/m, 0.016 nm^2) in Figure 2c.

6.02 nm (Figure 3a). This value is approximately double the calculated length of L12, which is 3.13 nm. Therefore the film

Letters

J. Phys. Chem. B, Vol. 102, No. 43, 1998 **8355**
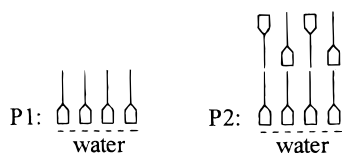
SCHEME 3

SCHEME 4

of L12 on water at A3 must have two identical bilayers, each being 6.02 nm long and each containing two monolayers.

Surface potential−area measurements help to reveal the molecular packing manner in the bilayer (Scheme 2). Molecular simulations of L12 give a permanent dipole moment, whose projection along the long molecular axis directs to the hydrocarbon tail of L12 (Scheme 1). The initial SP increase with compression, as shown in Figure 1b, reflecting that the molecular dipole moments gradually stand up on water, with the chiral head attaching water and the hydrocarbon tail pointing to the air. The SP plateau with compression between A1 and A2 indicates that the molecular dipole moments of the second layer are statistically oriented. The number of molecular dipoles between the two electrodes should increase with compression. To keep the SP constant, it is required that in the second layer the dipoles pointing upward be as many as the dipoles pointing downward (Scheme 2). This is the same as H. Gruler's bilayer structure.[7] The final increase of SP with compression between A2 and A3 implies that the film of L12 on water develops from bilayer to tetralayer, with a "rolling-over" mechanism.[5]

(2) L10. The behavior of L10 on water is different from that of L12 (Scheme 3). It is concluded from the $\pi-A$ isotherm and SP−area isotherm in Figure 2 that L10 forms a tight monolayer at P1 (0.21 nm^2), and a bilayer at P2 (0.12 nm^2). However, the surface potential of L10 decreases with compression in the range 0.07−0.12 nm^2, which is different from that of L12 in this range. Observed under polarized microscope, the film of L10 transferred at P3 (0.07 nm^2) onto quartz substrates shows crystalline domains, indicating a collapse to an undefined state. X-ray diffraction measurement of this film on silicon gives no Bragg peaks for 2θ in 1−5°; also indicating the collapse.

(3) L8, L6, L4, and L2. L8, L6, L4, and L2 all have similar $\pi-A$ isotherms, and, for this reason, only the $\pi-A$ isotherm of L6 is shown in Figure 2c. At the collapse point Q, L6 has an area of 0.0073 nm^2, which is strikingly less than its estimated cross-sectional area 0.18 nm^2. The film at Q should be about $0.18/0.0073 \approx 25$ molecules thick. The film of L6 on water was once-transferred at (20 mN/m, 0.016 nm^2) onto silicon substrates. X-ray diffraction measurement of this film gives patterns (Figure 3b) like those of smectic LC phases or Z-type LB multilayers, both of which have a layer spacing approximately equal to the molecular length. Table 1 compares the calculated molecular length with the experimental d spacings of Ln ($n = 2, 4, 6, 8$) "once-transferred" at a certain molecular area. It is seen from Table 1 that d_{001} is approximately equal to the molecular length and that $d_{001} = 2d_{002} = 3d_{003}$. The X-ray diffraction patterns were obtained with the scattering vector perpendicular to the substrate surface. Therefore the molecules in the films should stand nearly normal to the substrate surface. The multilayer structure of the films of L2, L4, L6, and L8 at their deposition areas is depicted in Scheme 4. X-ray diffraction measurements also reveal that such a structure does not exceed 2 days on silicon substrates. In addition, such a structure is not like ordinary smectic phases, since the film transferred on quartz is observed to be uniformly dark under a polarized microscope.
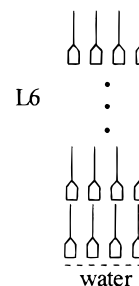
TABLE 2: d Spacings of Once-Transferred Films of Ln Produced by "Freely Dropping" a Certain Volume on the Water Area 33.5 cm^2

Ln	concn (mg/mL)	volume (μL)	d_{001} (nm)	d_{002} (nm)	d_{003} (nm)
L2	1.8	35	2.12	1.04	
L4	2.3	45	2.12	1.06	0.705
L6	1.8	75	2.35	1.17	0.778
L8	3.6	60	2.61	1.29	

Polarized FT-IR studies of the films of L6 once-transferred onto CaF$_2$ substrates show that L6 stands with its long molecular axis nearly normal to the substrate surface. The hydrocarbon chains $-(CH_2)_6-$, the $>C=N-$, the ether linkage, and the two benzene planes are oriented preferentially normal to the substrate surface. Temperature-variable FT-IR studies reveal that when heated to 75 °C, the $>C=N-$, the ether linkage and the two benzene planes become more normal to the substrate surface, indicating a transition from the solid crystalline phase to the smectic LC phase. The phase behavior of L6 in the bulk has been studied by DSC,[8] polarized microscopes,[8] and temperature-variable FT-Raman spectroscopy.[10] By comparing the phase behavior of L6 in the bulk with that in the "once-transferred films", it is concluded that in the films L6 is somewhere between the ordinary solid crystalline phase and the smectic LC phase. In addition, FT-IR studies of the "once-transferred films" on CaF$_2$ detect no water, thereby excluding the involvement of water in the multilayer formation.

The multilayer structure of Ln ($n = 2, 4, 6, 8$) has formed spontaneously after dropping their chloroform solution onto water, rather than due to the compression of barriers. First, the surface potential and pressure of L2, L4, L6 and L8 on water do not change with barrier movement in the range 0.06−0.6 nm^2. Second, the following "free-dropping" experiment without barrier movement also produces such multilayers. The Ln was dropped from their chloroform solution to a small water area of 33.5 nm^2. During dropping, the water surface was observed with eyes, and the dropping was stopped when small crystallites were seen. After dropping, 10 min was left for sheets of films to appear. Appropriate dropping quantity is when sheets of films were seen to pack closely on water, but no crystallites appeared. Table 2 lists the d spacings of these films once-transferred onto silicon, measured by X-ray diffraction. These d spacings are the same as those in Table 1.

4. Discussions

The spontaneous multilayer formation of L2, L4, L6, and L8 on water is interesting and has never been reported. A relevant finding maybe that some smectic liquid crystal molecules deposited on solid substrates by thermal evaporation in vacuo

8356 *J. Phys. Chem. B, Vol. 102, No. 43, 1998*

Letters

can have layered structures.[11] The mechanism of this spontaneous behavior is up to now not clear. It is not straightforward that because the L*n* is smectic in the bulk, it should form smectic multilayers on water. Miscellaneous LC compounds with LC transition in the room-temperature range or higher have been spread onto the water surface. According to the reviews by Ulman,[3] they do not form multilayers spontaneously. The self-assembly of L2, L4, L6, and L8 on water seems to be related with their hydroxyl. H. Gruler's HOBACPC [7] is much like L6, but does not have the hydroxyl. HOBACPC forms successively monolayer, bilayer, trilayer under the compression of barriers, rather than due to self-assembly. Another molecular feature for this self-assembly is the number of CH_2 groups in the terminal group. As described above, the L8 with $(CH_2)_8$ can self-assemble into multilayers, while the L10 with $(CH_2)_{10}$ cannot self-assemble.

In another paper we shall report the spontaneous multilayer formation of L2, L4, L6, and L8 on aqueous $Ni(CH_3COO)_2$ subphase, where the hydroxyls of two L*n* incorporate one Ni^{2+}.

Supporting Information Available: Microscopic images of FTIR studies (1 page). Ordering and accessing information is given on any current masthead page.

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