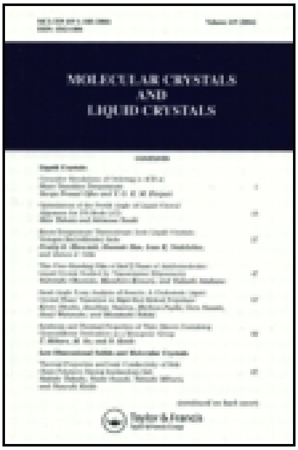

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Yoko Matsuzawa [a] & Mutsuyoshi Matsumoto [a]

[a] Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan

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LB MONOLAYERS COMPOSED OF AMINIMIDE DERIVATIVES HAVING TWO ALKYL CHAINS. WETTING PROPERTIES AND ALIGNMENT OF NEMATIC LIQUID CRYSTALS

Yoko Matsuzawa and Mutsuyoshi Matsumoto*
Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, AIST Tsukuba Central 5-2, 1-1-1 Higashi, Tsukuba, Japan 305–8565

LB monolayers were prepared using a series of aminimide derivatives having two alkyl chains. One of the alkyl chains had 19 carbons, while the number of carbons of the other alkyl chain was systematically changed from 12 to 20. Inter-chain packing and conformational order of the alkyl chains in the monolayer were affected by the length of the two alkyl chains. Static and dynamic contact angles of a series of aprotic liquid having low surface tension were measured investigate surface properties of the films with varying molecular organization of alkyl tail groups. Contact angle hysteresis on the monolayers were sensitive to the sort of probe liquids owing to the interaction between the uppermost portion of the alkyl chains and contacting probe liquids through steric and van der Waals interaction. Nematic liquid crystals (LC) aligned homeotropically on the fluid-like monolayers. In contrast, the monolayer containing well-ordered and well-packing alkyl chains indicate low wettabilities, small hysteresis and random orientation of LC.

Keywords: homeotropic alignment; hysteresis; sessile drop method; surface tension; Wilhelmy plate method

INTRODUCTION

The alignment of liquid crystals (LC) to result in an uniform orientation may not only be achieved by electric or magnetic fields but also by action suitable prepared surfaces on solid surfaces. The interfacial properties of LC are of great interest of basic science understanding and for practical application to LC devices. Solid-LC surface interactions are described by means of surface tension of both materials and the FCK rule has been

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*Corresponding author. Tel. & Fax: +81-298-61-4669, E-mail: yoko-matsuzawa@aist.go.jp widely supported by experimental data [1]. However, taking microscopic processes into consideration lack in the FCK rule.

In this work, we prepared LB monolayers on solid surface as surface active agent using amphiphilic aminimides having two alkyl chains (Fig. 1). One of the alkyl chains tethered at amide position has fixed length ($C_{19}H_{39}$), while the length of other alkyl chain at amine position is systematically changed. We have employed this strategy for the preparation of LB films because the two alkyl chains of almost the same length will give planar surface, whereas molecules having two alkyl chains of different length will be give molecularly rough surfaces.

LB monolayers of these aminimides are subjected to the static and dynamic contact angle measurements using aprotic organic liquids and investigated their ability to control of alignment of nematic liquid crystals in LC cells. Surface properties of the films will be reflected in the contact angles because the interaction of a solid-liquid interaction is influenced

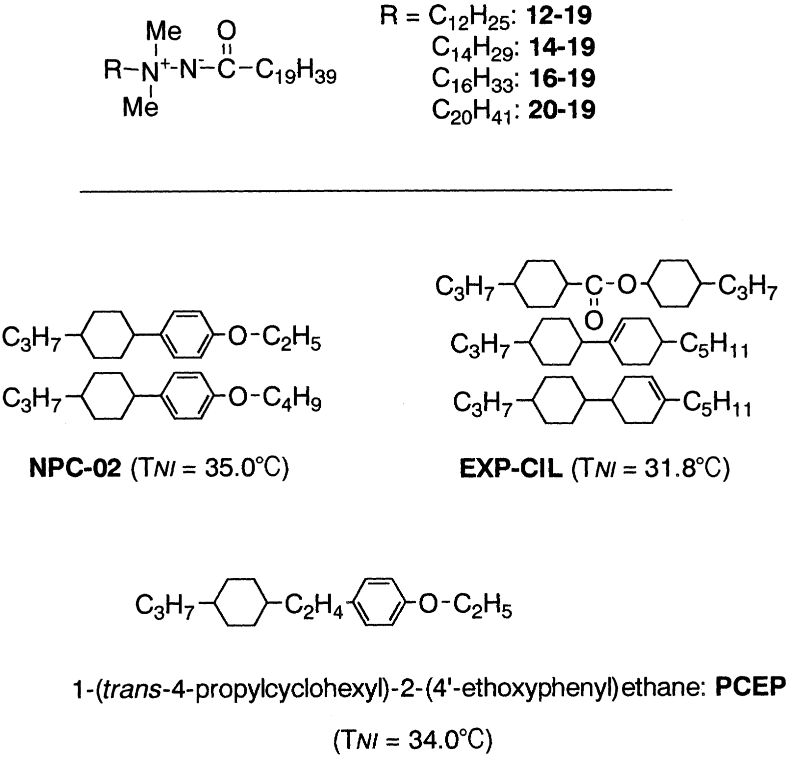

FIGURE 1 Structural formulae of aminimide derivatives and nematic liquid crystals.

only by atoms at or close to the interface [2,3]. Especially we focused on and discussed about hysteresis between advancing and receding contact angles. Alignment of LC on the LB films showing variations in the surface properties is determined.

EXPERIMENTAL

Materials

Details of the synthesis of the aminimide derivatives used in this study (Fig. 1) were described in literature [4]. All probe liquids used in contact angle measurements were purchased from KANTO Chemical Co., Inc. A liquid crystal used to fabricate LC cells (EXP-CIL in Fig. 1) is kindly donated by Rodic Co., Ltd.

Contact Angle Measurements

Langmuir monolayers were transferred onto substrates using LAUDA FW-II film balance at $25\,\mathrm{mN\,m^{-1}}$ at a dipping speed of $5\,\mathrm{mm\,min^{-1}}$. The temperature was set at 20°C by a water circulating system equipped with a thermostat (RC6, RCS: LAUDA). Contact angles of probe liquids on the aminimide LB monolayers transferred on solid substrates were measured using both the sessile drop method and the Wilhelmy balance method. As for the sessile droplet method, we used a contact angle measuring device, CA-X equipped with SA-11 system (Kyowa Interface Science) at ambient condition. A glass syringe with a 28-guage Teflon coated steel needle was used to produce as liquid drop. The typical volume was *ca.* 1 µl. Advancing and receding contact angles were measured according to the method described in literatures [5,6]. Following this technique, small liquid drops were formed on the solid surface using the syringe. While the drop was still in contact with the syringe needle, additional liquid was added to advance the drop edge as slowly as possible. After cessation of the movement of the three-phase contact line, the advancing contact angle (θ_a) was measured. Receding contact angles (θ_r) were measured following the same procedure after withdrawing the liquid from the previously advanced drop. The values reported in this paper are the averages of 10 measurements made on different areas of the sample surface. The advancing and receding contact angles were also measured using the Wilhelmy plate method with a dynamic contact angle analyzer (DCA322, CAHN Instruments). The measured force acting on a thin plate which is partially immersed in a liquid can be represented by the force balance equation [7,8]

$$F = -\rho gtwd + 2(t + w)\gamma_{lv} cos\,\theta$$

where F is the measured force on the equipment, ρ is the liquid density, g is the gravitational acceleration, t is the thickness of the plate, w is the width of the plate, d is the immersion depth, γ_{lv} is the surface tension of the liquid, and θ is the contact angle at the air/solid/liquid three phase contact line. The first term is the buoyancy force and the second term is the interfacial interaction force (wettability force of the liquid on the plate). Probe liquid was poured in a beaker and place inside the closed test chamber. Immersion and emersion of the LB monolayer transferred onto a mica plate were carried out by raising and lowering the beaker stage at a constant speed of $20\,\mu\mathrm{m\,min}^{-1}$.

LC Cells Preparation

The aminimides monolayers transferred onto glass plates by LB technique were paired and spaced with *ca.* 25 μm-thick films of PET to form optical cells. Nematic liquid crystals (Fig. 1) was heated into its isotropic phase, drawn into optical cells by capillary action, and cooled to their nematic phase by leaving at ambient temperature. A polarizing microscope (Olympus: BH3) was used to observe optical textures of the liquid crystals.

RESULTS AND DISCUSSION

Surface Properties of the Aminimidesmonolayers

The all four Langmuir monolayers were deposited onto solid substrates in good transferred ratios. In order to acquire information detailed about monolayer structure, IR-RA and IR-T spectroscopy were performed. According to IR spectroscopic measurements, the film structure becomes less vulnerable to thermally induced disordering with increasing chain length. The alkyl chains in the **20-19** monolayer take *all-trans* conformation while those in the other films contain a considerable amount of *gauche* conformation because of loose packing near the uppermost region of the films.

Many spectroscopic methods have been employed to investigate surface properties of organic thin films such as XPS, optically ellipsometry and scanning force microscopy. In this study, we have used “a wetting method” to measure the surface properties because it is remarkably useful and sensitive in characterizing surface functionality and structure, and is simple. In order to investigate the surface properties of low-energy surfaces whose outer-part is covered with methyl or methylene moieties, we chose aprotic and apolar liquids as probe liquids. This approach assumes that the liquid and the solid interact purely through *van der Waals* interactions.

n-Alkanes (dodecane:**2D**, tridecane:**3D**, tetradecane:**TD** and hexadecane:**HD**) and naphthalene derivatives (decaline:**DL**, tetraline:**TL**, 1-chloronaphthalene:**Cl**, 1-methoxynaphthalene:**MeO**, and 1-chloromethyl naphthalene:**CH_2Cl**) were used in this study.

The difference between the advancing and receding contact angles are plotted in Figure 2 as a function of the chain length at amine position in the monolayers. Large hysteresis was observed for **14-19** and **12-19**. Wetting hysteresis is most often ascribed to surface roughness, chemical heterogeneity or specific interaction between the probe liquid and the surface [9]. n-Alkane, one dissolved in the liquid-like outer part of the monolayer. Will give rise to a combinational contribution to the entropy. The hysteresis becomes large due to increment of degree of interaction between n-alkane liquids and the aminimide monolayers consisting of unsymmetric aminimides. On the other hand, such a relationship is not evident between the hysteresis observed for naphthalene derivatives are not readily dissolved in the hydrocarbons of the monolayers even if the hydrocarbons are liquid-like. Contribution of polarity of naphthalenes might be dominant in this system.

In order to gain an insight into the interaction between the aminimide monolayers and liquids having low surface tension, the Wilhelmy balance method was performed. The Wilhelmy balance method has advantage over the sessile drop method for the following reasons, high reproducibility and elimination of operator's subjectiveness [10]. We applied the method to the aminimide monolayers of **12-19** and **20-19** using **HD** and **DH** as probe liquids.

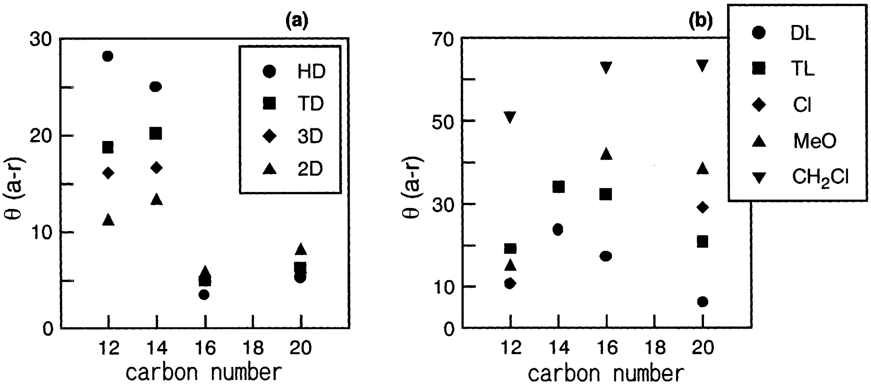

FIGURE 2 The difference between the advancing and receding contact angles as a function of the number of carbons of the alkyl chains tethered at amine position. The measurements were using two series of probe liquids, (a) n-alkanes and (b) naphthalene derivatives.

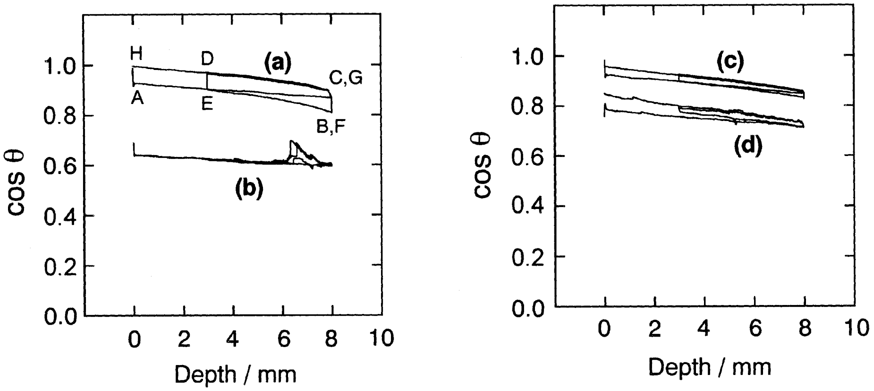

FIGURE 3 Wilhelmy hysteresis loops for the LB films measured using two kinds of liquids. Left: (a) **12-19/HD** and (b) **20-19/HD**. Right: (c) **12-19/DH** and (d) **20-19/DH**. Moving cycle of a plate are A-B-C-D (cycle 1) and E-F-G-H (cycle 2) as shown in (a).

The results are summarized in Figure 3. The location of the loop within the plot and the shape of the loop are affected by the interaction between the monolayers and the probe liquids. As the critical surface tension is larger for the **12-19** monolayer (Fig. 3-a) than that for the **20-19** monolayer (Fig. 3-b), the position of the loop of the former is higher compared with the latter. This trend is observed for the both force loop obtained using **HD** and **DH**, respectively. As for the width of the loop indicating hysteresis in the contact angle, a remarkable difference is evident when **HD** used. The width for the **12-19** monolayer probed by **HD** is larger than that of **20-19** (Fig. 3-a and b). On the other hand, the loop width obtained using **DH** is insensitive to the variation of structure of the surface (Fig. 3-c and d). These results are consistent with those obtained by using the sessile drop method. The results obtained by these two techniques to measure the contact angle of liquid having low surface tension on the low-energy organic surface strongly suggest that the interaction between the molecularly rough outer part of the surface and n-alkane having cylindrical shape is increased due to the solution or penetration of the probe molecules at the interfacial region.

Alignment of LC on the Aminimides Monolayers

Figure 4 shows polarizing micrographs of LC cells using the LB monolayer of **12-19** and **20-19**. The LC molecule exhibits drastic changes in their alignment depending mainly on surface properties of the LB films. The

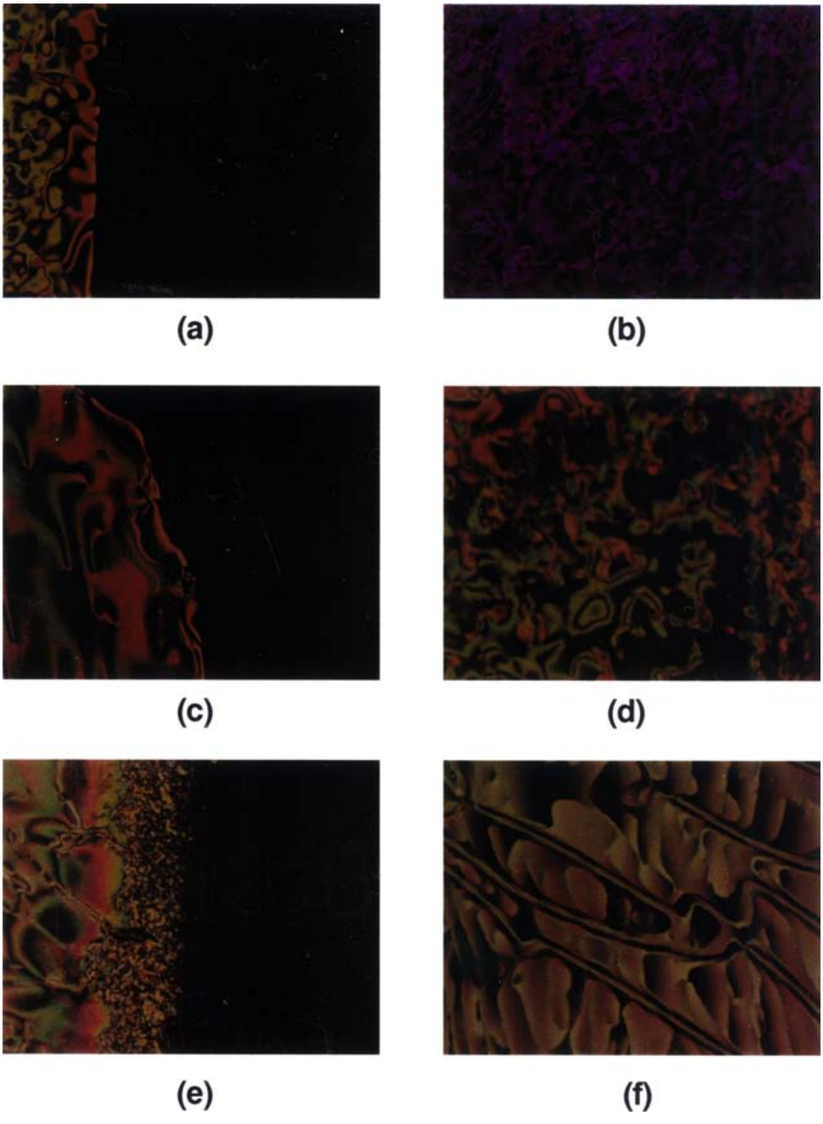

FIGURE 4 Polarizing micrographs of the LC cells prepared aminimides LB monolayers and LC, EXP-CIL (a: **12-19** and b: **20-19**), NPC-02 (c: **12-19** and b: **20-19**) and PCEP (e: **12-19** and f: **20-19**). (See COLOR PLATE V)

12-19 monolayer composed of unsymmetric aminimides having relatively short alkyl chain at amine position produce homeotropically anchored nematic phases for nematic liquid crystals (Fig. 4-a, c, and e). This LC cell maintained the homeotropic alignment even after 1 month. These results suggest that the hydrocarbons of the nematic LC and n-alkanes should dissolve or penetrate into the hydrocarbon region of the molecularly rough surface of the **12-19** monolayer. The nematic liquid crystals interacting with the surface should be oriented perpendicularly to the surface due to mainly to the steric effect. This orientation at the interfacial region will be transferred into the adjacent bulk of nematic liquid crystals by the elastic interaction forces. In contrast, the **20-19** monolayer of the aminimide having two alkyl chains of similar length causes non-uniform planar anchoring (Fig. 4-b, d and f). The orienting surface action is small for smooth and rigid surface of the **20-19** monolayer because dissolution or penetration of LC (and n-alkanes) will not occur. This results in random-planar orientation of LC.

CONCLUSION

We investigated length effect on alkyl tail groups of amphiphilic aminimide derivatives on molecular organization and surface properties of the LB monolayers. Static and dynamic contact angles were measured to characterize of the LB monolayers. Fluid-like monolayers composed of unsymmetrical aminimide derivatives indicated high wettabilities, large contact angle hysteresis, and ability to align liquid crystals homeotropically. On the other hand, the well-ordered monolayer composed of symmetrical aminimides indicated low wettabilities, small hysteresis, and random orientations of LC.

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