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The formula of dielectric polarization of Langmuir monolayers with $C_{\infty v}$-symmetry has been derived, using orientational order parameters expressed by Legendre polynomials. It is shown that Maxwell Displacement Current (MDC) measurement coupled with Optical Second Harmonic Generation (SHG) measurement is helpful for the study of orientational orders and the phase transitions in monolayers. Using this measurement, monolayers of 4′-n-octyl-4-cyanobiphenyl (8CB) on the water surface was examined by monolayer compression. The phase transition from planar to polar orientational alignment phase was clearly predicted in the region of low surface pressure.

Keywords: Maxwell displacement current; second harmonic generation; Langmuir monolayer

INTRODUCTION

Organic monolayers on the surface of materials show specific electrical and optical phenomena as a two-dimensional system due to symmetry breaking at the interface. For example, they have spontaneous polarization due to their non-centrosymmetric structure, and optical second harmonic generation (SHG) is allowed. Over the last ten years, we have been investigating organic monolayers from the viewpoint of dielectric physics, keeping in mind the difference between the bulk materials and organic ultra-thin film. The authors recently wrote a book entitled "*The Physical Property of Organic Monolayers*" [1], where they stressed the importance of the study of organic monolayer films from the viewpoint of electronics and dielectric physics. Among the preparation technique of organic monolayers, the simplest and easiest way would be to form monomolecular films on the water surface. As such, the physico-chemical property of monolayers at the air-water interface has been a research subject for physicists, chemists and biologists since the discovery of the preparation technique of floating monomolecular films by Langmuir [2].

Obviously, the physical property of organic monolayers depends on their structure. Thus many researches have been done to clarify the relationship between the dynamical features of monolayer systems and their structures. From the theoretical side, the monolayer systems are viewed as quasi two-dimensional (2D) systems and their states are characterized by the positional and orientational distributions of constituent molecules. In corresponding to these two distributions, two order parameters are used. One is the *in-plane* planar order parameter that expresses the positional distribution of the heads of amphiphilic molecules and the other is the orientational order parameter that expresses the orientational distribution of hydrophobic long-tails of the molecules. The physico-chemical properties of monolayers are expressed using these two parameters. Among these two kinds of parameters, the latter one is essentially important for monolayers because this parameter expresses the specific property of monolayers that is induced due to symmetry breaking at the interface [3]. Thus by studying the orientational orders and tilting behavior of monolayers, we could obtain very important insight in monolayer physics.

Along with this idea, we have investigated monolayers on the water surface from the viewpoint of dielectric physics, where the knowledge of the polarization of monolayers in association with the orientational parameters is very important. The topic discussed here is related to the detection of the phase transition of monolayers as well as to the determination of orientational order parameters by Maxwell-Displacement Current (MDC) measurement [3] coupled with SHG measurement [4,5,6,7].

In the present paper, we derive the formula to express the linear and nonlinear polarization of monolayers with a $C_{\infty v}$-symmetry. We then show that MDC measurement coupled with SHG measurement is helpful for the study of orientational orders of organic monolayers that have non-centrosymmetric structure [3,6,7]. We also show that the technique is very helpful for the detection of the phase transition of these monolayers. Finally we show some experiments on 4′-n-octyl-4-cyanobiphenyl (8CB) monolayers during monolayer compression.

ANALYSIS

It is well known that monolayers on water surface exhibit various phases such as liquid-crystalline, solid phases and others [2]. For simplicity, we here assume that monolayer is composed of uniaxial rod-like polar molecules with a permanent dipole moment μ along its molecular long axis, and with anisotropic electronic polarizabilities $\alpha_{\perp}$ and $\alpha_{\parallel}$. Obviously this model is very simple, but we can obtain very important insight in

physics of monolayers, especially concerning the orientational orders and phase transitions [1]. To analyze the dielectric property of monolayers, we here derive the formula of dielectric polarization of monolayers as follows. We choose the coordinate system in such a way that the monolayer plane is parallel to the water surface ($x-y$ plane) and the monolayer normal falls along the positive z-axis, as shown in Figure 1. The angle that the dipole at the origin makes with the layer normal is denoted by θ. The dipole at the origin is facing on the water surface. The molecule orientates with a counter-clockwise azimuthal angle ϕ from y-axis. The coordinate system (x', y', z') is attached to the dipolar molecule at the origin with z'-axis pointing toward the molecular long axis, and x'-axis on the $x-y$ plane with a counter-clockwise angle ϕ away from x-axis. The polarization of monolayers is the sum of the spontaneous polarization $\mathbf{P}_0$, linear polarization $\mathbf{P}_d$ and nonlinear polarization $\mathbf{P}_N$.

The main contribution to the generation of MDC is the spontaneous polarization $\mathbf{P}_0$ in the direction toward air, normal to the surface. This polarization changes by external stimuli such as compression and photoirradiation. The vertical component of spontaneous polarization $\mathbf{P}_z$ is calculated, assuming $\mathbf{n} = (0, 0, 1)$ is the unit vector normal to the water surface (z-axis), and $\mathbf{m} = (\sin\theta_t, 0, \cos\theta_t)$ is the tilting-direction of monolayers in the $z-x$ plane on the water surface (see Fig. 1). It is given by

$$P_0 = N\mu S_1(\mathbf{n}\cdot\mathbf{m}). \tag{1}$$

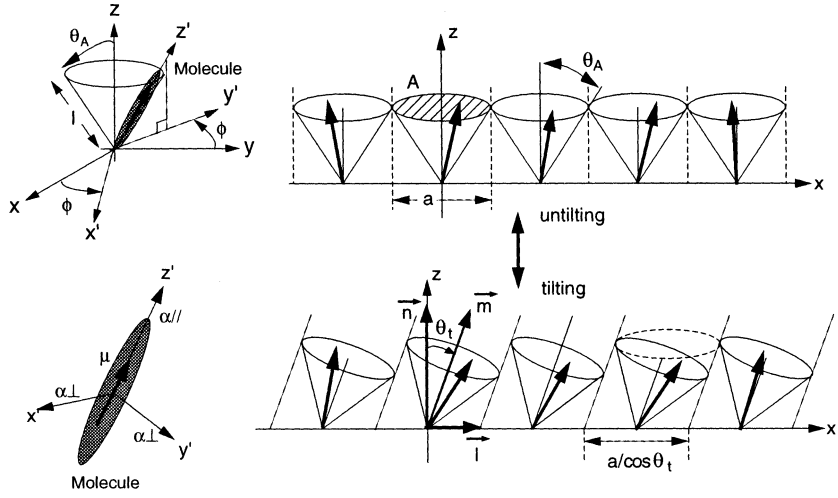

FIGURE 1 Model of molecule and monolayers. Untilting monolayers and tilting monolayers are shown.

Here N_s is the surface density of molecules, and S_1 is the orientational order parameter defined as $S_1 = \langle \cos\theta \rangle$. θ is the tilt angle of the molecular-long axis from the normal direction to the water surface and $\langle\ \rangle$ represents the thermodynamic average all over direction of molecules. For example, in a special case that molecular motion is restricted within the angle $0 < \theta < \theta_A$ due to hardcore repulsive interaction among molecules as shown in Figure 1(a), both **n** and **m** become (0,0,1), and thus S_1 is calculated as $(1 + \cos\theta_A)/2$ [8]. On the one hand, in the case that molecules lie on the water surface due to the electrostatic coulomb attractive force working between the molecules and the water surface, the molecular motion is restricted to the case only with an angle $\theta_A = \pi/2$, and S_1 becomes 0. The latter case appears when the molecular area A is greater than $A_0 = \pi l^2$ (l : the length of long chains of polar molecules), and the former case appears when the molecular area A is smaller than $A_0 = \pi l^2$. Thus it is postulated that the phase transition from planar to orientational alignment phase happens at the molecular area A_0 by monolayer compression [9].

On the other hand, the main contribution to the generation of the SHG is the nonlinear polarization $\mathbf{P}_N$ induced by laser irradiation. For monolayers with $C_{\infty v}$-symmetry that are composed of non-chiral molecules standing vertically to the substrate surface, $\mathbf{P}_N$ is expressed using three molecular SOS components ($s_{pq}; p, q = 1, 2, 3$) in a vector form as [3]

$$\mathbf{P}_N = (s_{33} - s_{31} - s_{15})(\mathbf{n}\cdot\mathbf{E})^2\mathbf{n} + s_{15}(\mathbf{n}\cdot\mathbf{E})\mathbf{E} + s_{31}(\mathbf{E}\cdot\mathbf{E})\mathbf{n}. \tag{2}$$

Here s_{15}, s_{31} and s_{33} are the components of second order susceptibility (SOS) tensor of a monolayer, and they are defined using the components of molecular SOS, i.e., β_{ijk} $(i, j, k = 1, 2, 3)$, and the molecular orientational order parameters S_1 and S_3 expressed by Legendre polynomials, i.e., $S_1 = \langle \cos\theta \rangle$ and $S_3 = \langle (5\cos^3\theta - 3\cos\theta)/2 \rangle$. The suffixes (1, 2, 3) are commonly referred to the laboratory frame (x, y, z) and the molecular frame (x', y', z'). The components of SOS tensor s_{15}, s_{31} and s_{33} are given by

$$\begin{aligned}
s_{15} &= N_s(S_1 - S_3)(2\beta_{333} - \beta_{322} - \beta_{311})/5 \\
&\quad + N_s(3S_1 + 2S_3)(\beta_{223} + \beta_{232} + \beta_{113} + \beta_{131})/10 \\
s_{31} &= N_s(S_1 - S_3)(2\beta_{333} - \beta_{223} - \beta_{232} - \beta_{113} - \beta_{131})/10 \\
&\quad + N_s(4S_1 + S_3)(\beta_{322} + \beta_{311})/10 \\
s_{33} &= N_s(S_1 - S_3)(\beta_{322} + \beta_{311} + \beta_{223} + \beta_{232} + \beta_{113} + \beta_{131})/5 \\
&\quad + N_s(3S_1 + 2S_3)\beta_{333}/5.
\end{aligned} \tag{3}$$

It is interesting here to discuss the change of polarization induced by the phase transition. Firstly, as mentioned earlier, it is postulated that the phase transition from planar to orientational alignment phase happens at the molecular area A_0 by monolayer compression. At this molecular area,

the polar molecules take off from the water surface. Thus the spontaneous polarization $\mathbf{P}_z$ changes from 0 to $N_s\mu S_1$ (see Eq. (1)). Similarly, the vertical component of nonlinear polarization P_z^N changes from 0 to $\mathbf{P}_N \cdot \mathbf{n}$ (see Eq. (2) and Fig. 1).

Secondly, as described in our previous paper, the tilting to a nearest neighbor (NN) and to a next-nearest neighbor (NNN) is observed for monolayers such as fatty acids and others [8,11] using x-ray and other spectroscopic techniques. Thus it is interesting to discuss the change of polarization in monolayers induced by the Untilting to tilting (U-t) phase transition. It is postulated that the symmetry of monolayer is changed to C_s when monolayers with $C_{\infty v}$-symmetry experience this transition. In this case when director of constituent molecules in monolayers tilts with an angle θ_t from the normal (z-axis) in the $x-z$ plane (see Fig. 1), the amount of nonlinear polarization $\mathbf{P}_N$ given by Eq. (2) changes to

$$\mathbf{P}_N = (s_{33} - s_{31} - s_{15})(\mathbf{m} \cdot \mathbf{E})^2\mathbf{m} + s_{15}(\mathbf{m} \cdot \mathbf{E})\mathbf{E} + s_{31}(\mathbf{E} \cdot \mathbf{E})\mathbf{m}. \qquad (4)$$

Here $\mathbf{m}$ is the unit vector that represents the tilting direction (see Fig. 1). By expanding Eq. (4) into the elements of P_x, P_y and P_z, we can easily check that the polarization given by Eq. (4) represents the polarization of monolayers with C_s-symmetry in the laboratory frame (see Table I in ref. [12]).

In the MDC measurement, the change of the spontaneous polarization P_z in the normal direction is measured during monolayer compression. Thus the MDC is helpful for the detection of both phase transitions mentioned above. On the other hand, in the SHG measurement, we can detect signals such as s-polarized component or p-polarized component of the reflected and transmitted SH wave from monolayers by the laser irradiation [4]. As a result, the generation of SHG signal depends on the states of monolayers. In more detail, for simplicity, if no account is taken of the local field correction factors such as Lorentz factor, the intensity of SHG is proportional to the square of $\mathbf{E}_{\text{out}} \cdot \mathbf{P}_N$, where $\mathbf{E}_{\text{out}}$ is the unit vector of the SH electric field after passing through the output polarizer. Thus the SHG measurement is helpful for the study of such phase transitions mentioned earlier. Furthermore, it is needless to say that we can determine the orientational order parameters S_1 and S_3 from the MDC and SHG measurements, because the polarization of monolayers at various states are expressed by using these parameters and the polarization of monolayers is detected in MDC and SHG measurements [6,7]. Based on the above discussion, we may conclude that MDC and SHG measurements are helpful for the study of orientational orders of monolayers as well as the detection of tilting phase transition.

EXPERIMENTAL

Method

Figure 2 shows a schematic diagram of MDC measurement coupled with SHG measurement, where electrode 1 is suspended in air and it is placed parallel to the water surface, and electrode 2 is immersed in water. These two electrodes 1 and 2 are connected to each other through an electrometer. The induced charge on electrode 1 changes in accordance with the orientational motion of molecules on the water surface as well as the change of surface density of molecules. In the MDC measurement, monolayers are compressed with aid of two moving barriers. MDC flows through the closed circuit (see Fig. 2). The charge induced on electrode 1 suspended in air due to the spontaneous polarization is expressed as [1]

$$Q_1 = -P_z B/L - C\phi_s \ , \tag{5}$$

where B is the working area of electrode 1, C is the capacitance between electrode 1 and the water surface, L is the distance between electrode 1 and the water surface, and ϕ_s is the surface potential of water. Assuming that molecules lie on the water surface in the range of low surface pressure due to the electrostatic coulomb interaction working between polar molecules and water, i.e., the orientational order parameter $S_1 = 0$, the order parameter S_1 defined by Eq. (5) is calculated [1]. Furthermore it is clear from Eq. (5) that the MDC flows due to the change in orientational order parameters. Thus it is postulated that we can easily detect such phase transitions described in previous section.

On the other hand, optical second harmonic light is generated from monolayers by laser irradiation. In Figure 2, the experimental arrangement

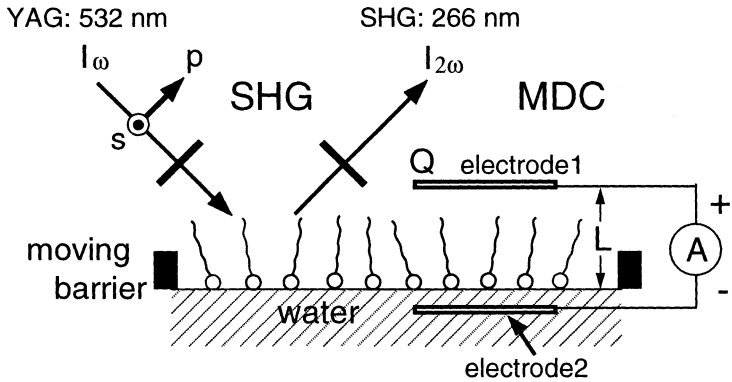

FIGURE 2 MDC and SHG measurement.

is shown. The angles θ_{in} and θ_o represent the incident and the output ones, respectively (see Fig. 3). The angles δ and γ represent the polarized angles of incident light and output SH light, respectively. The SH generation is due to the electronic polarization induced by external electric field. The input light is the sum of *s*- and *p*-polarized waves and it is expressed as

$$\mathbf{E}_{\text{in}} = S_\omega \mathbf{s}_{\text{in}} + P_\omega \mathbf{p}_{\text{in}}\,, \tag{6}$$

where $\mathbf{s}_{\text{in}}$ and $\mathbf{p}_{\text{in}}$ are unit vectors for *s*- and *p*-polarized waves, and S_ω and P_ω represent the amplitude of *s*- and *p*-polarized waves, respectively. Assuming that the incidence plane is in the $x-z$ plane (see Fig. 3), the elements of $\mathbf{s}_{\text{in}}$ and $\mathbf{p}_{\text{in}}$ are given by $(0,-1,0)$, $(\cos\theta_{\text{in}}, 0, \sin\theta_{\text{in}})$, respectively. Further the angle of the polarizer is chosen as δ for the input light (see Fig. 3), S_ω and P_ω are given by $S_\omega = \mathbf{E}_{\text{in}} \sin\delta$ and $P_\omega = \mathbf{E}_{\text{in}} \cos\delta$, respectively. Similarly, output light is the sum of the *s*- and *p*-polarized waves. Taking into account them, we could show that the output light intensity $I_{2\omega}$ is proportional to the square of $\mathbf{E}_{\text{out}}(2\omega) \cdot \mathbf{P}_N$. Thus by choosing appropriate angles δ and γ, the orientational order parameters of monolayers can be estimated [3]. Furthermore, it is clear that the SHG intensity is dependent of polarization and the direction of the electric field of output signals. Thus we may conclude that the phase transitions such as the transition from the planar to orientational alignment phase and tilting phase transition can be detected by the SHG measurement.

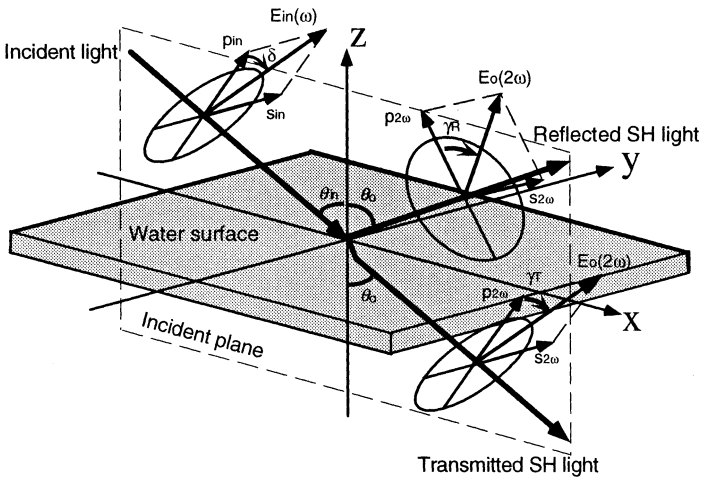

FIGURE 3 Optical arrangement for SHG measurement.

Measurement

The MDC and SHG experiments were performed using the experimental setup described in our previous paper [6,7]. Briefly, the experimental setup consists of Langmuir-trough equipped with a two-electrode arrangement for the MDC measurement and optical measurement arrangement with a Q-switched Nd:YAG laser (wavelength 0.532 μm, pulse duration <7 nsec, fundamental pulse rate <15 Hz) for the SHG measurement (see Figs. 2 and 3). The rectangular-shape Langmuir-trough (600 mm × 150 mm in length and width, 10 mm in depth) is composed of polytetrafluoroethylene (PTFE) and it is filled with pure water (electrical resistivity $> 17\,\mathrm{M\Omega\cdot cm}$). One transparent silica glass slide plate is attached to the bottom of the LB trough for the SHG measurement. For MDC measurement, transparent glass slide coated with Indium Tin Oxide (ITO) is used as electrode 1. It is placed in air parallel to the water surface at a distance of 1 mm. Electrode 2 is a gold-wire (1 mm ϕ and 500 mmL) and it is immersed in the water. Electrodes 1 and 2 are connected to each other through an electrometer (Keithley 617) whose internal electrical resistance is negligibly small. For the SHG measurement, the Q-switched laser is irradiated onto monolayer at an intensity of about 6 mJ with a pulse rate of 2 Hz. The laser spot size was about 56 mm^2. The fundamental light was incident to the water surface with an incident angle (θ_{in}) of 60°. The surface pressure of monolayer is measured during monolayer compression by a Wilhelmy plate.

Monolayers of 8CB were used in the experiment. The 8CB monolayers were compressed at a speed of 10 $\mathrm{mm\,min^{-1}}$ (0.056 $\mathrm{nm^2\,min^{-1}\,molecule^{-1}}$). It is expected that the permanent dipole moments of methyl and cyano groups in 8CB molecules make the contribution to the generation of MDC, whereas the electronic polarization of biphenyl group with alkyl and cyano-groups makes the contribution to the SHG. It should be to note that as monolayers are placed on the water surface, the contribution of hydrophilic part is diminished owing to the screening effect by the water with a high dielectric constant. Thus, although the dipole moment of methyl group is negligible in comparison with that for the nitorile, the long alkyl chain parts also make the contribution to the generation of MDC, in a manner as we can see the similar results for fatty acids monolayers [9,10].

RESULTS AND DISCUSSIONS

Figure 4 (a) and (b) show a typical example of the MDC-SHG measurement for 8CB monolayers corresponded to *p*-output and *s*-output, respectively, where the laser irradiation was carried out with a wavelength of 0.532 μm. The absorption peak of 8CB molecule which could be assigned to the lowest $\pi - \pi^*$ transition is located at around 280 nm in absorption spec-

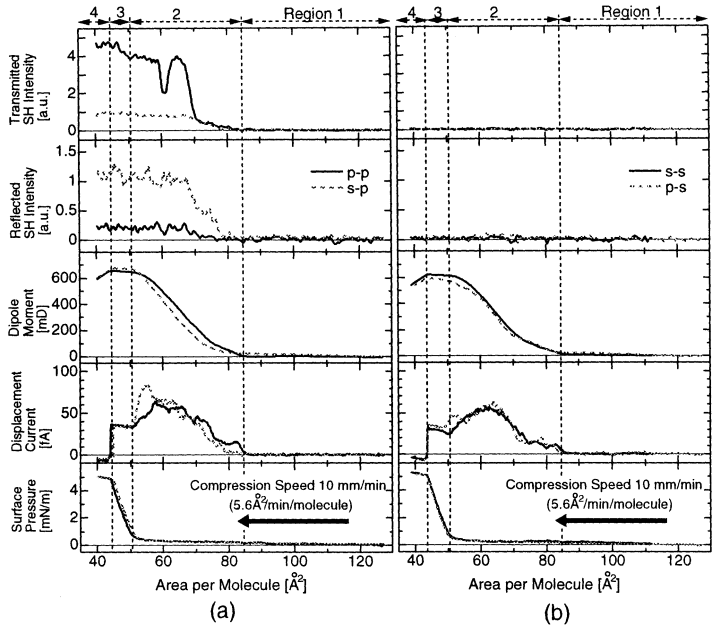

FIGURE 4 Typical examples of SHG and MDC of 8CB monolayers by monolayer compression. (a) p-polarized light is radiated, and (b) s-polarized light is radiated.

trum. From the quantum mechanical consideration, resonance enhancement of SHG occurs, when the wavelength of the second-harmonics is located at the optical absorption band. As a result, the S/N ratio is expected to increase in the SHG measurement. The incident and output lights are polarized waves, and they are as indicated in the figures such as $p-p, s-p$ and others. From bottom to top, the surface pressure-area, MDC-area, dipole moment-area, reflected SH intensity-area, and transmitted SH intensity-area are plotted. As we can see in the figure, the MDC and SHG signals are generated in nearly stable, except for some fluctuation due to domain formation of LC molecules and the thermodynamical motion of the water surface, and they are generated in accordance with the change of molecular area. The isotherms can be divided into four regions as shown in the figure. In the region 1, MDC is very small and almost zero. Similarly the SH intensity is also very small. These results suggest that the molecules lie on the water surface and the molecules are randomly distributed on the water surface. That is, the monolayer is in the planar and isotropic state. On the other hand, the MDC begins to flow by monolayer compression in region 2. Similarly, the SHG is observed for the *p*-polarized light radiation, whereas it is not observed for the *s*-polarized light radiation. Although the

two-photon fluorescence is also observable in the SHG measurement, the null signal obtained under the $s-s$ polarization condition suggests that two-photon fluorescence makes no contribution to the SH signal. These results suggest that the molecules take off on the water surface by monolayer compression, and the nonlinear polarization is induced by laser irradiation. This polarization is expressed by Eq. (2). That is, the monolayer of 8CB has a $C_{\infty v}$-symmetry in this region. In our previous study, we concluded that the planar to polar orientational alignment phase transition happens at the onset of region 2 during compression. Our present experimental results support our previous conclusion [9,10]. Furthermore the SHG experiments suggest to us that the molecular structure in region 2 is $C_{\infty v}$-symmetry. In our previous study, we only speculated this monolayer structure based on the MDC measurement, but the present experiment using the MDC coupled with the SHG measurement clearly shows the experimental evidence of this structure. In more detail, the permanent dipole moments of methyl and cyano groups in 8CB molecules make the contribution of the generation of MDC, whereas the electronic polarization of biphenyl group with alkyl and cyano-groups makes the contribution to the SHG. Thus from the experimental result, we may postulate that the core of 8CB molecules and long alkyls rotate in a similar way by monolayer compression. In region 3, MDC flows steadily by further compression. SH light is also generated stably, where the transmitted light slightly increases by compression whereas the reflected light is generated steadily. At the end of region 3, MDC current decreases abruptly by further compression, whereas the SHG generation is in a way similar to that in region 3. These experimental results support the conclusion that the transition from one layer to a three-layer smectic structure is induced in region 4 by monolayer compression [13].

As mentioned above, using MDC measurement coupled with SHG measurement, we examined the orientational behavior of 8CB monolayers on the water surface. The measurement employed here will be helpful for a better understanding of the dielectric behavior of monolayers on the water surface.

CONCLUSION

The dielectric polarization of organic monolayers at the air-water interface has been analyzed. The formula of polarization of organic monolayers is derived and it is expressed using orientational order parameters expressed by the Legendre polynomial. It was revealed that MDC measurement coupled with SHG measurement is helpful for the determination of these orientational order parameters as well as the detection of phase transitions.

Monolayers of 8CB on the air-water interface were examined during monolayer compression and the phase transition from planar to polar orientational order state was confirmed.

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