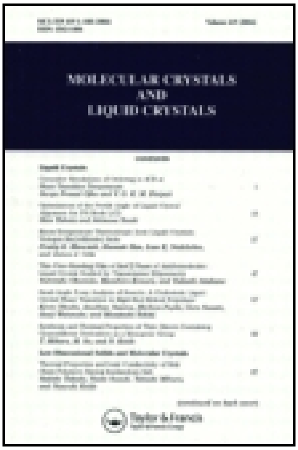
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DETECTION OF PHASE TRANSITION OF 4-HEPTYLOXY-4′-n-CYANOBIPHENYL LANGMUIR FILMS BY MAXWELL DISPLACEMENT CURRENT AND OPTICAL SECOND HARMONIC GENERATION MEASUREMENT

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We investigated 4-heptyloxy-4′-n-cyanobiphenyl (7OCB) Langmuir films by monolayer compression using Maxwell displacement current (MDC) and optical second harmonic generation (SHG) measurements. In the region with a slope in the surface pressure – area (π-A) isotherm, it was found that the s-s and p-s SH signals were suddenly generated by monolayer compression, although the change of MDC was very gentle. This result reveals the appearance of phase transition accompanying the monolayer structural change from $C_{\infty v}$ to Cs-symmetry, due to the shear induced azimuthal in-plane reorientation in monolayers.

Keywords: Langmuir film; Maxwell displacement current; MDC; phase transition; second harmonic generation; SHG

INTRODUCTION

The rich polymorphism and phase transitions in monolayers of amphiphilic molecules have been recognized from the existence of kinks or plateaus in the surface pressure – area (π-A) isotherms. Recently, a variety of experimental techniques coupled with π-A isotherm measurement have been

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developed for a profound understanding of the property of monolayers in association with the monolayer structure [1,2]. The authors have been paying attention to the dielectric polarization phenomena in monolayers, originating from the symmetry breaking at the interface [3], and have been developing a novel instrument equipped with Maxwell displacement current (MDC) and optical second harmonic generation (SHG) measurement system [4–6]. Using this instrument, liquid crystal monolayers such as 4-pentyl-4′-n-cyanobiphenyl (5CB) have been examined. The orientational order parameters have been determined [7] and the phase transition behaviors such as the transition from planar – isotropic phase to the polar orientational phase with $C_{\infty v}$-symmetry have been clarified [8]. In all of these studies, the orientational change in molecules in direction normal to the surface was essential.

In this paper, we report our experiment on 4-heptyloxy-4′-n-cyanobiphenyl (7OCB) Langmuir films by monolayer compression, and show for the first time the successful detection of the phase transition originating from the compression shear induced azimuthal in-plane reorientation [9,10] which accompanies the monolayer symmetrical change from $C_{\infty v}$ to Cs, that is the phase transition which does not accompany the orientational change in molecules in direction normal to the surface. In other words, we show the transition which accompanies neither the change in the vertical component of dipole moment by means of MDC and SHG measurements.

MDC AND SHG MEASUREMENTS

The polarization of monolayers on the water surface is given by the sum of spontaneous, linear and nonlinear polarization [11]:

$$\mathbf{P} = \mathbf{P}_0 + \chi^{(1)} \cdot \mathbf{E} + \chi^{(2)} : \mathbf{EE} + \chi^{(3)} : \mathbf{EEE} + \cdots, \tag{1}$$

where $\mathbf{P}_0$ is the spontaneous polarization, $\chi^{(1)}$ is the linear susceptibility, $\mathbf{E}$ is the external electric field and $\chi^{(n)}$ $(n \geqq 2)$ is the n-th order nonlinear susceptibility. The spontaneous polarization $\mathbf{P}_0$ is expressed as $\mathbf{P}_0 = P_0\mathbf{m}$, where $\mathbf{m}$ is unit vector expressing the director. The polarization P_0 is function of dipolar orientation around director $\mathbf{m}$. As the monolayer symmetry is broken at the air-water interface, nonlinear polarization is induced in monolayers due to the interaction between electrons in molecules and external electro-magnetic waves [11]. This induced nonlinear polarization is dependent on the monolayer structure and can be expressed using second order susceptibility (SOS) tensor. For example, the monolayer with C_∞-symmetry for $\mathbf{m}$ is expressed as [4]

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

where s_{ij} are the components of SOS tensor expressed as the function of order parameters of molecular orientation around director **m**.

Figure 1 shows an experimental setup of MDC and SHG measurement system. In the MDC measurement, as the charge $Q\ (= -B_s(\mathbf{P}_0\cdot\mathbf{n})/d_0)$ induced on electrode 1 due to the spontaneous polarization of monolayers on the water surface changes by monolayer compression, MDC flows through the closed circuit. Here B_s is the working area of electrode 1, d_0 is the distance between electrode 1 and the water surface, **n** is unit vector defined in the direction normal to the water surface toward air. MDC is the transient current and it is given by

$$\mathrm{MDC} = -\frac{dQ}{dt} = B_s\frac{dP_0(\mathbf{n}\cdot\mathbf{m})}{dt}. \qquad (3)$$

It is found that MDC is sensitive to the orientational motion of the director **m**, whereas it is not to the azimuth orientational motion.

In the SHG measurement, the induced nonlinear polarization $\mathbf{P}^N$ is detected. Figure 2 shows an optical arrangement for the SHG measurement. Assuming $\mathbf{m} = (\sin\theta\cos\phi,\ \sin\theta\sin\phi,\ \cos\theta)$, we obtain the expression of nonlinear polarization for SHG waves. For example, nonlinear polarization for the generation of s-s wave from monolayers with induced

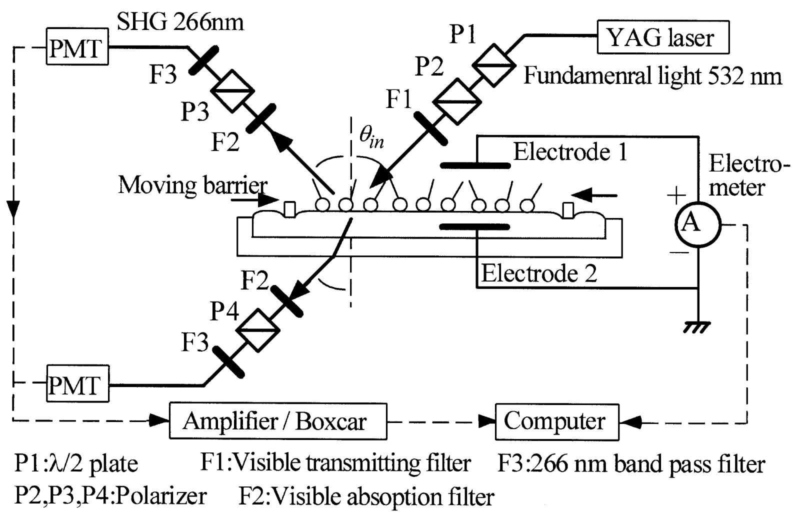

FIGURE 1 An experimental setup of MDC and SHG measurements.

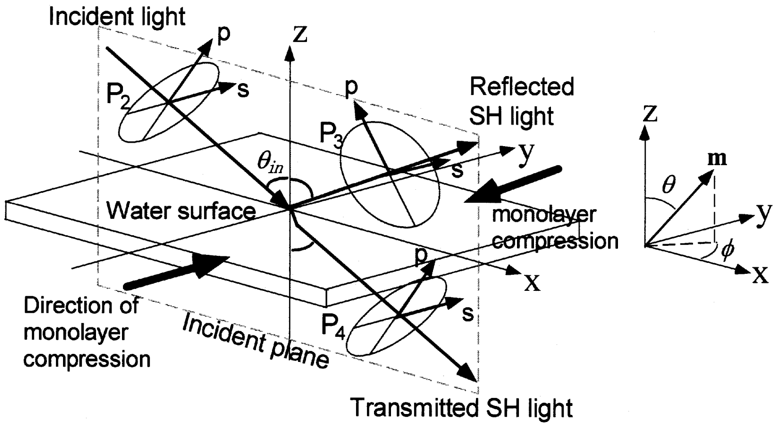

FIGURE 2 A coordinate system of SHG measurement.

nonlinear polarization $\mathbf{P}^N$ given by Eq. (4) can be described as

$$\mathbf{P}_{ss}^N \propto \mathbf{P}^N \cdot \mathbf{s} = \{(s_{33} - s_{31} - s_{15}) \sin^3\theta \sin^3\phi + (s_{31} + s_{15}) \sin\theta \sin\phi\} E_s^2, \tag{4}$$

under assumption $\mathbf{E} = E_s\mathbf{s}$, where $\mathbf{s} = (0,\ 1,\ 0)$.

From Eq. (4) we have the prediction: s-s SH signal is not generated for monolayers with $C_{\infty v}$-symmetry where $\theta = 0$, whereas s-s signal is generated if $\theta \neq 0$ and $\phi \neq 0$. Similarly, we can have the prediction that p-s SH signal is not generated, whereas s-p and p-p signals are generated for monolayers with $C_{\infty v}$-symmetry ($\theta = 0$). By contrast, if $\theta \neq 0$ we have the prediction that s-p, p-p and p-s signals are detected.

It should be noted here again that MDC is very sensitive to the orientational motion of polar molecules, whereas it is not sensitive to the rotational motion on the surface (azimuthal orientational motion). By contrast, SHG can detect the in-plane monolayer symmetrical change. Thus in combination with MDC and SHG measurements, we can gain further information on the phase transition of monolayers by monolayer compression.

EXPERIMENT

The Langmuir-trough is the same as used in our previous study [12]. It is made of polytetrafluoroethylene (PTFE) and filled with pure water (electrical resistivity > 17 MΩ·cm). The transmitted light can pass through a silica glass side attached to the bottom of this trough. The monolayer

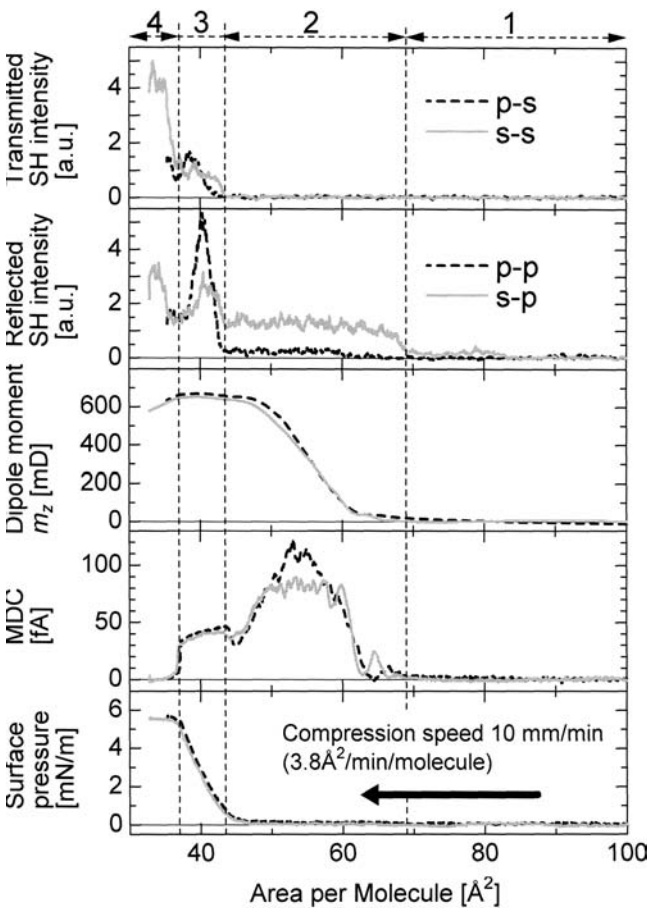

FIGURE 3 A typical example of 7OCB monolayer by compression.

covering area is controlled between 180 ~ 600 mm × 150 mm by moving two barriers. For the MDC measurement, two electrodes 1 and 2 connected through an electrometer (Keithley 617) are used. Electrode 1 is a round shape glass slide coated with Indium Tin Oxide (ITO) with a diameter of 76 mm and it is placed in air to be parallel to the water surface. An air gap is 1 mm. Electrode 2 is a spiral shaped gold wire and it is immersed in the water subphase. For the SHG measurement, Q-switched Nd:YAG laser is used as a light source (Continuum Minilite II). The laser power irradiated onto monolayer, wavelength, pulse rate and irradiated area were about 3 mJ, 532 nm, 2 Hz and about 56 mm^2, respectively. The linearly polarized light by the polarizer (P2) is incident on the monolayer on the water surface at an incident angle of $\theta_{in} = 60°$. The reflected and transmitted SH signals are detected by the photomultiplier-tube (PMT) through the filters (F2, F3) and the polarizers (P3 and P4). The π-A isotherm is also recorded during monolayer compression. In this experiment, we are focusing on the monolayer symmetry. Therefore, s-s, p-s, p-p and s-p signals are measured.

Langmuir films of 7OCB were examined at a monolayer compression of 10 mm/min, after spreading 130 μL chloroform solution with a density of 1 mmol/l onto a water surface using a micro-syringe.

RESULTS AND DISCUSSION

Figure 3 shows a typical example of the MDC and SHG measurement of 7OCB monolayer during compression. p-s and s-s SH transmitted signals and p-p and s-p SH reflected signals are measured.

In region 1, MDC, SHG and surface pressure signals are negligibly small. This result indicates that molecules lie on the water surface, due to the electrostatic attractive Coulomb interaction between molecules and water [3].

In region 2, MDC and the p-p and s-p SH signals begin to rise up and gradually increase by monolayer compression, although the surface pressure and the p-s and s-s SH signals remain nearly zero. These results indicate molecules stand up gradually with randomly azimuthal distribution, i.e., the monolayer has a $C_{\infty v}$-symmetry structure in this region.

In region 3, the surface pressure increases monotonously by further compression. In this region, molecules are packed closely. MDC signal changes smoothly and the vertical component of dipole moment m_z is nearly constant. These results indicate that the change of polar orientational angle is very small. By contrast, p-p, s-p, p-s and s-s SH signals are observable over the entire region 3. Of interest is the successful detection of the p-s and s-s signals in this region, suggesting that monolayers with $C_{\infty v}$-symmetry change to another symmetry such as C_s. That is, this sudden generation of the p-s and s-s signals indicates the phase transition. Here the change of SH signals are due to the reorientation of azimuthal distribution of molecules. In other words, the most possible explanation is that the domains with the polarization given by Eq. (2) are distributed in region 2, and the azimuthal orientation is induced by monolayer compression along and against the y-axis [13]. In more detail, the generation of the s-s signals occurs only when $\langle \cos\phi \rangle$ and $\langle \cos^3\phi \rangle$ are non-vanishing, where $\langle\ \rangle$ denotes the average over the domains in the laser irradiated area. That is, $\langle \cos\phi \rangle = \langle \cos^3\phi \rangle = 0$ and $\theta = 0$ in region 2, whereas $\langle \cos\phi \rangle = \langle \cos^3\phi \rangle \neq 0$ and $\theta \neq 0$ in region 3. Similarly we can explain the generation of the s-p, p-p and p-s signals in these regions. This explanation is confirmed by smooth generation of MDC at the transition. This phase transition corresponds to the shear induced azimuthal reorientation reported by Fullers [9] and Schwartz [10] group by the observation techniques such as Brewster angle microscopy (BAM) and fluorescence microscopy.

In region 3 and 4, all p-s, s-s, p-p and s-p SH signals are detected, though fluctuations are observed from sample to sample. These results also indicate the azimuthal motion of domains induced by flow happens in monolayers. Finally it is interesting to note that for nCB monolayers, p-s and s-s signals are not generated over the entire range of molecular area. That is, the monolayer symmetry does not change to Cs from $C_{\infty v}$ by monolayer compression.

CONCLUSION

Using the MDC and SHG measurement, we examined 7OCB Langmuir films by monolayer compression. The phase transition from a $C_{\infty v}$-symmetry monolayer structure to Cs one accompanies the change of azimuth angle of domains induced by compression, and it is detected in the region of initial rise of surface pressure. From these observations, it was found that MDC measurement coupled with SHG measurement is very helpful for the study of monolayer.

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