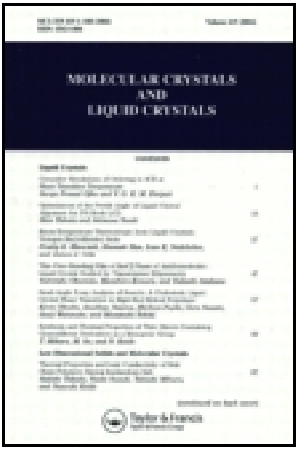

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

Mol. Cryst. and Liq. Cryst., 2001, Vol. 367, pp. 53-60
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Using Maxwell displacement current (MDC) and second harmonic generation (SHG) measurements, the linear and nonlinear dielectric properties of organic monolayer films on a material surface can be examined. In this study, we have developed a novel experimental system which can detect MDC and SHG signals, and examined the molecular motion of 4-cyano-4′-n-alkyl-biphenyls (5CB) on the water surface by monolayer compression. The orientational order parameters expressed by using Legendre polynomials were successfully determined from both MDC and SHG signals, and the difference in the determined order parameters was discussed in association with the molecular motion of 5CB monolayers.

Keywords: MDC; Maxwell displacement current; SHG; second harmonic generation

INTRODUCTION

Monolayers at the air/water surface exhibit very interesting and specific electrical and optical properties due to their non-centrosymmetric structure, i.e., symmetry breaking. Maxwell displacement current (MDC)[1,2] is generated by monolayer compression and second harmonic generation (SHG)[3-6] signals are generated. It is interesting to clarify the specific dielectric properties of organic monolayers on the water surface from the viewpoints of science and electronics. Generally, the polarization of organic monolayers is expressed by

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

where $\mathbf{P}_0$ is the spontaneous polarization, and $\chi^{(1)}$ and $\chi^{(n)}$ ($n \geqq 2$) are the linear susceptibility and the n-th order nonlinear susceptibility, respectively. This polarization $\mathbf{P}$ is approximately given by the sum of the first and second terms in Eq.(1) when the external electric field $\mathbf{E}$ is small, whereas the higher order terms cannot be ignored when the electric field $\mathbf{E}$ is high. The spontaneous polarization $\mathbf{P}_0$ is proportional to the orientational order parameter S_1 defined as $S_1 = < \cos\theta >$, where $< >$ denotes a thermodynamics average over the molecular orientations, and θ represents the tilt angle of polar molecules away from the normal direction to the material surface. Similarly, the susceptibility $\chi^{(1)}$ and the n-th order susceptibility $\chi^{(n)}$ are expressed as functions of order parameters $S_m = < P_m(\cos\theta) >$, where P_m is the m-th Legendre polynminals. Therefore it is very important to determine the orientational order parameters to clarify the dielectric property of organic monolayers. Using the MDC measurement, we can determine the orientational order parameter S_1 of monolayers. Similarly, using the optical SHG measurement, orientational order parameters S_1 and S_3 can be determined. Therefore MDC measurement coupled with the SHG measurement will be helpful for better understanding of the linear and nonlinear dielectric properties of monolayers. In this study, we made a MDC measurement system equipped with the SHG measuring system, and then examined 5CB monolayers by monolayer compression.

MDC AND SHG MEASUREMENTS

In this section, we briefly summarize the principle of MDC and SHG measurements for the determination of orientational order parameters.

MDC Measurement [1,2]

Consider rod-like amphiphilic molecules are distributed on a water surface and they are pointing toward the air at a tilt angle θ_m from normal direction to the water surface. The average vertical component of dipole moment of the molecule is written as

$$m_z = \mu S_1, \tag{2}$$

where μ is the permanent dipole moment of the molecule, and $S_1 = \langle\cos\theta_m\rangle$ is the orientational order parameter. In the MDC measurement, the charge Q induced on electrode 1 due to m_z changes by monolayer compression, and MDC flows through the closed circuit (see Figure 1). MDC $I(t)$ is given by[2]

$$I(t) = -\frac{dQ}{dt} = \frac{N\mu}{d}\frac{d}{dt}S_1 + \frac{\mu S_1}{d}\frac{d}{dt}N + \frac{\varepsilon_0 B}{d}\frac{d}{dt}\phi_s, \tag{3}$$

assuming that the relative dielectric constant of air is unity. Here N is the number of molecules under electrode 1, d is the distance between electrode 1 and the water surface, and ε_0 is the dielectric constant of vacuum, B is the working area of electrode 1, and ϕ_s is the surface potential of water. When monolayers on pure water surface are compressed, the 3rd term is smaller than the 1st and 2nd terms and is negligible. Thus the orientational order parameter S_1 is determined from the following relation

$$S_1 = \frac{d}{\mu N}\int_0^t I(t)dt, \tag{4}$$

assuming that the orientational order parameter $S_1 = 0$ before monolayer compression, i.e., molecules lie on the water surface so that the vertical component of dipole moment is zero before compression. When molecules do not lie on the water surface, $S_1 = 0$ before compression or an initial electric charge Q_0 is taken in account and S_1 is determined similarly.

SHG measurement[3-5]

SHG is known as one of optical phenomena, where the light with an angular frequency of 2ω is generated from non-centrosymmetric materials by the irradiation of incident light with an angular frequency ω. Generally, floating monolayers on a water surface have the non-centrosymmetric structure, where the hydrophilic groups protruding into water and hydrophobic groups pointing toward air. Therefore optical second harmonics may be generated from monolayers on the water surface. Second order nonlinear polarization induced by the irradiation of an external electric field $\mathbf{E}(\omega)$ is expressed as

$$\mathbf{P}(2\omega) = \chi^{(2)} : \mathbf{E}(\omega)\mathbf{E}(\omega). \tag{5}$$

Assuming that the molecular symmetry of monolayer is $C_{\infty v}$, where the constituent molecules have only the 2nd order molecular polarizability $\beta_{z'z'z'}$ along the molecular long axis, their molecular long axes tilt at an angle θ_s normal to the material surface, and their azimuth angles distribute randomly, $\chi^{(2)}$ is written as

$$\chi^{(2)} = \begin{pmatrix} 0 & 0 & 0 & 0 & \chi_{xzx} & 0 \\ 0 & 0 & 0 & \chi_{yyz} & 0 & 0 \\ \chi_{zxx} & \chi_{zyy} & \chi_{zzz} & 0 & 0 & 0 \end{pmatrix} \tag{6}$$

with two independent components

$$\chi_{zzz} = \frac{1}{5} n_s (2S_3 + 3S_1)\beta_{z'z'z'} \tag{7}$$

and

$$\chi_{zxx} = \chi_{zyy} = \chi_{xzx} = \chi_{yyz} = \frac{1}{5} n_s (S_1 - S_3)\beta_{z'z'z'}. \tag{8}$$

Here n_s is the surface molecular density, $S_1 = <\cos\theta>$ and $S_3 = (5 < \cos^3\theta_s > -3 < \cos\theta_s >)/2$ are orientational order parameters. The optical second harmonic (SH) intensity generated from monolayers by irradiating light with a laser beam intensity $I(\omega)$ becomes

$$I(2\omega)=\frac{32\pi^2\omega^2}{25c^3\varepsilon_1^{1/2}(2\omega)\varepsilon_1(\omega)}n_s^2\beta_{z'z'z'}^2\tan^2\theta_{in}\left|(AS_1+BS_3)\right|^2I^2(\omega). \quad (9)$$

Here θ_{in} is an incident angle of the laser beam away from the surface normal and it is equal to θ_{out}, the output angle of the generated second harmonics. c is the light velocity, $\varepsilon_1(\Omega)$ is the dielectric constant of monolayers at an angular frequency $\Omega\,(=\omega$ or $2\omega)$. A and B are constants with incident angle θ_{in}, output angle θ_{out}, and polarized angles of incident light ($\theta_{in}{}^{P}$) and output SH light ($\theta_{out}{}^{P}$). S_1 and S_3 are determined using Eq.(9).

EXPERIMENTAL SETUP

Figure 1 shows our MDC measurement system coupled with the SHG measurement system. The trough is filled with pure water (electrical resistivity > 17 MΩ /cm), where the transmitted light can pass through a silica glass side attached to the bottom of this trough. The monolayer covering area is controlled between 200 ~ 600 mm × 150 mm by moving two barriers. For MDC measurement, two electrodes 1 and 2 are used. Electrode 1 is a round shape glass slide coated with ITO with a diameter of 76 mm and it is placed in air to be parallel to the water surface. An air gap between electrode 1 and the water surface is adjusted to 1 mm. Electrode 2 is a gold wire and it is immersed in the water subphase. Electrodes 1 and 2 are connected to each other through an electrometer (Keithley 617). A femto-ampere order current is detectable using this system. For SHG measurement, Q-switched Nd:YAG laser was used as a source of fundamental wave (Big Sky Laser Technologies, Inc, maximum power 50 mJ, wavelength 1.064 μm, pulse duration < 7 nsec, fundamental pulse rate < 20 Hz). The incident light is linearly polarized by quarter-wavelength plate (P1) and input polarizer (P2). The linearly polarized light is incident on the water surface at an incident angle of θ_{in}. The reflected and transmitted SH signals are detected by the photomultiplier-tube (PMT) through the IR absorption filter (F2), band pass filter (F3) and output polarizer (P3). These signals are measured by a boxcar averager. The angle of the incident and output lights can be changed in the range between 10° and

80 °. The polarizers are used to change polarized directions in the range over 360 °. The surface pressure of monolayer is measured using a Wilhelmy plate. In this study, monolayers of 4-cyano-4'-pentylbiphenyl (5CB) were examined. Briefly, after spreading a 180 μl chloroform solution with a density of 1 mmol/l onto a water surface using a micro-syringe, we kept it for about 10 minutes and then started MDC and SHG measurements. The speed of the moving barrier was 20 mm/min during monolayer compression. For the SHG measurement, the incident and out put angles were set at $\theta_{in} = \theta_{out} = 60$ °, and the angle of polarizer for incident light $\theta_{in}{}^{P}$ was at 31 °. The angles of polarizer $\theta_{out}{}^{P}$ for reflected and transmitted SH lights were set at -63 ° and 18 °, respectively, for the determination of S_3 (A=0 for Eq.(9)) and S_1 (B=0). The laser power irradiated onto monolayer, pulse rate and irradiated area were about 30 mJ, 2 Hz and about 16 mm², respectively.

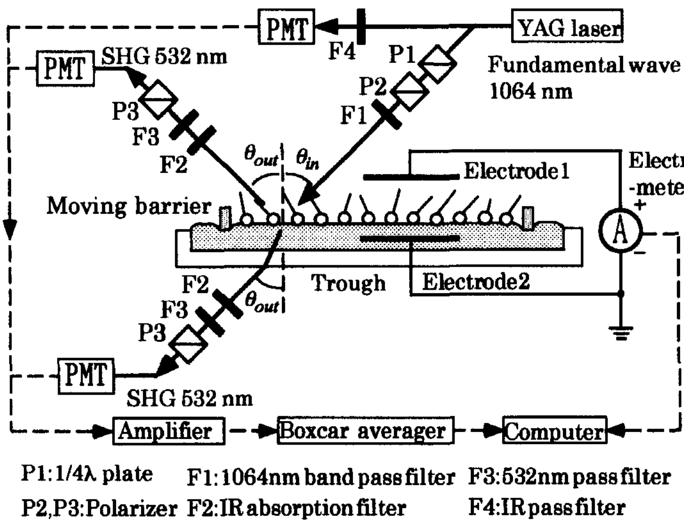

FIGURE 1 Experimental setup of MDC and SHG measurement system.

RESULTS AND DISCUSSION

Figure 2 shows an example of the MDC and SHG measurement of

5CB monolayers during compression, where surface pressure, displacement current, and SH intensity change with molecular area. More specifically, immediately after starting the compression at the molecule area of 90 Å^2 the SHG increases, whereas the MDC begins to increase at 70 Å^2. By further compression, the dipole moment m_z decrease slightly in the range of molecular area < 43 Å^2. The dipole moment was calculated using Eq.(4), assuming MDC reaches maximum at 43 Å^2, where S_1 should be 1.

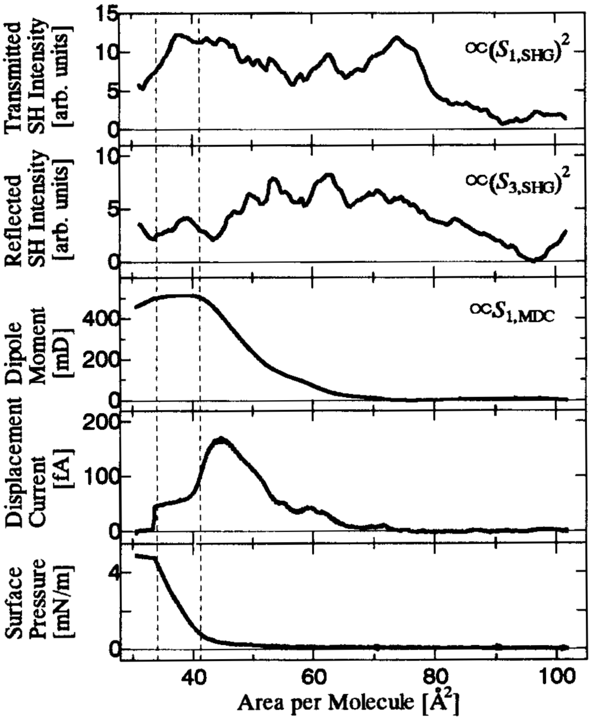

FIGURE 2 MDC and SHG of 5CB monolayer.

In the MDC measurement, permanent dipole moments of methyl and cyano groups in 5CB molecules make a contribution to the generation of MDC, that is, the orientational order parameter S_1 gives a thermodynamics average of the vector sum of these two dipole moments. On the one hand, in the SHG measurement, the main contributor is the electronic polarization of biphenyl group with alkyl- and cyano-groups. These difference lead to the difference in the generation between SHG and MDC. More specifically, SHG signals tell us that the biphenyl group in 5CB molecule stands on the water surface with a tilt angle even in the range of molecular area > 70 Å^2, whereas MDC tells that S_1 = 0 because the MDC gives information on the thermodynamics average of the vector sum of permanent dipoles. For further clarifying the details, investigation is proceeded.

CONCLUSION

Using MDC and SHG measurement, the orientational order parameters of 5CB monolayers at the air/water interface were successfully determined. The difference in the order parameters determined from MDC and SHG signals were discussed in association with the molecular motion of 5CB monolayer. The developed SHG and MDC measurement system will be helpful for the study of molecular motion in monolayers and molecular motion of liquid crystals at the interface.

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