Nano-interface Surface Dielectric Polarization Phenomena:
Detection and Application

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Nanointerfacial dielectric polarization phenomena were discussed from the viewpoint of electronics, paying attention to the alignment of dipoles and dipolar energy. Firstly, we summarized dielectric polarization phenomena of monolayer comprised of polar molecules, and showed that monolayer is quite different from bulk materials, and the unique dielectric properties of monolayers can be discussed in terms of orientational order parameters. Maxwell-displacement-current (MDC) measurement coupled with optical second harmonic generation (SHG) measurement is shown as an effective way for detecting unique dielectric polarization phenomena of surface monolayers. Then, the importance of dielectric energy is discussed from the viewpoint of monolayer pattern formation and pointed out that the control of dipolar energy can be a new pattern formation technology.

Key Words: MDC, SHG, dipolar energy, monolayer pattern

1 INTRODUCTION

Organic materials have attracted much attention in electronics [1]. Successful preparation of films with high mobility and high electrical conductivity motivated us to study organic devices such as organic field-effect transistors (OFET). Similarly, successful preparation of organic monomolecular films such as self-assembly films and Langmuir-Blodgett films, etc. motivated us to study electronic devices operating at molecular level. It is now an urgent task to gain an insight into physics of organic materials for electronics; especially the understanding of nano-interfacial electrostatic phenomena is essential. Interfacial energetic problems at organic-metal interfaces are usually discussed based on the concept of Fermi-level alignment between metal and organic materials, and the concept of energy level alignment is naturally introduced to discuss interfacial phenomena of molecular films [1]. However, such concept is not necessarily valid when an interfacial dipole layer is formed at organic/metal interfaces due to the alignment of polar molecules. Furthermore, if the electrical conductivity of prepared organic films is sufficiently low such as electrical insulating polymers, the establishment of thermodynamic equilibrium over the entire bulk region of the prepared organic films is generally very difficult due to the long-lasting dielectric relaxation phenomena [2]. As a result, the alignment of energy level is restricted at interfaces and the concept of surface Fermi-level becomes more helpful [2, 3]. This means that theoretical and experimental approaches based on dielectric physics are quite important to clarify nano-interfacial phenomena of organic materials.

Among many interfacial phenomena, orientational alignment of polar molecules and displacement of electrons at the metal-film interface is most basic and important ones. Thus, the establishment of theory and experiment related to these two dielectric polarizations should be the first step [2-4]. Paying attention to the orientational alignment of polar molecules, the authors have been developing a Maxwell-displacement-current (MDC) measuring technique coupled with optical second harmonic generation (SHG) measurement [5, 6]. Further to study the dipolar energy effect in association with the two-dimensional texture of surface monolayers, optical method (Brewster angle microscope) has been very recently introduced [7-9]. Based on the experiments using these techniques, we have been developing a theory of monolayers on the water surface keeping in mind that surface organic monolayer is a precursor and model film of organic films used in electronic and optical devices. In this paper, we briefly summarize our study on nano-interface phenomena of organic monolayers due to the alignment of dipoles. We show monolayer possesses both liquid crystalline and lattice properties due to the positional and orientational constriction imposed on constituent polar molecules. Finally, we discuss that the control of dipolar energy should be a new way to pattern formation technology, and thus the study of physics of organic monolayer is of great importance for electronics.

2 SURFACE POLARIZATION DUE TO ORIENTATIONAL ORDERING OF POLAR MOLECULES

2.1 Orientational Order Parameters

The state of surface monolayer composed of rod-like polar molecules, e.g., 4'-n-pentyl-4-cyanobiphenyl (5CB), is expressed...
using two kinds of order parameters [10], i.e., positional and orientational order parameters. The former expresses the molecular configuration describing the positional distribution of molecular heads on the surface, and the latter expresses the orientational distribution of molecules normal to the surface. Therefore, the physical properties of monolayers are naturally connected to these two parameters. Among them, the orientational order parameter is more important and helpful to specify the unique dielectric polarization of monolayers. It is instructive to note here that material system composed of rod molecules is classified using orientational order parameters $S_n$ ($n=1, 2, 3$) defined by the thermodynamic average of the Legendre polynomials, $P_n(\cos \theta)$ ($n=1, 2, 3$), of the orientational angle $\theta$ of molecules from the z-direction normal to the surface (see Figure 1) [10, 11]. Figure 1 (a) shows the state of isotropic bulk materials, where rod molecules are randomly distributed, i.e., $S_1 = <P_1(\cos \theta)> = 0$, $S_2 = <P_2(\cos \theta)> = <P_2((3\cos^2 \theta - 1)/2)> = 0$, and $S_3 = <P_3(\cos \theta)> = <(5\cos^3 \theta - 3\cos \theta)/2> = 0$. Figure 1 (b) shows the state which corresponds to nematic phase of bulk liquid crystals, where the orientational direction of molecules is restricted in space, though constituent molecules are randomly pointing up and down, i.e., $S_1 = 0$, $S_2 \neq 0$, but $S_3 = 0$. Figure 1 (c) shows the state of surface monolayer comprised of rod molecules, where all molecules are pointing upper direction, and thus $S_1, S_2, S_3 \neq 0$. From Figure 1, we find that the physical properties of nematic LCs is characterized by non-zero orientational order parameter $S_2$ [12]. On the other hand, the specific physico-chemical property of monolayers ascribed to symmetry breaking at the interface is connected to non-zero order parameter $S_1$ and $S_3$.

This means that the monolayer is the most generalized system, and this is the reason why monolayer shows various phenomena that cannot be seen for bulk materials. Further it should be noted that as monolayer is a system comprised of non-zero order parameters $S_1$, $S_2$, and $S_3$, monolayer must have the liquid crystalline property due to non-zero $S_1$ and also have the property related to non-zero order parameter $S_1$ and $S_3$. That is, monolayer possesses both liquid crystalline and lattice properties because of the positional and orientational constriction imposed on the constituent polar molecules.

The dielectric polarization of monolayer with $C_{2v}$-symmetry is expressed using complete sets of orientational order parameters, $S_1$, $S_2$, and $S_3$.
S, S, and S [3, 13]. Thus, the specific properties of the organic monolayers such as spontaneous polarization and nonlinear polarization are interpreted with these unique parameters S, S, and S. It is easy to expect that the characteristic texture of 2D-monolayer is connected to nano-interfacial electrostatic phenomena associated with dipolar energy originating from S ≠ 0 [14], while the 2D-monolayer possesses liquid-crystalline property.

In the development of SHG-MDC spectroscopy, the determination of the orientational order parameters and the coupling with observation technique such as BAM are especially important to clarify the dipolar structure of monolayers. Further it is instructive to note from viewpoint of electronics that the use of electrical and optical phenomena related to non-zero order parameter S, S, and S in electronic and optical devices leads to a new way to electronics and optical phenomena related to non-zero order parameter S, S, and S. Under Onsager approximation [15]. Of interest is that the dipolar polarization in case of S = 0 gives nothing but the Debye-Langevin equation which expresses the orientational polarization in the isotropic bulk state [16]. In other words, the linear surface polarization P is different from the linear bulk polarization due to the spatial restriction imposed on surface monolayers as shown in Figure 1 (c). In the frequency region of light, electronic polarization P, is a main contribution to the linear polarization, and dipolar polarization can be ignored. This fact indicates that orientational order parameter S, can be explored by means of optical method. In the BAM system, reflected light from the monolayer on the water surface is detected at an incident angle of the Brewster angle of water, θ = 53.1° [7-9]. This means that orientational order parameter S, can be explored by the BAM system through analyzing the reflected light from monolayers. Nonlinear polarization is induced by the interaction of laser beam with electrons in molecules. Nonlinear polarization P (P) of monolayer can also be expressed using the parameters S, S, and S. This polarization P is the sum of the polarization P, associated with the chirality of monolayer and the polarization P, associated with the achiral component of the susceptibility of monolayer. In case of achiral monolayers with C-symmetry, the nonlinear polarization reduces to [6, 13]

\[ P = (s_1, s_2, s_3) (n \cdot E)^3 n + s_1 (E \cdot E) n + s_2 (n \cdot E) E, \]  

where E is the external electric fields, and s is the susceptibilities expressed using the orientational order parameters S, S, and S. Thus, the nonlinear dielectric polarization of achiral monolayer is only a function of the order parameters S, S, and S. As mentioned above, surface polarization induced in monolayers can be expressed using orientational order parameters S, S, and S, and the surface polarization of monolayers is completely described by S, S, and S. The experiment shown in Figure 2 is the result of the detection of S, S, and S in Eqs. (1) and (2) as described below.

The experimental system consisting of a Langmuir-trough equipped with a two-electrode arrangement for the MDC measurement, optical measurement arrangement for the SHG measurement and BAM system has been developed by the present authors'
group. Figure 4 shows the schematics:

MDC generated from monolayers due to the change of spontaneous polarization $P$, enables us to determine orientational order parameter $S$. Transmitted and reflected SH signals with a wavelength $2\omega$ generated from monolayer by laser irradiation with a wavelength $\omega$ enables us to determine the orientational order parameters $S_0$ and $S_1$. Similarly, the reflected light of BAM configuration enables us to determine orientational order parameter $S$. In this way, complete sets of orientational order parameters of monolayer can be determined. MDC-SHG-BAM technique becomes now a new way to characterize dipolar polarization and to detect related phenomena of organic monolayers.

It is instructive here to note that the nonlinear dielectric polarization $P_s$ is strongly dependent on the monolayer structure, and the equation representing the corresponding polarization is obviously different from Eq. (2). On the other hand, the output SH light intensity $I_{\omega}$ is proportional to $e_{\omega}(2\omega)\cdot P$, where $e_{\omega}(2\omega)$ is electric field vector of the SH signal. Therefore, the monolayer structure, phase transition of monolayers, etc can be explored by SHG, and MDC can do these similarly [6].

3 LIQUID CRYSTALLINE AND LATTICE PROPERTIES OF ORGANIC MONOLAYERS

From viewpoints of monolayer symmetry, spontaneous and nonlinear dielectric polarization of organic monolayers originates from their non-centrosymmetric structure (see Figure 1), where non-zero order parameter $S_0$ and $S_1$ reflects the non-centrosymmetric structure. The spontaneous polarization given by Eq. (1) changes with monolayer compression and this change leads to the generation of MDC. This fact implies that monolayers possess the piezoelectric property, where change of surface molecular density $N_s$ and orientational order parameter $S_i$ are the main origins. For 8CB monolayers, these changes occur homogeneously over the entire region of monomolecular films. That is, director $m(=n)$ can be defined over the entire region of monolayer covering area. However, this is not the case for 4-heptyloxy-4-cyanobiphenyl (7OCB) monolayers and others that experience compression-shear-induced tilt azimuthal orientation [17].

As is well known, variety of textures appear in liquid crystals and monolayers. This means that director $m$ distributes spatially in bulk LCs and monolayers. That is, $\nabla \cdot m \neq 0$, and $\nabla \times m \neq 0$. Of course, to give such spatial distribution, elastic deformation such as splay, bend and twist deformation must be induced in monolayer in a manner similar to the case of nematic LCs, as those have been theoretically pointed-out by Ono, Zocher, and Frank [18]. These effects give rise to so-called flexoelectric effect discovered by Meyer [19]. For nematic LCs, bend and splay deformations are origins of flexoelectric effect, whereas for monolayers, all constituent rod-molecules are facing the water surface and pointing toward air (upper direction, see Figure 1(c)) due to symmetry breaking. Thus, the flexoelectric effect in monolayer must be different from that in LCs, if the monolayer possesses liquid crystalline property [20].

For monolayers such as fatty acids with long alkyl chains, it has been revealed by microscopic observation, e.g., BAM, fluorescence spectroscopy, etc [21-24] that the monolayer has the hexagonally closed packing structure, but the constituent molecules can tilt in the N-N (nearest neighbor) direction and N-N-N (next nearest neighbor) direction, in L2 and L2' phases, respectively. This property is of course the lattice property observed in crystals, and can be reasonably explained by assuming lattice energy of monolayers. However, this is no longer sufficient to specify the dynamical property of monolayers. As the constituent molecules posses long chains, monolayer can shows the property that be explained by the Eriksen-Leslie (EL) theory under the flow of water surface. That is, the EL theory, well accepted in LC science, can be applied to the monolayer dynamics by assuming that the average orientation of polar molecules as directors defined in LC science. Of course, as above-mentioned L2 and L2' phases are static ones, such dynamical property should not be needed considered when we discuss the property of monolayers at a fixed molecular area. However, this situation changes, when we discuss the monolayers during compression. For example, in our experimental system shown in Figure 4, monolayers on the water surface are compressed at a constant barrier speed. This means that the monolayer experiences shear-compression during monolayer compression; that is, the shear given by $d_{01}=-\lambda(0)-\lambda(t)$ is induced in monolayers in the direction normal to the compression barriers. Here $\lambda(0)$ and $\lambda(t)$ are molecular area at $t=0$ and at $t=t$, respectively. This shear induced in monolayers gives tremendous effect on some monolayers during monolayer compression. We can see such an example for the MDC-SHG experiment on 7OCB monolayers [20]. Figure 5 shows an example of the MDC-SHG experiment on 7OCB monolayers, where we can see the generation of $s-s$ and $p-s$ SH signals in the region 2. These signals never appear when monolayer is compressed homogeneously all over directions, and the structure of monolayer is expected as C$_{19}$-symmetry structure, that is, s-p and p-p SH signals are due to the liquid crystalline property of monolayer induced by shear-compression, indicating that monolayer posses the liquid crystalline property.

![Figure 5 MDC-SHG experiment on 7OCB monolayer. s-s, and p-s SH signals are due to the liquid crystalline property of monolayer induced by shear-compression, indicating that monolayer posses the liquid crystalline property.](image-url)
generation is only expected, as has been detected in 8CB monolayers. This result can be explained by assuming that the shear flow induced director orientation in monolayers in a manner similar as in bulk LCs. As has been described above, monolayer posses both the liquid crystalline and lattice properties. This is the most important and interesting feature of monolayers that cannot be seen in bulk LCs as well as bulk materials (see Figure 1).

4 DIPOLAR ENERGY AND TEXTURES OF 2D-INTERFACE

When we discuss the texture of monolayers composed of the dipolar molecules, we need to more focus on the dipolar energy stored by oriented dipoles, especially when we discuss domain formation on the water surface, as suggested by McConnel [25, 26]. The dipole-dipole interaction prefers the elongation of domains whereas the line tension prefers the circle-domains. The osmotic surface pressures described by Gibbs free energy density difference between outer (fluid) and inner (solid) phases, dipole-dipole interaction among oriented polar molecules and line tensions are main contributions to define shape domains of monolayers.

In a manner similar to the derivation of shape energy of a 3D vesicle by Helfrich and Ou-Yang [30, 31], the shape energy of a 2D domain with permanent dipoles pointing toward air normal to the water surface, corresponding to the state $S_1=1$, is formalized [14], and the domain energy is derived naturally taking into account the contribution of elongation by dipole interaction [25, 26] and circularly shape formation tendency according to the 2D Young and Laplace law as

$$F = \Delta P s dA + \lambda \int \frac{s}{2} ds + \alpha \int \kappa' ds$$

Here $\Delta P$ represents the Gibbs free energy density difference between outer (e.g., fluid) and inner (solid) phases, i.e., $\Delta P = \gamma_{01} = \gamma_{02}$ because solid phase is more stable than fluid one. $\lambda = \frac{\mu I}{2} \ln \frac{L}{h}$ is total line tension which is positive or negative depending on the line tension $\gamma$, length of domain $L$, the dipole density $\mu$, and the monolayer thickness. $\alpha = \frac{11}{96} \mu I^2$ is certainly positive, and regarded as the modulus of line curvature elasticity or 1D bending rigidity. Eq. (3) is very similar to the 3D shape energy of vesicle [28]. Here we should note that in the derivation of the 2D shape equation, the dipole energy is introduced, replacing the curvature energy used for the derivation of the 3D shape equation. From Eq. (3), it is found that 2D line tension is size- and shape-dependent, where dipolar energy stored in domains due to the alignment of dipoles by the symmetry breaking makes a significant contribution. The variation of the domain energy yields an equilibrium domain shape equation, and the solutions of the shape equation clearly predict various textures of monolayers such as circle and torus, depending on the difference in Gibbs free energy between the solid and fluid phases and the total line tension [15]. Figure 6 predicts the three cases depending on the sign of $\lambda$ and $\alpha$. That is, two circles and two tori, only one circle, and no compact circular domain.

Such shapes with a micrometer size were found as domains in monolayers experimentally by BAM, fluorescence spectroscopy, etc [21-24]. Our experimental BAM system attached to the MDC-SHG experimental system have also visualized such textures in monolayers [29]. The control of dipolar energy is an important way to open up the fabrication of two-dimensional patterns. Finally, it should be noted that the dipolar energy effect is a key to control monolayer pattern and we can produce novel electrical and optical phenomena available for electronics by coupling it with nano-technology. Further, we should note that the control of dipolar energy is also essential to bring biomaterials into electronics.

5 CONCLUSION AND REMARKS

According to Maxwell's electro-magnetic field theory, total current flowing across organic film is sum of the conduction current and displacement current. In section 2, it was shown that surface polarization phenomena due to alignment of dipoles leading to spatially homogeneous spontaneous polarization be an origin of Maxwell-displacement current, as described in section 2.2. On the other hand, inhomogeneous alignment of polar molecules resulting into spatial director distribution characterized by $\mathbf{V} \cdot \mathbf{m} \neq 0$ and $\mathbf{V} \times \mathbf{m} \neq 0$ gives rise to the generation of MDC originating from the flexoelectric effect. It should be noted that such effect is originating to the liquid crystalline property of monolayers, and can be detected in the dynamic process of monolayers, such as seen in Figure 5 in the observation of the $s$-$s$ and $p$-$s$ SHG during the shear induced monolayer compression.

![Figure 6](image-url)
In order to clarify the details of two-dimensional surface polarization phenomena, the coupling with MDC-SHG experiment with BAM observation is thus effective. Of course, the development of theory with consideration of dipolar energy arising from non-zero order parameter is also essential. From the viewpoint of two-dimensional system, we need to extend it to the generalized one so that we can treat a variety of molecules with characteristic shapes such as banana-shape, helical structure, etc. This will be of help for understanding the origin of chirality of monolayers, origin of spontaneous curvature in monolayers, and more focus on the $\theta$-space structure of monolayers from the viewpoint of electronics. By solving shape equation derived from Eq. (3) and related equations \[30\], we can predict monolayer patterns characterized such as clover, etc. This means that the control of dipolar energy in two-dimensional system can be a new pattern formation method in electronics, in replacing of nano- or micro-lithography technique, and will force us to study electron and photon behaviors in two-dimensional patterns in future from the viewpoint of informatics.

Finally we should remark that as seen in organic monolayers, organic material, especially monolayer has many aspects and show a variety phases, gaseous, liquid, liquid-crystalline, solid, etc. This means that we need a variety of knowledge in physics, chemistry, biology and others to understand the properties of monolayers. Interestingly, monolayer is widely used in electronics, e.g., as alignment layer in LCs, as a tunneling barrier in electron devices, etc. As mentioned in section 2, monolayer is the most generalized system from the viewpoint of orientational order parameters. To find a new way to electronics, it is important to study the physics of organic monolayers, and catch the important concept coming from monolayers, e.g., liquid-crystalline properties and lattice properties.

References


