

Molecular twist transition in chiral and racemic phospholipid monolayers detected by Maxwell-displacement-current measurements

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The physicochemical properties of chiral and racemic phospholipid (α -phosphatidylcholine dipalmitoyl) monolayers at the air-water interface were investigated using Maxwell-displacement-current (MDC) and surface pressure measurements by monolayer compression. The chiral and racemic phospholipid monolayers exhibited the same pressure-area isotherm with a pressure plateau at a temperature of 20 °C. However, some critical MDC peaks were generated with different amplitude and sign depending on the chirality of the phospholipids in the plateau region. This anomalous MDC generation is theoretically interpreted on the basis of the molecular twist transition induced by monolayer compression. [S1063-651X(99)07902-7]

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The origin of biomolecular homochirality and searching of the possible mechanism for transition of biomolecules have been topics of interest to biologists, chemists, and physicists since the 19th century and they are still continuous study subjects and now have become urgent research topics [1]. Phospholipids (PCL) are one of the main amphiphiles of biomembranes and they contain one phosphatidylcholine (polar hydrophilic) head group and two long alkyl chains with a carbonyl (hydrophobic) group (see Fig. 1). Usually, the hydrophilic and hydrophobic groups are not located in the same plane containing the two hydrocarbon chains. Thus the PCL molecules are referred to as chiral due to the lack of the mirror plane symmetry. Another remarkable physicochemical property of the amphiphiles is that they can show a variety of structures in the bulk of aqueous solutions, and their thermodynamics and intra-aggregate forces in the bulk of solutions have been extensively investigated [2]. Unfortunately, the role of the chirality of the amphiphiles in the structure multiplicity has not been studied clearly. Since monolayers at the air-water interface show some different phases during monolayer compression and can reveal more information on the molecular conformation than in bulk, it is important to examine the molecular conformation of chiral and racemic compounds in the monolayer state. For the similar purpose, Lundquist [3] found that for monolayers of 2-alkanos and certain derivative racemates, pure enantiomers form different crystal-like phases. The studies of chiral and racemic 12-hydroxyoctadecanoic acids (12HOA) later showed that the molecules at the water-air surface can take the two conformations with straight chain and bent chain, respectively, while the packing molecular models are proposed with rectangular and oblique lattices for racemic and chiral 12HOA's, respectively [4]. The same dependence of both kinds of lattice depending on the chirality has been discovered in an amphiphilic monolayer [5]. Although the measurement of surface pressure-area (π -A) isotherm is performed really in the monolayers at water-air interface, the

above measurement of molecular packing and conformation is carried out by transferring the monolayers onto mica [5] or calcium fluoride plate [4] using the Langmuir-Blodgett technique [6]. This process may cause a change in both molecular packing and conformation affected by the substrate specific. Therefore, it is a challenge to detect the molecular conformation in monolayer at the air-water surface without transfer so that the monolayers are not destroyed.

Over the past few years, we have developed an approach to study monolayer properties using Maxwell displacement current (MDC) measurement [7], and applied it to investigate the *cis-trans* photoisomerization in the monolayers of azobenzenes [8] and their mixtures with PCL [9]. The MDC technique has an advantage in that the MDC can reveal the polar orientational ordering and conformational ordering of the amphiphiles [10] that are not able to be detected by the conventional π -A measurement; for example, the polar orientational change of monolayers in the range of immeasur-

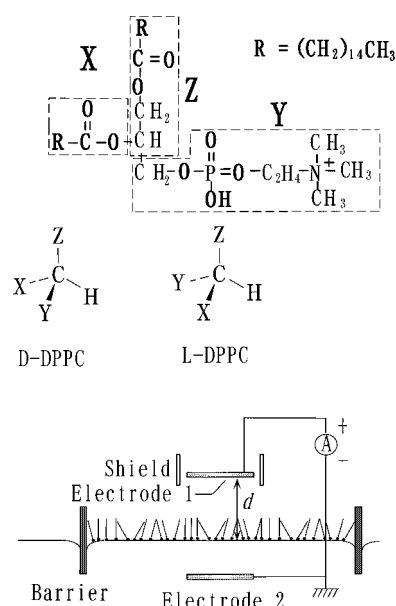


FIG. 1. Schematic diagram for molecule DPPC (above) and experimental setup (below).

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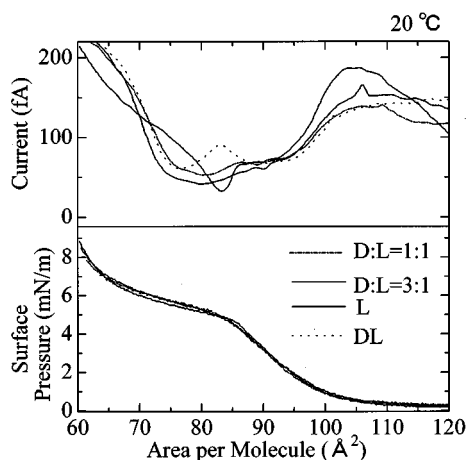


FIG. 2. π -A isotherms (below) and corresponding Maxwell-displacement currents (above) measured in four DPPC monolayers composed of pure L-DPPC, PL-DPPC, and mixtures with molar ratios of D-L-DPPC = 1:1, 3:1, respectively.

ably low surface pressures can be detected by the MDC technique. The aim of our present study is to examine the MDC behavior in chiral and racemic PCL monolayers in combination with their π -A isotherms. Our experiment shows that for the α -phosphatidylcholine dipalmitoyl (DPPC) monolayers (Fig. 1), the π -A isotherms for pure chiral enantiomers (D-DPPC and L-DPPC), their mixtures, and the racemic molecular compound (DL-DPPC) agree well with each other (Fig. 2). However, it is found that in the plateau region of the π -A isotherms, some critical MDC peaks are generated with different amplitude and sign depending on the chirality. This anomalous MDC generation is theoretically interpreted as the molecular twist transition induced by monolayer compression.

The D-, L-, and DL-DPPC molecules used in the experiment were purchased from SIGMA, and they were used as freshly received. Besides the detailed molecular form of D-DPPC [11], Fig. 1 shows the schematic of our experimental setup, which is similar to that used in our previous study [7–9]. The main setup is a usual Wilhelmy-type film balance system in a Langmuir trough ($15 \times 73 \text{ cm}^2$). Two electrodes 1 and 2 are connected to each other through a sensitive ammeter and they are placed parallel to the water-air surface: Electrode 1 is suspended in air above the water surface and electrode 2 is immersed in the water subphase. The effective working area of electrode 1 is 45.6 cm^2 and the spacing between electrode 1 and water surface (d) is manually adjusted to 1.15 mm and the water subphase (pH 6) is kept at a constant temperature of $20 \pm 0.2 \text{ }^\circ\text{C}$. The monolayers of mixtures of D- and L-DPPC in designed ratios are formed on the water surface by spreading their dilute chloroform solutions onto the water surface of the Langmuir trough using a microsyringe. The monolayers of DPPC formed on the water surface were compressed with two floating barriers at a constant barrier velocity of 40 mm/min. The MDC and π -A isotherms were simultaneously measured during the monolayer compression. Figure 2 shows the typical experimental results of the measurement for four samples: pure L-DPPC and DL-DPPC monolayers and their mixtures with a molar ratio of D-L-DPPC = 1:1, 3:1, respectively. As shown in Fig. 2, the π -A isotherms of these four samples are almost the

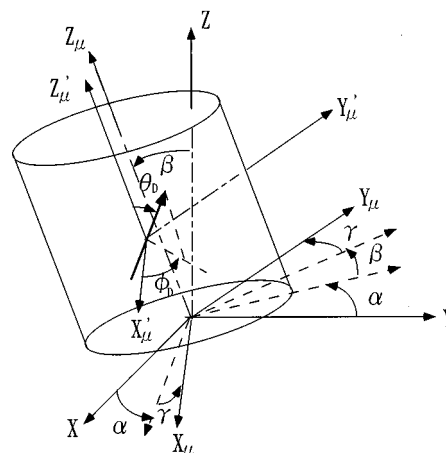


FIG. 3. Sketch of rodlike molecular model for PCL monolayers at the air-water surface. The cylinder represents the molecular long axis and the side dipole flanking the cylinder with polar angle θ_D and twist angle ϕ_D . The latter serves to describe the chirality of the molecules, $\phi_D = 0$ and π for racemic, otherwise for chiral.

same function of molecular area A containing nearly the same pressure plateau in the range of $65\text{--}85 \text{ \AA}^2$ of molecular area at a temperature of $20 \text{ }^\circ\text{C}$. The latter was usually referred to two-dimensional (2D) phase transition region from the expanded monolayer to condensed one. In Ref. [4], with the help of the x-ray diffraction, the 2D positional transition was also argued to associate with the molecular conformation change from bent chain state to straight chain state. In our recent work [10,12], the plateau region is interpreted to involve the phase transition of molecular orientation from isotropic to polar orientation. From the present π -A measurement, it seems that the mentioned phase transitions are obviously independent of the chirality of the molecules composed in the monolayers. However, the result of measurement in MDC shown in Fig. 2 above reveals that although the main shapes of the MDC viewed as a function of the molecular area A are roughly similar for the four samples of DPPC, there exist some essential differences between them: The most striking characteristic is the generation of MDC peak that appears in the beginning of the pressure plateau, $A = 85 \text{ \AA}^2$, with different amplitude and sign for the four examples. From the viewpoint of molecular level, the four examples of the DPPC monolayers differ only from their chirality: DL-DPPC is racemic, L-DPPC and D-DPPC both are chiral with different optical activity. Therefore, the mentioned MDC peak should reveal some molecular conformation change relating to the molecular chirality. In other words, this anomalous MDC generation may be of significant help to understand the chiral discrimination from molecular conformation level. Due greatly to the problem being of critical importance in physics, chemistry, biology, and geology [13], in what follows we present a theory to describe the chirality dependence of the MDC peak of a monolayer, and discuss the anomalous MDC generation.

As mentioned earlier, chiral PCL molecules must be lacking in the mirror plane symmetry (see again, Fig. 1). Hence, our previous models for the study of uniaxial [10(a)] and biaxiality [10(b)] ordering of molecular orientation in a monolayer are inconsistent with the requirement of chiral symmetry: The uniaxial model assumes the molecular dipole

is along the molecular long axis of cylindrical symmetry and the biaxial one only revises the molecular dipole direction with a tilted angle θ_D . Therefore, a plane containing the dipole and the long molecular axis must be a mirror-symmetry one. It is essential to present a model to describe the chiral symmetry by the modification of our previous molecular model, because the MDCs are generated in a similar manner in the entire range of the molecular area except in the range involving the anomalous MDC generation, as shown in Fig. 2.

Thus the basic geometry used in the present theory remains as a one-dipole model (see Fig. 3). However, the dipole \vec{P} is not located in the molecular long axis but it is in a cylindrical surface, i.e., describing in the molecular frame as

$$\vec{r}_0 = (x_\mu, y_\mu, z_\mu) = (a, 0, h), \quad (1)$$

where z_μ is along the molecular long axis. Besides an angle θ_D ($0 \leq \theta_D \leq \pi$) away from \vec{z}_μ , it is assumed that the dipole is not in the plane of $y_\mu = 0$, but with a tilted angle ϕ_D to it ($0 \leq \phi_D \leq 2\pi$), i.e., in the molecular frame

$$\vec{P}/P = (\sin \theta_D \cos \phi_D, \sin \theta_D \sin \phi_D, \cos \theta_D). \quad (2)$$

It is easy to check that $\phi_D \neq 0$ represents the chirality and $\phi_D = 0$ and π mean racemic states with biaxiality ordering [10(b)]. In the case of $\theta_D = 0$ and $\theta_D = \pi$, Eq. (2) reduces to the simplest uniaxial symmetry [10(a)]. Other geometry of the monolayer composed of the dipolar molecules is the same as that in [10], as illustrated in Fig. 3: The average orientation direction of the molecular long axis is upright to the water surface and referred to the z direction of the laboratory frame. It is then obvious that the molecular orientation is confined in the range of $0 \leq \beta \leq \theta(A) = \arcsin \sqrt{A/A_0}$ (see Fig. 3) due to the effect of hard-core intermolecular repulsive force working among molecules, where β is the angle between \vec{z} and the molecular long axis, $A_0 = \pi l^2$, l is the partial length of the molecules along their long axis above the water surface, and A is the mean molecular area. Besides the repulsive force, the distribution of β is also affected by the attractive Coulomb force working from the image of the molecular dipole in the bulk water, i.e., the interaction energy is [14]

$$W(\beta) = -P^2 \left(\frac{\epsilon_w - \epsilon_m}{\epsilon_w + \epsilon_m} \right) \frac{1 + \cos^2 \theta_L}{32\pi\epsilon_0(r_0 \cos \theta')^3}, \quad (3)$$

where ϵ_m and ϵ_w are the dielectric constants of monolayer and the water, respectively, ϵ_0 is the permittivity of free space, θ_L is the angle of the dipole direction from \vec{z} , and $d = r_0 \cos \theta'$ is the distance of the dipole above the water surface; hence, $r_0 = |\vec{r}_0| = \sqrt{a^2 + h^2}$ and θ' is the angle between \vec{z} and the direction of the position vector of the dipole \vec{r}_0 .

To describe the apparent relations of both θ_L and θ' with the geometry given in Fig. 3, we introduce the relationship between the molecular frame $\vec{r}_\mu = (x_\mu, y_\mu, z_\mu)$ and the laboratory one $\vec{r} = (x, y, z)$ with Euler angles (α, β, γ) defined as the convention in [14],

$$\vec{r} = R(\alpha, \beta, \gamma) \cdot \vec{r}_\mu, \quad (4)$$

where 3×3 matrix $R(\alpha, \beta, \gamma)$ is the usual Euler rotation matrix (see (3) in [10(b)]). From Eq. (4) we have, in the molecular frame,

$$\vec{z}/z = (-\sin \beta \sin \gamma, -\sin \beta \cos \gamma, \cos \beta) \quad (5)$$

and obtain from Eqs. (1), (2), and (5),

$$\begin{aligned} \cos \theta_L = (\vec{z}/z) \cdot (\vec{P}/P) &= -\sin \theta_D \sin \beta \sin(\gamma + \phi_D) \\ &+ \cos \theta_D \cos \beta, \end{aligned} \quad (6)$$

$$r_0 \cos \theta' = \vec{r}_0 \cdot (\vec{z}/z) = -a \sin \beta \sin \gamma + h \cos \beta. \quad (7)$$

Substituting Eqs. (6) and (7) into Eq. (3) yields the apparent expression for the molecular distribution function

$$f(\beta, \gamma) = \frac{e^{-W(\beta, \gamma)/kT}}{Z}, \quad (8)$$

where Z is the single-particle partition function

$$Z = \int_0^{2\pi} d\gamma \int_0^{\theta(A)} e^{-W(\beta, \gamma)/kT} \sin \beta d\beta. \quad (9)$$

Here k is the Boltzmann constant and T is the temperature. By using the approximation in a manner as carried out by Onsager [15],

$$e^{-W(\beta, \gamma)/kT} = 1 - W(\beta, \gamma)/kT, \quad (10)$$

and with a lengthy calculation [16], we obtained from Eq. (9) the analytic form for the partition function

$$\begin{aligned} Z = Z(A, \theta_D, \phi_D) &= 2\pi [1 - \cos \theta(A)] + \pi \eta \left\{ (1 + \cos^2 \phi_D \sin^2 \theta_D) [\tan^2 \psi \sin^{-3} \alpha - (1 + \tan^2 \psi) \sin^{-1} \alpha] \right. \\ &+ (\cos^2 \theta_D - \cos^2 \phi_D \sin^2 \theta_D) \left[(3 \cos^2 \psi - 2)(\sin^{-1} \psi - \sin^{-1} \alpha) - \sin^2 \right. \\ &\times \psi (\sin^{-3} \psi - \sin^{-3} \alpha) + (2 - 3 \cos^2 \psi) \ln \frac{1 + \sin \psi}{(1 + \sin \alpha) \cos \theta(A)} \left. \right] + \sin^2 \theta_D (2 \cos^2 \phi_D - 1) \\ &\times \left[\tan^2 \psi (\sin^{-1} \psi - \sin^{-1} \alpha) + \ln \frac{1 + \sin \psi}{(1 + \sin \alpha) \cos \theta(A)} \right] - \sin 2\theta_D \cos \phi_D \sin \psi \cos \psi \\ &\times \left[3(\sin^{-1} \psi - \sin^{-1} \alpha) - \tan^2 \psi (\sin^{-3} \psi - \sin^{-3} \alpha) - 3 \ln \frac{1 + \sin \psi}{(1 + \sin \alpha) \cos \theta(A)} \right] \left. \right\}, \end{aligned} \quad (11)$$

where $\theta(A)$ has been defined above, $\tan \psi = h/a$, and $\cos \alpha = \cos \psi / \cos \theta(A)$. The dimensionless parameter $\eta = P^2[(\epsilon_w - \epsilon_m)/(\epsilon_w + \epsilon_m)]/32\pi\epsilon_0 r_0^3 kT$ describes the relative strength of the dipole-medium interaction energy with respect to kT . Given these, the minimization of the free energy ($F = -kT \ln Z$), or saying maximum of Z , can reveal some interesting effect of molecular conformation transition during the compression of monolayers.

First, let us consider the transition between the two racemic states of $\phi_D = 0$, and π . It is worth noting that in Eq. (11), except the last term associated with $\cos \phi_D$, $\phi_D = 0$, and π make no difference for other terms. Therefore, we obtain the condition for conformation transition from $\phi_D = 0$ to $\phi_D = \pi$ as

$$3(\sin^{-1} \psi - \sin^{-1} \alpha) - \tan^2 \psi (\sin^{-3} \psi - \sin^{-3} \alpha) - 3 \ln \frac{1 + \sin \psi}{(1 + \sin \alpha) \cos \theta(A)} \geq 0. \quad (12)$$

Similarly, Eq. (12) is also the criterion for chiral state transition from ϕ_D ($0 < \phi_D \leq \pi/2$) to $\pi - \phi_D$ or from ϕ_D ($3\pi/2 \leq \phi_D < 2\pi$) to $\phi_D - \pi$. We refer the transition to the molecular twist transition.

Second, we shall prove the anomalous MDC generation; the MDC peak described earlier, corresponds to the molecular twist transition. According to Eqs. (2), (8), and (10), we can calculate the average molecular dipolar moment in the \vec{z} direction,

$$\langle P_z \rangle = \frac{P}{Z} \int_0^{2\pi} d\gamma \int_0^{\theta(A)} \cos \theta_L \left(1 - \frac{W}{kT}\right) \sin \beta d\beta. \quad (13)$$

In the actual calculation, for the sake of simplicity, we take an approximation of

$$-\cos \theta_L \frac{W}{kT} = \frac{\eta(\cos \theta_L + \cos^3 \theta_L)}{(a \sin \beta \sin \gamma + h \cos \beta)^3} \approx \frac{\eta \cos \theta_L}{(a \sin \beta \sin \gamma + h \cos \beta)^3}.$$

We then have from Eq. (13) the following formula on $\langle P_z \rangle$:

$$\begin{aligned} \langle P_z \rangle = & \frac{\pi P}{Z} \cos \theta_D \sin^2 \theta(A) + \frac{\pi P \eta}{Z r_0^3} \{ \cos \theta_D [(2 - 3 \cos^2 \psi) \\ & \times (\cos^{-1} \theta_A \sin^{-1} \alpha - \sin^{-1} \psi) \\ & - \sin^2 \psi \cos^2 \psi (\sin^{-3} \psi - \cos^{-3} \theta_A \sin^{-3} \alpha)] \\ & + \tan \psi \cos^2 \psi \sin \theta_D \cos \phi_D (3 \cos^{-1} \theta_A \sin^{-1} \alpha \\ & - 2 \sin^{-1} \psi - \sin^2 \psi \cos^{-3} \theta_A \sin^{-3} \alpha) \}. \quad (14) \end{aligned}$$

It is now clear that the above ϕ_D ($0 < \phi_D \leq \pi/2$) to $\pi - \phi_D$ or ϕ_D ($3\pi/2 \leq \phi_D < 2\pi$) to $\phi_D - \pi$ molecular twist transitions have to induce the great change of $\langle P_z \rangle$ at the critical area $A = A_c$ that makes Eq. (12) as identity; then the MDC peak occurs at the critical area independent on the racemic or chiral examples. This is in good agreement with experiment as shown in Fig. 2 above.

On the other hand, for certain examples the values of both ϕ_D have to be determined by their chirality, so the anomalous MDC peaks have different amplitude and sign. Roughly speaking, the amplitude of the MDC peak for the transition between both racemic states of $\phi_D = 0, \pi$ should be the largest due to $|\delta \cos \phi_D| = 2$ being maximal for the change of $|\delta \cos \phi_D|$. This is also confirmed by the MDC peak of the DL-DPPC monolayer given in experiment (Fig. 2 above). Briefly, we can estimate that the MDC change flowing through the circuit due to the molecular twist transition is approximately related to $\eta \sin \phi_D$, from the chiral effect on $\langle P_z \rangle$ explicitly expressed in factor $\cos \phi_D$ [the last term in Eq. (14)]. This reveals that the larger the interaction (which is proportional to η), the more striking the molecular twist transition will be.

From the above discussion, we show that the generation of the MDC from racemic and chiral monolayers can reveal the molecular twist transition. The transition-induced MDC peak can serve to estimate the molecular structures. This may have significance in biology, chemistry, and physics.

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