Characterization of Ultrathin Organic Membranes by Vibrational Spectroscopy

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ABSTRACT : We first deal with a new method for quantitative evaluation of the molecular orientation in thin Langmuir-Blodgett (LB) films by Fourier transform infrared (FT–IR) transmission and reflection–absorption (RA) spectroscopy. The method was applied to the study of the 7–monolayer LB film of cadmium stearate. The orientation angle of the hydrocarbon chain axis around the surface normal was found to be $7°$, being in good agreement with the average of the previous data obtained by other investigators. Then, we applied the same method to the study of temperature dependence of the molecular orientation in alternate LB films consisting of a phenylpyrazine-containing long-chain fatty acid and deuterated stearic acid, and in the corresponding alternate LB films of their barium salts. At the same time, pyroelectricity of these films was measured on heating the sample, and the results are discussed in connection with the molecular structure and orientation. It was concluded that the pyroelectricity is ascribed to changes of spontaneous polarization due to a structure modification of the polar groups of the constituent molecules with the highly oriented all-trans hydrocarbon chains.

KEY WORDS   Molecular Orientation / Infrared Transmission Spectrum / Infrared Reflection-Absorption Spectrum / LB Film / Alternate LB Film / Structure-Function Relationship / Pyroelectricity / Metal Stearate / Phenylpyrazine Moiety /

Infrared and Raman spectra of ultrathin organic films such as Langmuir–Blodgett (LB) films have been expected to provide useful information about molecular structure and orientation, and afford an excellent insight into the structure-function relationship in these molecular assemblies. In this paper, we first deal with a new method for quantitative evaluation of the molecular orientation in thin LB films by Fourier transform infrared (FT–IR) transmission and reflection–absorption (RA) spectroscopy. Then, we discuss about the relationship between the molecular orientation evaluated by the above method and pyroelectricity in alternate LB films consisting of a phenylpyrazine-containing long-chain fatty acid and deuterated stearic acid.

A NEW METHOD FOR QUANTITATIVE EVALUATION OF
MOLECULAR ORIENTATION IN THIN LB FILMS

In the normal-incident transmission measurements of LB films, the electric vector of the infrared beam is parallel to the film surface. Therefore, only absorption bands which have the transition moments parallel to the film surface can be detected by this method. On the other hand, in the RA measurements, in which the p-polarized infrared beam is incident upon the LB film prepared on Ag film at a large angle of incidence ca. 85°, we have a strong electric field perpendicular to the film
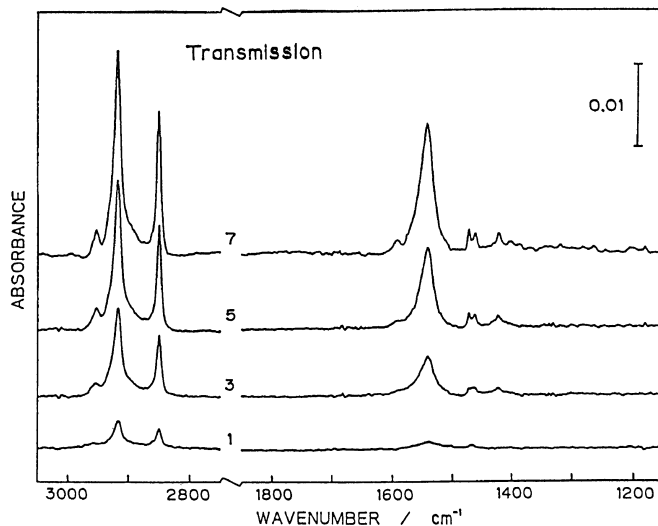

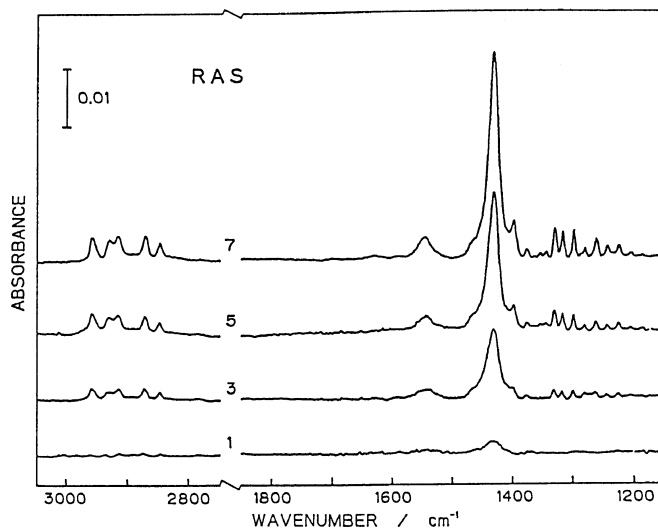Figure 1. FT-IR transmission spectra of 1-, 3-, 5-, and 7-monolayer LB films of cadmium stearate on ZeSe plates.[2]

Figure 2. FT-IR reflection-absorption spectra of 1-, 3-, 5-, and 7-monolayer LB films of cadmium stearate on evaporated Ag films.[2]

surface as a consequence of the interference between the incident and reflected beams. Therefore, in this measurement, only absorption bands which have the transition moments perpendicular to the film surface can be detected with some intensity enhancement due to the presence of the Ag film.[1] Thus, if the molecules are highly oriented in the LB films, the peak intensities of particular bands should be different between the transmission and RA spectra.

Figure 1 shows the FT-IR transmission spectra of the 1- , 3-, 5-, and 7-monolayer LB films of cadmium stearate prepared on ZnSe plates. Figure 2 illustrates the RA spectra of the same LB films deposited on evaporated Ag films.[2] Apparently, the peak intensities of the respective bands are quite different between the transmission and RA spectra. The antisymmetric and symmetric CH_2 stretching bands (2919 and 2852 cm^{-1}) of the hydrocarbon chains and the antisymmetric COO stretching band (1543 cm^{-1}) of the carboxylate group are strongly observed in the transmission spectrum (Figure 1). But, the symmetric COO stretching band (1433 cm^{-1}) of the carboxylate group and so called "band progression" (1400–1200 cm^{-1}) due to the CH_2 wagging vibration of the hydrocarbon chains appear exclusively in the RA spectrum (Figure 2).

If the molecule of cadmium stearate with the all-trans hydrocarbon chain is oriented perpendiculary to the film surface, the two CH_2 stretching vibrations and the antisymmetric COO stretching vibration which have the transition moments parallel to the film surface should be obserbed strongly in the transmission measurements. However, the symmetric COO stretching and CH_2 wagging vibrations which have the transition moments perpendicular to the film surface should be strongly obserbed in the RA measurements. Since these expectations were fully realized in observed transmission and RA spectra, we can conclude that the molecular axis is almost perpendiculary to the film surface.

On the basis of these experimental results and discussion, we tried to establish a new method for quantitative evaluation of the molecular orientation in the thin LB films using FT-IR transmission and RA spectra. Here, we assume an uniaxial orientation of the transition moment with an angle ϕ around the normal axis, Z, to the LB film surface i.e. the XY plane. As shown by Eq.(1), the absorbance in the transmission spectrum, A_T, is proportional to the x component of the absorption coefficient, K_x. On the other hand, the absorbance in the RA spectrum, A_R, mainly depends upon, the z component of the absorption coeffi-

Table I. Calculation of the ϕ and γ values for 7-monolayer LB film of cadmium stearate.[2]

Assignment	A_T	A_R	A_T/A_R	m_z	m_x	ϕ	
$v_a CH_2$	0.01130	0.00325	3.48	10.7	0.133	$\beta=85°$	$\gamma = 7°$
$v_s CH_2$	0.00803	0.00217	3.69	10.8	0.129	$\alpha=85°$	
$v_a COO^-$	0.00735	0.00339	2.17	13.7	0.048	83°	
$v_s COO^-$	0.00027	0.03490	0.004	13.9	0.042	18°	

cient, K_z, multiplied by the z component of the intensity enhancement factor, m_z, due to the presence of the Ag surface, and partly on k_x multiplied by m_x. After a simple calculation under the condition of the uniaxial orientation, we have Eq.(2) relating the absorbance ratio, A_T/A_R, with the orientation angle ϕ.

$$A_T/A_R = K_x/(m_z k_z + m_x k_x) \qquad (1)$$

$$= \sin^2\phi/(2m_z\cos^2\phi + m_x\sin^2\phi) \qquad (2)$$

The enhancement factors m_z and m_x can be calculated precisely by Hansen's formulas[3] for optics of thin multilayer film.

Then, we calculated the ϕ values for the transition moments of the major bands of the 7-monolayer LB film of cadmium stearate by Eq.(2) using the observed absorbance ratios between the transmission and RA spectra. The results are shown in Table I. Apparently, the m_x values are almost one per cent of the m_z value. This means that the electric field obtained by the RA experiments is practically perpendicular to the film surface, as was described above. From the values

Figure 3. Schematic illustration of the orientation of cadmium stearate in the LB film.[2]

of A_T/A_R, m_z and m_x, we obtained the results of the angles ϕ. Both angles (α and β) of the transition moments of the antisymmetric and symmetric CH_2 stretching vibrations are 85°, and those of the antisymmetric and symmetric COO stretching vibrations are 83° and 18°, respectively. Since the transition moments of the antisymmetric and symmetric CH_2 stretching vibrations and the hydrocarbon chain axis are mutually perpendicular, the orientation angle γ of the hydrocarbon chain axis from the surface normal can be obtained to be 7° by the orthogonal relation

$$\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1 \qquad (3)$$

using $\alpha = \beta = 85°$. These results for the cadmium stearate LB film are schematically illustrated in Figure 3, which gives a clear indication for the almost perpendicular orientation of the molecule. The tilt angle of 7° for the hydrocarbon chain axis agrees well with the result of 8°±5° [4] which is the average of several data obtained for cadmium salts of long-chain fatty acids by other investigators.[5-9] This is also in good agreement with the result of 10° obtained from the long spacing determination of cadmium salts of long-chain fatty acids by X-ray analysis.[10,11]
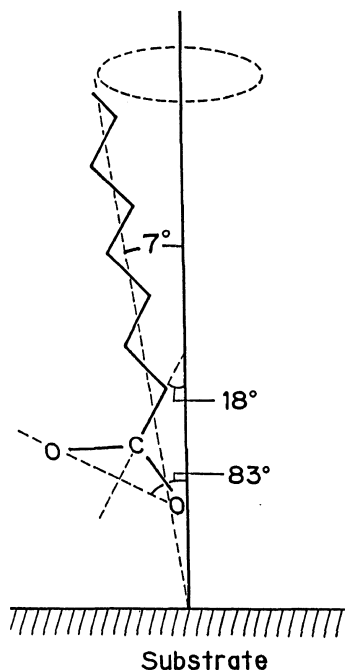
RELATIONSHIP BETWEEN THE MOLECULAR ORIENTATION AND PYROELECTRICITY IN ALTERNATE LB FILMS

It has been known that the X- and Z-type LB films, and alternate LB films consisting of two different amphiphiles have noncentrosymmetric structures, and therefore, are expected to give piezoelectric, pyroelectric, and various nonlinear optical properties.
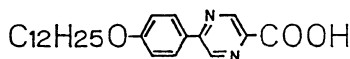
$$C_{12}H_{25}O \text{—} \bigcirc \text{—} \langle N \rangle \text{—} COOH$$

Figure 4. Structure of DOPC.

In this view point, we fabricated alternate LB films consisting of 5-(p-dodecyloxyphenyl)pyrazine-2-carboxylic acid (DOPC, Figure 4) synthesized by Takehara et al.[12] and deuterated stearic acid (St-d_{35}). Hereafter, I will symbolize DOPC by P and deuterated stearic acid by S. The alternate LB film was prepared by n-time depositions of the unit PS layer on the first monolayer of S. We designate this structure by S(PS)$_n$. Then, we measured pyroelectricity and temperature dependence of the molecular orientation in these films[13] using the above-mentioned method[2] by FT-IR transmission and RA spectra. The same studies were also performed for the alternate LB films of their barium salts, S(PS)$_n$-Ba.[13]

For pyroelectric measurements, we used an arrangement shown in Figure 5 with two Al electrodes. The electric current gaenerated on linearly heating the LB film was measured by picoammeter in the temperature range between -30 and 60 °C. The pyroelectric coefficient p is calculated from the pyroelectric current I by

$$I = pA (dT/dt) \tag{4}$$

Here A is the area of the electrode (1.7 cm^2) and dT/dt is the rate of the temperature change (2.2 K/min).

Figure 6 shows the current-temperature (I-T) curves for the alternate (noncentrosymmetric) S(PS)$_9$ and S(PS)$_9$-Ba films. For reference, the I-T curve for the homogeneous (centrosymmetric) SP$_{18}$-Ba film is also
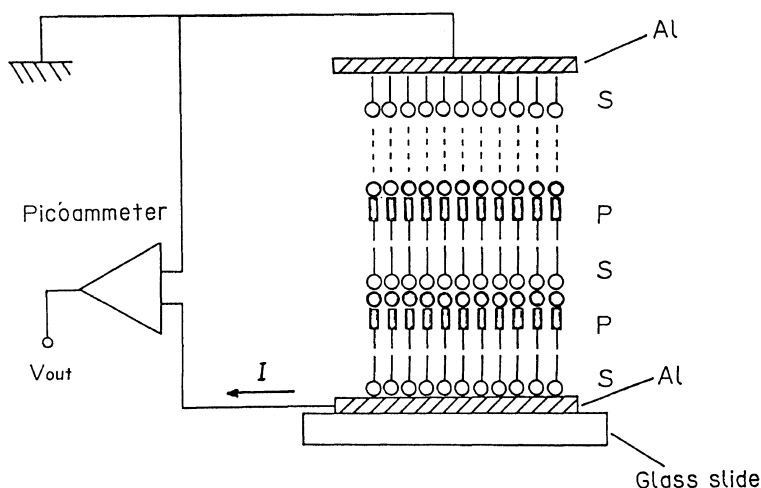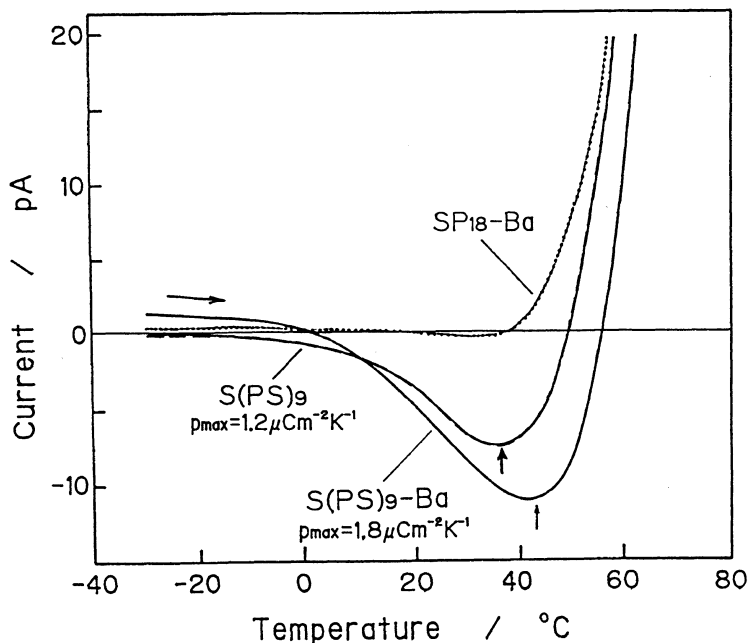

Figure 5. Arrangement for pyroelectric measurements.[13]

Figure 6. The current-temperature curves for alternate S(PS)$_9$ and S(PS)$_9$-Ba films and for homogeneous SP$_{18}$-Ba film. [13]

shown in Figure 6. For both alternate LB films, the negative current is increased on heating above 0°C. After passing through the minimum points around 40 °C, the curves rise rapidly on further heating. For homogeneous SP$_{18}$-Ba film, on the other hand, almost no current is obtained up to 40 C°, and then the positive current increases. Therefore, the negative current observed only for the alternate films can be regarded as pyroelectric currents which may be due to changes in the spontaneous polarization in the films. Maximum pyroelectric coefficient, P$_{max}$, calculated by Eq.(4) is 1.8 μC/m^{2}K at 43 °C for the alternate film of barium salt and 1.2 μC/m^{2}K at 37 °C for the alternate film of acid. The positive currents observed above 50 °C for the all LB films will be discussed later in connection with the molecular orientation.

Figure 7 represents FT-IR transmission spectra of the alternate S(PS)$_9$-Ba film at various temperatures from 0 to 120 °C. Two intense bands at 2919 and 2852 cm^{-1} are the antisymmetric and symmetric CH$_2$ stretching bands of DOPC, respectively, and two intense bands at 2192 and 2088 cm^{-1} are the antisymmetric and symmetric CD$_2$ stretching bands of St-d$_{35}$, respectively. Furthermore, two bands at 1610 and 1514 cm^{-1} are assigned to the antisymmetric COO stretching vibrations of DOPC and St-d$_{35}$. Intensities of the CH$_2$ and CD$_2$ stretching bands apparently decrease with the increase in temperature. Figure 8 shows RA spectra of the same alternate film in the same temperature range. The CH$_2$ and CD$_2$ stretching bands are much weaker in the RA spectra than in the corresponding transmission spectra.

Using these transmission and RA spectra as well as Eq.(2), we calculated the temperature dependence of the orientation angles, γ, for the
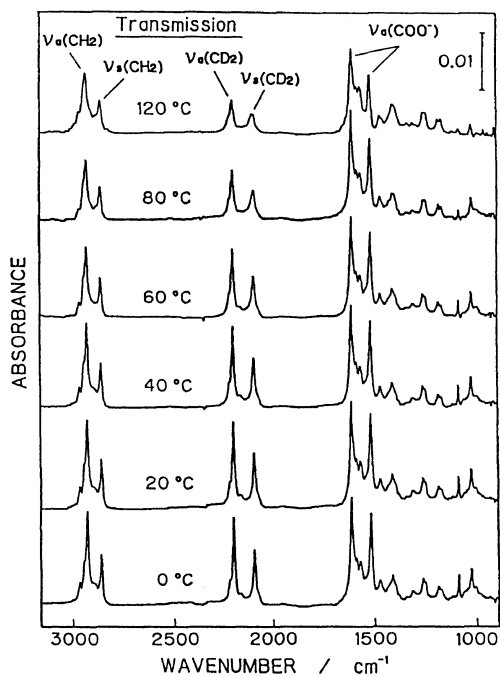
Figure 7. FT-IR transmission spectra of alternate S(PS)$_9$-Ba film at various temperatures.[13]
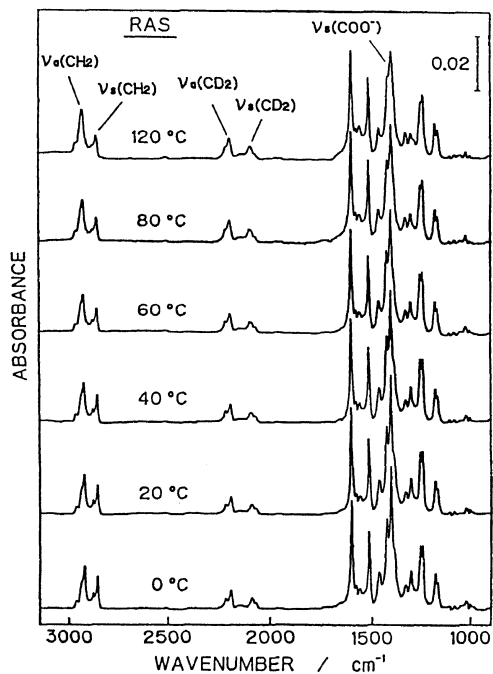
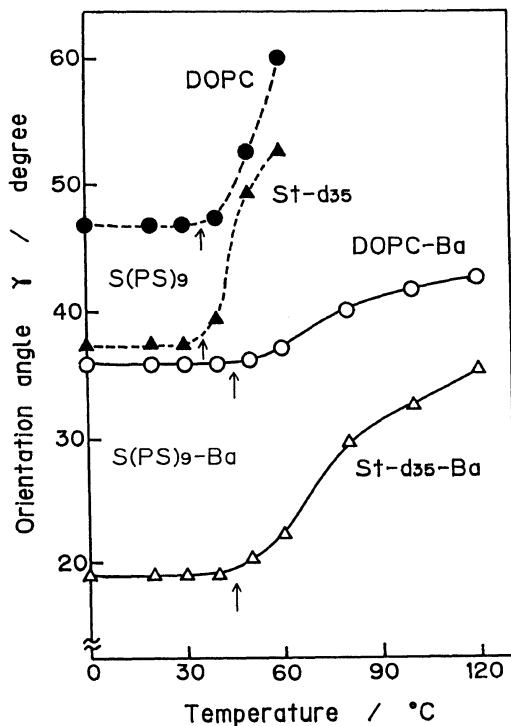Figure 8. FT-IR reflection-absorption spectra of alternate S(PS)$_9$-Ba film at various temperatures.[13]

Figure 9. Temperature dependence of the orientation angles γ of the hydrocarbon chain axes of the constituent molecules in alternate $S(PS)_9$-Ba (——) and $S(PS)_9$ films (----).[13]

hydrocarbon chain axes of the constituent molecules of the alternate acid and barium salt films. The results are shown in Figure 9. Apparently, the γ values of the respective constituents in the alternate barium salts film are much smaller than those of the corresponding molecules in the alternate acid film. This reveals that the barium salt molecules are highly oriented as compared with the acid molecules. For the barium salt film, the γ values for both constituent molecules are almost constant up to ca. 45°C, and then gradually increase on further heating. For the acid film, the γ values for both constituents are also constant up to ca. 35°C, and then increase rapidly with increasing temperature. Therefore, the barium salt film are thermally more stable than the acid films. It is to be noted that the temperatures, 45 and 35 °C, at which the γ values start to increase for the alternate barium salt and acid films, respectively, are in good agreement with the above-mentioned temperatures (43 and 37 °C) at which the positive currents start to increase for the same films (Figure 6). Since it is reasonable to consider that the increases in the γ value at higher temperatures are mainly due to the increase in the conformational disorder of the hydrocarbon chains, the agreements of the temperatures suggest that the posi-

tive current can be ascribed to the increase in thermal motion of the hydrocarbon chains at higher temperatures.

Negative currents observed only for the alternate films below 50 °C were regarded as the pyroelectric currents due to the changes in spontaneous polarization. In this temperature region, the molecular orientation is kept unchanged for all the constituents as seen in Figure 9. Since, however, we observed the frequency changes of the antisymmetric and symmetric COO stretching bands for the barium salt films, it is conceivable that the changes in spontaneous polarization can be ascribed partly to a structure modification of the carboxylate groups of the constituent molecules with the highly oriented, all-trans hydrocarbon chains. Finally, it should be noticed that the higher value of the pyroelectric coefficient in the barium salt alternate film than that in the acid alternate film may be related to the higher orientation of the constituent molecules in the barium salt film than in the acid film.

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