

## FTIR-RA 분광법을 이용한 스테아르산 단분자막에서 분자구조의 온도의존성 고찰

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## Study on Temperature Dependence of Molecular Structure in Stearic Acid LB Films Using FTIR-RAS

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**요 약.** 물 표면 위의 스테아르산 단분자막을 은을 입힌 유리판에 이전시켜 1층, 3층, 9층 및 21층의 Langmuir-Blodgett(LB) 분자막을 제조하였다. 표면압은 30 mN/m 이었으며 FTIR-RA 분광법을 이용하여 31~72°C에서 적외선 흡수 스펙트럼을 얻었다. 31°C에서 탄화수소 사슬이 보다 더 수직적인 배향을 나타내고 있었으며 1층의 경우에는 C=O의 피크가 관찰되지 않았다. 이는 은표면에서 이미지 이중극 효과나 금속염을 형성하기 때문으로 본다. 1층과 3층의 경우에는 스테아르산의 트랜스 이성질체가 많고 21층의 경우에는 시스형이 많은 것으로 나타났다. 온도 변화에 대한 FTIR-RAS 측정에서 분자층의 수를 증가시키면 사슬의 녹는점이 높아졌으나 1층의 경우는 예외를 나타내는데 이는 1층의 경우 은기판과의 강한 상호작용에 의한 때문이다.

**ABSTRACT.** 1-, 3-, 9-, and 21-Monolayer Langmuir-Blodgett(LB) films of stearic acid were deposited on silver-coated glass slides at the surface pressure of 30 mN/m. Fourier transform infrared(FTIR) reflection-absorption spectra (RAS) of these LB films were recorded at various temperatures from 31 to 72°C. The spectra at 31°C exhibited characteristic features of highly perpendicular orientation of the hydrocarbon chain. In the 1-monolayer LB film, the C=O stretching band was not observed, presumably due to the image dipole effect on the silver surface. In the 1- and 3-monolayer LB films, the *trans* isomer of stearic acid was prominent, but the *cis* isomer was dominant in the 21-monolayer LB film. FTIR-RAS measurements at an elevated temperature indicated that the chain melting temperature increases and approached to the bulk melting point with increasing the number of monolayer, except for the 1-monolayer LB film which has a higher melting temperature than the 3-monolayer film due to the strong interaction with the silver substrate.

## INTRODUCTION

With the increased interest in Langmuir-Blodgett (LB) films as well-organized, functional molecular assemblies, much information about the molecular structure and orientation in thin LB films has been accumulated. However, from the diversity of molecular states in monolayers on the water surface and of the substrate material with different surface state (hydrophobic or hydrophilic, etc.), molecules within fabricated LB films take various structures and orientations. In that sense, the LB films is always a fresh subject of structural investigations.

In our previous report<sup>1</sup>, we postulated as drastic structural change in thin LB films of stearic acid with increasing the number of monolayers using Fourier transform infrared (FTIR) attenuated total reflection (ATR) spectroscopy. We also examined the effect of preparation method (vertical or horizontal) and speed on the polymorphs of stearic acid LB films by FTIR-ATR and X-ray measurement<sup>2</sup>. Further, we have investigated the intensity enhancement in the ATR spectra of stearic acid LB films by metal evaporations<sup>3-5</sup>. In these studies, the film was transferred at a surface pressure of 20 mN/m which the monolayer was in the liquid-condensed ( $L_2$ ) phase<sup>6,7</sup> (see Fig. 1).

In the present work, we transferred stearic acid monolayer at a surface pressure of 30 mN/m in the super liquid (LS) phase<sup>6,7</sup> onto silver-coated glass slides (see Fig. 1). We applied FTIR-RAS technique in order to examine the effect of thickness and temperature on the molecular isomerism, order, and orientation in these LB films<sup>8</sup>. This work also constitutes a series of investigations of thermostability in LB films<sup>9,10</sup>.

## EXPERIMENTAL

Stearic acid used in this study was the same as that reported on previously<sup>1</sup>. Water was purified by a modified Mitamura Riken Model PLS-DR automatic lab still consisting of a reverse osmosis module, an ion-exchange column, and a double distiller. The monolayer of stearic acid was

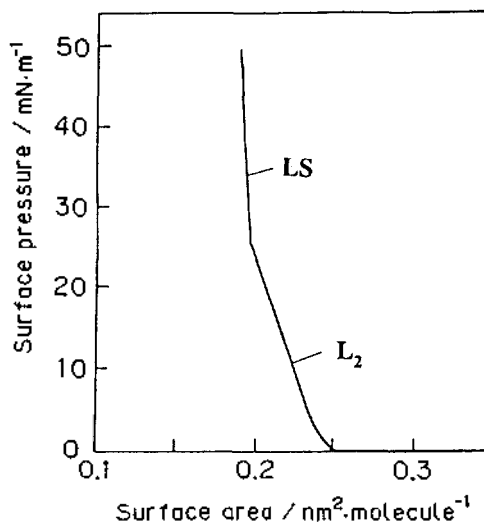


Fig. 1.  $\pi$ -A isotherm of stearic acid at 20°C.

prepared spreading 90  $\mu$ l benzene solution (ca. 1 mg/ml) on pure water at 20°C in Kyowa Interface Science Model HBM-AP Langmuir trough with a Wilhelmy balance. The monolayer was compressed by a speed of 20 cm<sup>2</sup>/min up to the surface pressure of 30 mN/m. Then, the monolayer was transferred by the vertical dipping method onto a 72×26×1.3 mm glass slide primed with a vacuum evaporated 100 nm thick silver layer. The dipping speed of the substrate was 10 mm/min and the transfer ratios were 0.99±0.02. After deposition of the first monolayer, the glass slide was kept dry in a desiccator with P<sub>2</sub>O<sub>5</sub> at least 15 h. Then, the depositions were repeated. The obtained LB film was immediately subjected to the FTIR measurement, although there has been no appreciable sign of the aging<sup>11</sup>. FTIR-RAS for *p*-polarized radiation through a Hitachi wire-grid polarizer were recorded using a Nicolet 710 spectrophotometer equipped with an MCT detector and a Harrick Model RMA-1DG/VRA reflection attachment. The angle of incidence was 85°. The spectral resolution was 4 cm<sup>-1</sup> and the number of interferogram accumulations was 3000. For RAS measurements at an elevated temperature, the sample was mounted on a heating cell made of an aluminum block with a built-in sheath heater<sup>9,12</sup> which is similar to one designed by Schlotter and

Rabolt<sup>13</sup>. After raising the temperature to a preset value and keeping it within  $\pm 1^\circ\text{C}$  for at least 10 min, we started the RAS measurement. The temperature reading was performed by a Keithley Model 177 voltohmmeter with a copper-constantan thermocouple, which is calibrated in advance recording RAS spectra of cast films of a series of *n*-fatty acids with known melting points.

## RESULTS AND DISCUSSION

FTIR-RAS of 1-, 3-, 9-, and 21-monolayer LB films of stearic acid at  $31^\circ\text{C}$  are shown in Fig. 2. From the Fig. 2, the spectral features in the CH stretching region appear to be of highly oriented hydrocarbon chains with appreciably strong intensities of the asymmetric ( $2,963\text{ cm}^{-1}$ ) and symmetric ( $2,876\text{ cm}^{-1}$ ) methyl stretching bands which are comparable to those of the antisymmetric ( $1,917\text{ cm}^{-1}$ ) and symmetric ( $2,849\text{ cm}^{-1}$ )  $\text{CH}_2$  stretching bands<sup>14-16</sup>. In a 7-monolayer LB film of cadmium stearate which had similar RAS features, we esti-

mated the tilt angle of the hydrocarbon chain axis as  $7^\circ$  from the surface normal, by comparison with its transmission spectrum<sup>15</sup>. If the tilt angle of the chain axis is around  $30^\circ$ , our analyses showed that the  $\text{CH}_2$  stretching bands have much stronger intensities than the  $\text{CH}_3$  stretching bands<sup>12,17,18</sup>. Therefore, the spectral features in Fig. 2 are quite different from one expected for the C-form crystal of stearic acid with the chain tilt angle of  $38^\circ$ <sup>19,20</sup>, which can be often obtained under the monolayer transfer at the surface pressure of  $20\text{ mN/m}$  (the liquid condensed  $L_2$  phase). The spectral features similar to Fig. 2 have been obtained for LB films of stearic acid/Al or Au<sup>11</sup>, icosanoic acid/Au<sup>21</sup>, docosanoic acid/Al<sup>22</sup> systems. Among various crystal polymorphs of stearic acid, the  $A_2$ -form which has higher degree of perpendicular chain orientation than other forms<sup>19,23</sup> is a possible form for these LB films. We deposited stearic acid LB films consisting of this form with a crystallographic long spacing of  $4.64\text{ nm}$ <sup>24</sup> by a low-speed horizontal lifting method<sup>2</sup>. Although the X-ray analysis was not successful in the present experiment, it is obvious that the spectral features in the CH stretching region in Fig. 2 is indicative of the highly perpendicular orientation of the hydrocarbon chain in the  $A_2$ -form crystal. It is also plausible if we consider the result of the synchrotron X-ray diffraction that the LS phase possesses a perpendicular chain orientation on the water surface, while the  $L_2$  phase has a tilted chain orientation<sup>25</sup>.

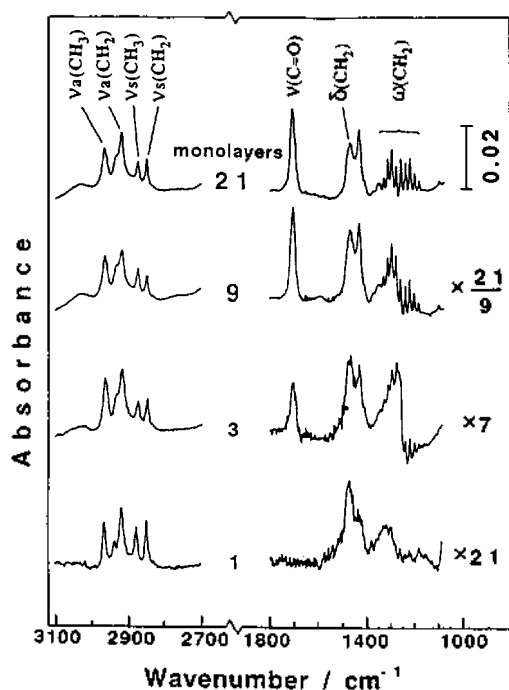


Fig. 2. FT-IR RA spectra of 1-, 3-, 9- and 21-monolayer LB films of stearic acid at  $31^\circ\text{C}$ .

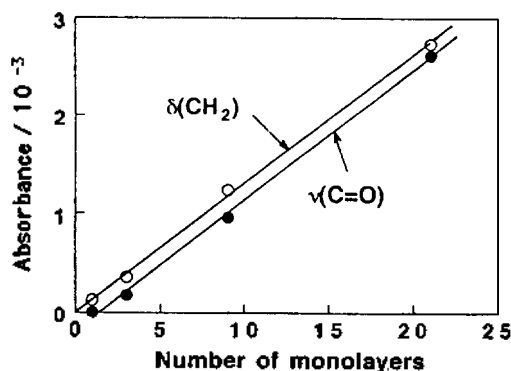


Fig. 3. Absorbances of the C=O stretching (●) and  $\text{CH}_2$  scissoring (○) bands plotted against the number of monolayers.

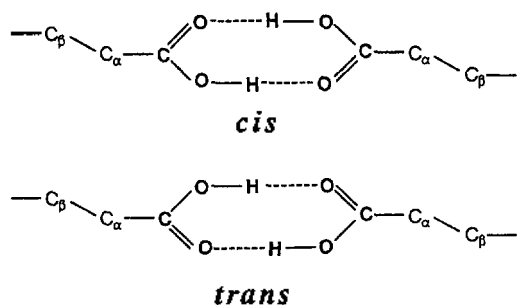


Fig. 4. *Cis* and *trans* isomers of stearic acid.

Another feature in Fig. 2 is the disappearance of the C=O stretching band at  $1,706\text{ cm}^{-1}$  in the 1-monolayer LB film. In Fig. 3, the peak absorbance of the C=O stretching band is plotted against the number of monolayers, together with that of the CH<sub>2</sub> scissoring band intensity has been taken into account, and the normalization of the CH<sub>2</sub> scissoring band intensity has been made so that its least-squares line parallels that for the C=O stretching band. The straight line for the C=O stretching band crosses the abscissa at the 1-monolayer position, seeing that the first monolayer in all the LB films has no intensity at this position. The similar phenomena has already observed in our previous ATR measurements of stearic acid LB films on germanium prism<sup>1</sup>. There are two possible reasons; one is the metal stearate formation on the substrate<sup>3,11</sup> and the other is the image dipole effect at a short distance from the silver surface<sup>1</sup>. Since there is no strong band either in the  $1,500\sim 1,600\text{ cm}^{-1}$  region where the antisymmetric COO<sup>-</sup> stretching band is expected for silver stearate<sup>26,27</sup> or around  $1,400\text{ cm}^{-1}$  where the strong symmetric COO<sup>-</sup> stretching band is expected<sup>3</sup>, we inclined to take the image dipole effect as in the previous case<sup>1</sup>. Another strong support comes from the fact that there is a broad band at  $1,300\sim 1,325\text{ cm}^{-1}$  characteristic to the coupling mode between the antisymmetric C<sub>α</sub>-C-O stretching and COH bending vibrations of the *trans* isomer (see Fig. 4) of stearic acid<sup>28,29</sup>. In RA spectra of metal salts of n-fatty acids, there is no strong band around  $1,300\text{ cm}^{-1}$ <sup>14-16</sup>. Although the presence of stearic acid (and thus the image dip-

ole effect) is almost certain, the final decision whether silver stearate exists or not awaits further clarifications by using perdeuterated stearic acid.

Another characteristic spectral feature observed in Fig. 2 is that in the 1- and 3-monolayer LB films, the coupling mode around  $1,300\text{ cm}^{-1}$  of the *trans* stearic acid is prominent. However, with increasing the number of monolayers to 9 and 21, the intensity of the band is decreased and instead the band progression due to the CH<sub>2</sub> wagging modes characteristic to the *cis* isomer (Fig. 4) of stearic acid<sup>28,29</sup> gains its intensity. This indicates that with the increase of the number of monolayers, the molecular assembly in the LB film enhances its perfectness at the A<sub>2</sub>-(or other similar) form crystal, since the *cis* isomer is a stable isomer in all the polymorphs except for the C-form where the *trans* isomer is stabilized<sup>23,28-31</sup>. The tendency is quite opposite to our previous observation<sup>1</sup> that the intensity of the *trans* band around  $1,300\text{ cm}^{-1}$  increased with increasing the number of monolayers, resulting from the C-form crystal formation in that case.

We performed FTIR-RAS measurements of these LB films at an elevated temperature. Results for the 9-monolayer LB film are presented in Fig. 5. The frequency ( $947\text{ cm}^{-1}$ ) and shape of the OH out-of plane bending band are similar to those of the polarized spectral component of the A<sub>2</sub>-form crystal of stearic<sup>32</sup> or palmitic<sup>23,33</sup> acid, although they are also close to those of the C-form crystals<sup>23,32,33</sup>. As the temperature increased, the originally weak antisymmetric and symmetric CH<sub>2</sub> stretching bands enhance their intensity slightly at first and drastically later (above  $68^\circ\text{C}$ ). This indicates the increased chain tilt and disorder due to the increase of the number of the gauche conformers in the hydrocarbon chains<sup>8,13,14,20</sup>. In addition, the band progression arising from the CH<sub>2</sub> wagging mode which is characteristic to the all-*trans* conformation of the hydrocarbon chain diminishes and finally disappears at  $68^\circ\text{C}$ . As a semiquantitative measure of the chain tilt and disorder, we calculated the peak intensity ratio of the antisymmetric CH<sub>2</sub> stretching band to that of

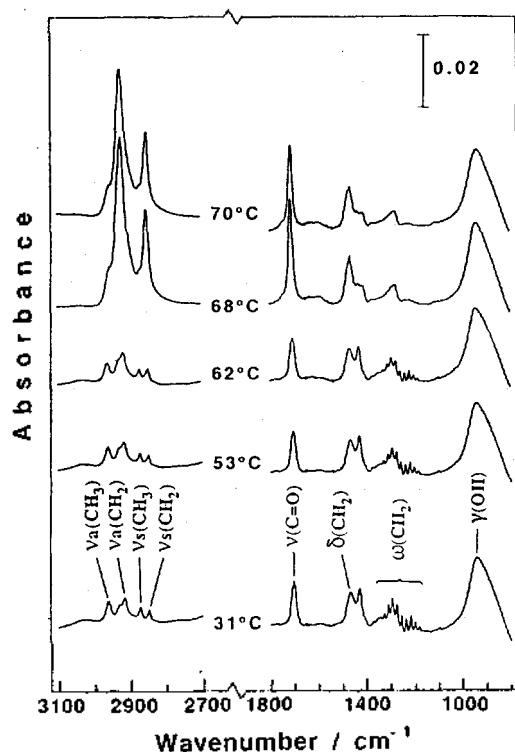


Fig. 5. FT-IR RA spectra of 9-monolayer LB film of stearic acid at elevated temperatures.

the symmetric  $\text{CH}_3$  stretching band, measuring the absorbance ratio of 2,990 and  $2,810\text{ cm}^{-1}$ . Then, we plotted it against temperature in Fig. 6, together with results for other numbers of monolayers. The intensity ratio was previously adopted in discussing changes in the chain order of the 12-hydroxystearic acid LB films by compression of its spread monolayer on the water surface<sup>34</sup>. In the 1-monolayer LB film, the intensity does not change very much. This implies that the interaction of the first monolayer with the silver substrate is strong enough to prevent that chain disorder (We have checked that the experimental reproducibility for the 1- and 3-monolayer LB films was good).

With increasing the number of monolayers, the highest intensity ratio at high temperatures increases, meaning that the chain disorder or the number of gauche conformers increases. This seems to come from the increase in internal pres-

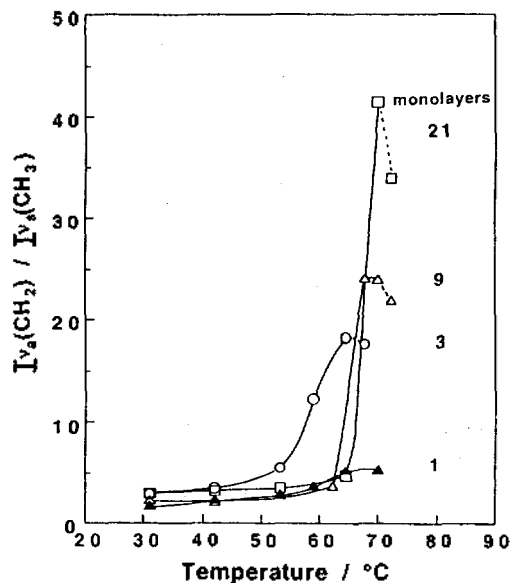


Fig. 6. Temperature dependence of conformational disorder of stearic acid LB films with various number of monolayers.

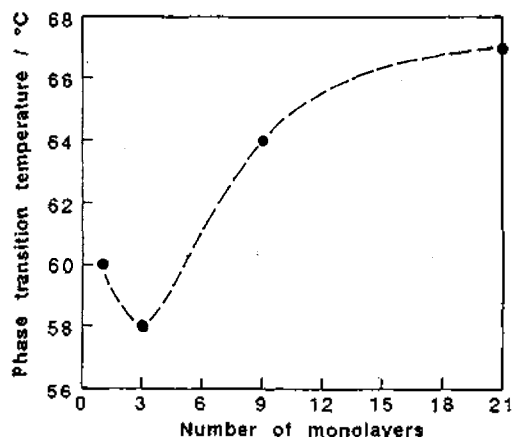


Fig. 7. Phase transition temperature (melting point) versus the number of monolayers.

sure, which originates from the attraction forces among molecules in the LB film, with the increase of the film thickness. In fact, it is well known that the molten hydrocarbon chain tends to be reduced incorporating the gauche conformers, as the pressure is increased<sup>35</sup>. After reaching a highest intensity ratio, it starts to decrease on further heating. This is due to the fact that the mol-

ten stearic acid LB film tends to slip off the substrate at these temperatures in the vertical setting of the RAS substrate. The phase transition temperature (melting point) which is defined by the middle point between the highest and lowest values of the intensity ratio, is plotted against temperature in Fig. 7. Except for the 1-monolayer LB film, it increases with increasing the number of monolayers, but they are still lower than the melting point of the bulk stearic acid at 69.5~70°C<sup>1</sup>. It is also noted that the phase transition temperatures given in Fig. 7 are higher than the melting point (44°C) of the spread monolayer on the water surface reported by Kajiyama *et al.*<sup>36</sup> The effect of substrate (water or silver) on the melting point (44 or 60°C) of the monolayer film is also clear.

### CONCLUSION

We have demonstrated the film transfer at the surface pressure of 30 mN/m (LS phase) gave LB films with the high perpendicular orientation of the hydrocarbon chain. The molecular conformation and chain melting phenomena of the stearic acid LB film are affected by the number of monolayers. With increasing the number of monolayers, the number of *cis* isomers increases, meaning that the molecular and crystal structure of the LB film gains its perfectness and approaches to that of the bulk A<sub>2</sub>- (or A<sub>2</sub>-like) form crystal. Concomitantly, the chain melting point increases with the number of monolayers. The first monolayer is always exceptional since it interacts strongly with the silver substrate by the physical effect including the image dipole effect.

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