Structure Disordering during Surface Pressure Relaxation of Langmuir Films of Stearic Acid as Studied by Infrared External Reflection Spectroscopy

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In situ FT-IR external reflection spectra of Langmuir films of stearic acid on the water surface were recorded during the surface pressure relaxation at two surface areas, corresponding to the liquid condensed (L_2) and super-liquid (LS) phases. In the L_2 phase, the surface pressure relaxation was minimal and so was the spectral change. In the LS phase, however, the structural change from the trans to gauche conformation was detected.

In a previous paper,[1] we have recorded Fourier transform infrared (FT-IR) external reflection spectra (ERS) of Langmuir (L) films of stearic acid and Cd stearate at various surface areas. In the stearic acid film, the gauche-trans conformational change upon monolayer compression was observed, supporting the result of Raman spectral measurements of L films of stearic acid-d_{35} and Cd stearate-d_{35}.[2] In that measurement,[1] the process was stepwise in that after compressing a certain amount of surface area, the FT-IR measurement was performed, and then it was repeated many times.

In the present work, we compressed the L film of stearic acid to a target surface area with a moderate speed, and then the surface pressure and FT-IR/ERS were recorded with the time lapse, to examine the structural change at the molecular level during the surface pressure relaxation. The plausible mechanism of the relaxation is either the collapse of the monolayer structure or inversely the promotion of crystallization within the two dimensional space.

We used a trough with a 80×22 mm^2 effective surface area attached to a Specac 19650 monolayer/grazing angle accessory.[1] The water level of the trough was kept constant during the experiment by using an external teflon reservoir connected by a siphon. First, the background spectrum was collected with 500 scans for the pure water surface at pH 6.2. Then, 10 ml of 8.12$\times 10^{-4}$ M benzene solution of stearic acid was spread on the water surface. After waiting for 10 min to allow the solvent to be fully evaporated, the L film was compressed at a velocity of 0.027 $nm^2 molecule^{-1} min^{-1}$ to 0.207 or 0.189 nm^2/molecule, which are typical of the liquid-condensed (L_2) or super-liquid (LS) phases, respectively (Figure 1). Immediately after the compression, 50 FT-IR/ERS of L films at each surface area were successively recorded with 100 scans (ca. 90s) each on a Nicolet 6000C FT-IR spectrophotometer equipped with an InSb detector with a resolution of 8 cm^{-1}, We used a bandpath (3400-2100 cm^{-1}) filter to remove the thermal agitation of the water surface by the infrared source. The angle of incidence was 38°. The surface pressure was measured with a Willhelmy balance attached to a Kyowa Interface Science Model HBM-AP Langmuir trough on the same condition as the FT-IR measurements.

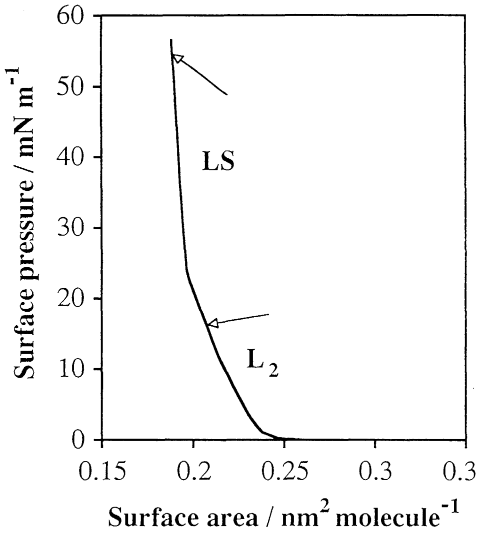

Figure 1. The π-A isotherm of stearic acid on the water surface at pH 6.2 and 23 °C. The arrows show two experimental points.

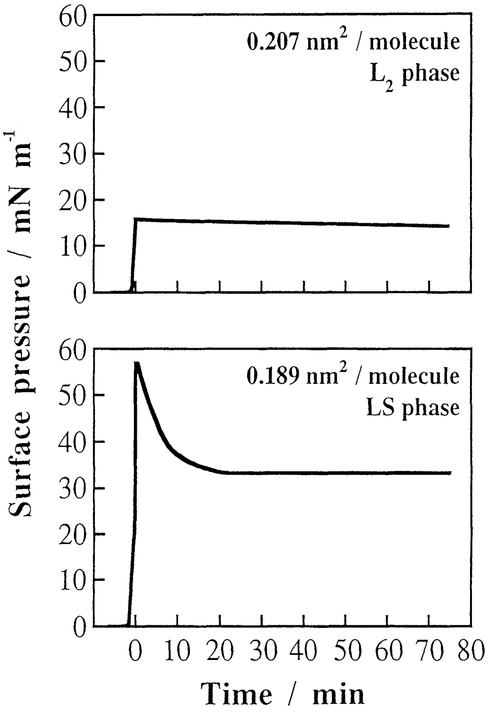

Figure 2. Surface pressure relaxation curves of stearic acid compressed to the surface area of 0.207 and 0.189 nm^2/molecule.

Figure 2 shows the surface pressure relaxations of L films of stearic acid compressed to the surface areas of 0.207 (L_2 phase) and 0.189 nm^2/molecule (LS phase). At the surface area of 0.207 nm^2/molecule, the surface pressure slightly decreases from 15.8 to 14.2 mN/m after 75 min. At 0.189 nm^2/molecule, on the other hand, the pressure sharply decreases from the initial value of 57.0 mN/m in ca. 20 min and finally reaches 33.2 mN/m.

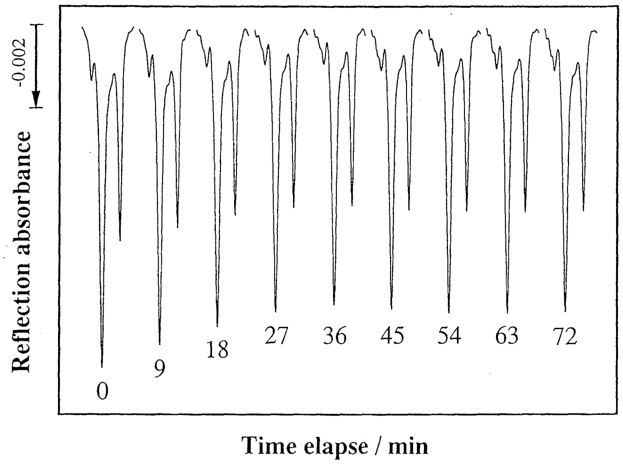

Figure 3. Time dependent FT-IR/ERS in the region 3000-2800 cm^{-1} of L film of stearic acid at surface area of 0.189 nm^2/molecule at 23 °C.

During the compression of this film, there has been no surface pressure drop often observed in the collapse process of the monolayer.[3] Since the solution to the subphase water or evaporation of stearic acid is very slow at room temperature,[3] the magnitudes of these relaxations are much larger than that expected from the loss by solution or evaporation.

In Figure 3, the change in FT-IR spectrum in the CH stretching vibration region (3000-2800 cm^{-1}) is demonstrated with the time elapse of the L film of stearic acid compressed to 0.189 nm^2/molecule. We find that the absolute value of the antisymmetric and symmetric CH$_2$ stretching modes appearing as the two bands with the intense and medium intensities decrease with time by ca. 27 min and then it stays roughly constant. Since the number of molecules under observation is invariant during the time elapse, this intensity decrease is ascribed to the conformational or orientational change. In Figure 4, the peak wavenumber of the antisymmetric CH$_2$ stretching band in L films of stearic acid compressed to 0.207 and 0.189 nm^2/molecule are plotted against relaxation time. In accord with the tendency of the pressure relaxation demonstrated in Figure 2, the wavenumber slightly changes from 2918.2 to 2918.5 cm^{-1} at 0.207 nm^2/molecule. At 0.189 nm^2/molecule, however, it increases largely from 2917.1 to 2917.6 cm^{-1} in 20 min and after 30 min, it stays almost unchanged at 2917.8 cm^{-1}. The increase in wavenumber of the antisymmetric CH$_2$ stretching band clearly indicates the increase in the gauche conformation or the chain disorder.[1] Thus, the most probable mechanism of the pressure relaxation is the collapse of the monolayer such that some molecules in the compressed monolayer slip out upward to form molecules with the disordered chain by gaining the free space. Then, the surface pressure could decrease owing to the decrease in number of molecules in the two dimensional monolayer spaces. In other words, the compression energy in excess is released by the monolayer collapse during pressure relaxation. The evidence of such a collapse is provided by the AFM experiments, though it is indirect because they are for LB films fabricated at high surface pressures.[4] The slight wavenumber increase at 0.207 nm^2/molecule indicates that even at this low surface pressure compared with the normally accepted collapse pressure (ca. 60 mN/m), the collapse already commences. This is reasonable if we consider the low equilibrium spreading pressure of stearic acid as low as 5 mN/m. The another mechanism that holes in the L film are gradually filled with surrounding molecules might be partly responsible for the gain of the free space in this case.

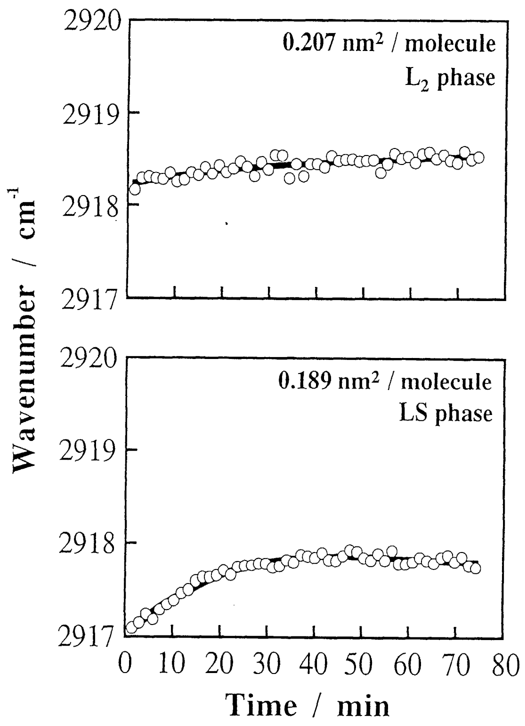

Figure 4. Wavenumber of ν_aCH$_2$ in L film of stearic acid vs. time after compression.

The collapse of two dimensional crystal under surface compression is just the inverse of the crystal growth under strain (stretching) of polymers,[5] although the relaxation of surface pressure or stress is observed in each case.

References and Notes

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