Selective Langmuir–Blodgett Transfer on Phase-Separated Films

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Mixed Langmuir–Blodgett (LB) films of arachidic acid (AA) and perfluorotetradecanoic acid (PA) took phase-separated structures with the monolayer domains of AA buried in the monolayer of PA. When two monolayers of AA were transferred on the 1/1 mixed LB films of AA and PA, AA was transferred only on the domains of AA in the mixed LB films.

The Langmuir–Blodgett (LB) technique has been used to fabricate supramolecular structures with multiple components.[1] Ease with which to fabricate multilayer LB films is an important aspect in that the LB films with noncentrosymmetric structures have been obtained to apply to nonlinear optics.[2] One of the important tasks to widen the possibilities of LB films is to explore the methodology to fabricate supramolecular multilayer LB films in which the upper layers probe the underlying films and are transferred only on one of the components. The directed transfer of this type will enable us to construct supramolecular films in which different functional units are positioned three-dimensionally in a planned manner.

In this study, we will first describe the fabrication of single-layer LB films of arachidic acid (AA) and perfluorotetradecanoic acid (PA). The phase-separated structures of the mixed LB films are investigated using IR, AFM and Friction Force Microscopy (FFM). Then we will demonstrate the directed transfer of the monolayers of AA on the phase-separated LB films.

Figure 1 shows surface pressure-area (π–A) isotherms of AA, PA and their mixtures at 20 °C. Spreading solvent was a mixture of hexane and THF (9/1 v/v). Within the experimental errors, the additivity rule seems to hold, suggesting that the two components are phase separated or ideally mixed.

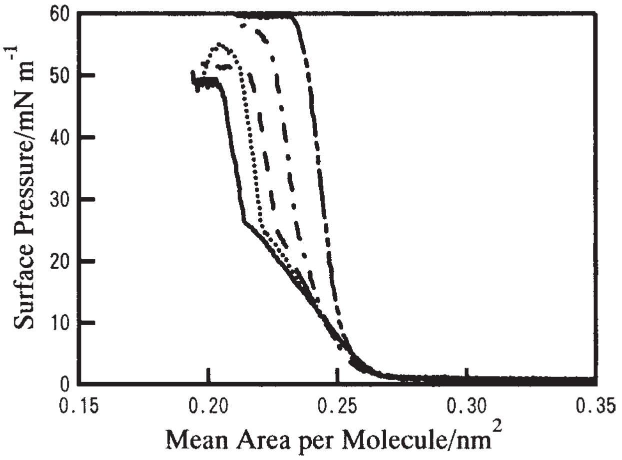

Figure 1. Surface pressure-area isotherms of AA, PA and their mixtures at 20 °C. Solid line: AA, dotted line: AA/PA=3/1, dashed line: AA/PA=1/1, dashed-dotted line: AA/PA=1/3, dashed-dotted-dotted line: PA.

Molecular packing and orientation in the LB films were investigated using IR spectroscopy. We focus on the CH stretching region and the CF stretching region of single-layer LB films transferred at 20 mN m^{-1}. Transmission IR (TIR) spectra of the LB films of AA and those of the mixtures of AA and PA on CaF_2 plates showed two absorption bands due to $\nu_a(CH_2)$ and $\nu_s(CH_2)$ at 2917 and 2850 cm^{-1}, respectively.[3] TIR spectra of the LB films of PA and those of the mixtures of AA and PA revealed two absorption bands at 1153 and 1207 cm^{-1} due to $\nu_s(CF_2) + \delta(CF_2)$ and $\nu(CF_2) + \nu(CF_3)$, respectively, with a shoulder at ca. 1240 cm^{-1}.[4] The intensities of the former two absorption bands increased linearly with the molecular density of AA and those of the latter two with the molecular density of PA, indicating that (1) the two components were transferred on the CaF_2 plates with the composition the same as in the spreading solution and that (2) the orientation of AA and PA was essentially the same in the pure and the mixed LB films.

On the basis of ratio of the intensity of the absorption band in the TIR spectrum to that in the reflection-absorption IR spectrum (substrate: hydrophobized glass plate coated with Au),[5,6] tilt angle of AA was estimated as 15–20° for pure and mixed LB films. These results show that AA is oriented almost perpendicularly in the LB films.

AFM (noncontact mode) was used to investigate the morphology of the LB films on mica. Figure 2 shows typical AFM images of single-layer mixed LB films of AA and PA. Domains are evident in both of the images though the shape and the size of the domains can change significantly depending on

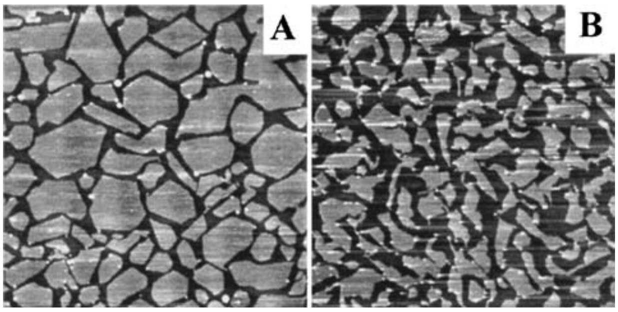

Figure 2. AFM images of single-layer mixed LB films of AA and PA on mica. A: AA/PA=3/1, B: AA/PA=1/1. The size of the images is 10 μm × 10 μm.

subtle variations in the fabrication conditions. The height of the domains is larger than the rest by 0.5 to 1.1 nm. This value agrees with the difference in molecular length of AA and PA. Area fraction of the domains was proportional to the area fraction of AA in the mixed LB films calculated from the π–A isotherms. FFM was used to probe the surface properties of the mixed LB films on mica. Friction was smaller at the domain region compared with the rest. According to the literature, friction is smaller on the hydrocarbon region than on the fluorocarbon region.[7] All these results indicate that the domains consist of AA and that the rest is comprised of PA. Similar phase-separated structures have been reported for other mixed LB films of hydrogenated and fluorinated molecules.[7–9] Completely different π–A isotherms and AFM images have been reported for AA and PA mixed films.[10] The different behaviors may be due to the differences in experimental conditions such as spreading solvent and temperature.

Monolayer transfer of AA on the phase-separated LB films was tried to investigate if the surface properties with local heterogeneity could affect the transfer manner. Figure 3A shows the AFM image of a 1/1 mixed LB film of AA and PA with two monolayers of AA transferred on it. It is evident that the AA overlayers are transferred as domains. Figure 3B shows the height distribution of the AFM image. The ordinate of this figure is proportional to the area fraction at each specific height. Three peaks that are evident in this figure show that there are three almost planar regions in the LB film. The lowest region (51% of the total area) corresponds to the surface of the 1/1 mixed LB film, the middle region (42%) to the surface of the overlayer of two monolayers of AA on the mixed film, and the highest region (7%) to the surface of the overlayer of four monolayers of AA, because the height difference of the adjacent regions is ca. 5 nm each which coincides with the thickness of two monolayers of AA. The highest region is a defect region where more monolayers than planned were transferred. Area fraction of the overlayer (total of the middle and the highest regions) agreed with the area fraction of AA in the 1/1 mixed LB film. When we examined the image more precisely, we could barely find small areas that are ca. 1 nm higher (slightly brighter) than the rest of the lowest region. The former should be the surface of the AA domains in the 1/1 mixed LB films, and the latter should be that of PA region. These results strongly suggest that the monolayers of AA were transferred selectively on the domains of AA in the mixed LB film except for some small areas. Lipophobicity of fluorocarbons should play an important role in this directed transfer.

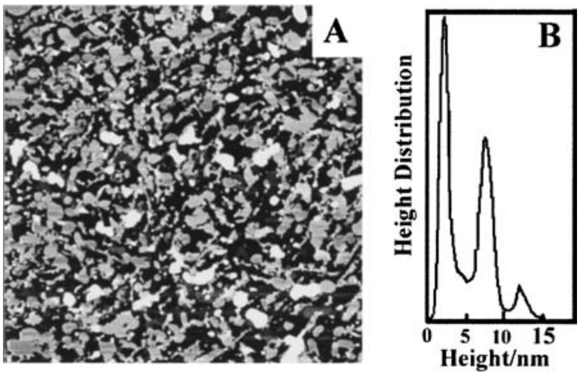

Figure 3. AFM images of a single-layer 1/1 mixed LB films of AA and PA with two monolayers of AA transferred on it. The size of the images is 10 μm × 10 μm. B: height distribution of the LB film. As to the abscissa, the position of "0 nm" does not have a definite meaning. Only the height difference that is shown by the difference in abscissa between the peaks is meaningful.

When two monolayers of AA were transferred onto 3/1 mixed LB films of AA and PA, the whole surface was covered with two monolayers of AA except for small defect regions. The domains in the mixed LB film were successfully imaged using AFM even through the AA overlayer. This shows that the AA overlayer bridges over the PA region owing probably to the small area fraction of PA.

In conclusion, we have shown that the monolayer of AA probes the phase-separated surface during the transfer and is deposited selectively on the lipophilic region under some conditions. The present methodology will provide us with a means to fabricate supramolecular films where different functional units are located three-dimensionally in a designed manner.

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