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Marbling with Amphiphilic Molecules on the Electron Microscopic Scale

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Electron microscopic technique allowed the visualization of a pattern in a monolayer similar to that in marbling with chinese ink on the electron microscopic scale. On the basis of the visualized pattern, the origin of structural defects in a monolayer was speculated.

A macroscopic pattern of the so-called marbling with chinese ink is visible to the naked eye, whereas a microscopic pattern of that is unable to be visually observed. A film of marbling with chinese ink having its thinnest film-thickness seems to be close to a monomolecular film prepared according to the procedure originally developed by Langmuir.[1)] The structure of a monolayer prepared on an aqueous subphase has been the subject of continuous studies. However, experimental techniques for probing interfaces selectively are still extremely limited and are mostly macroscopic in nature, although the interfacial behavior of amphiphilic molecules on the appearance of the molecular ordering at an air-water or air-solid interface in which the molecules lie have been studied for a better understanding between the structure and function of a Langmuir-Blodgett (LB) film system. Recently, we added a new replica method for the analysis of LB-film surface structure on the electron microscopic scale.[2)] In this letter, we demonstrate a marbling-like pattern in a mono- and multilayer of merocyanine dye (5-[2-(3-octadecyl-2-benzothiazolylidene)-ethylidene]-3-carboxylmethyl-2-thioxo-4-thiazolidinone, referred to NK 2684) on the electron microscopic scale.

The manipulation of a monolayer condensed at an air-water interface and the deposition of it onto a glass plate was carefully conducted under the same conditions as used in our previous report.[3] An aliquot of a mixed solution containing 1 x 10^{-4} $mol \cdot l^{-1}$ NK 2684 and arachidic acid (AA) with a molar ratio of [KK 2684] : [AA] = 1 : 2 in chloroform was delivered onto an aqueous subphase containing 1 x 10^{-4} $mol \cdot l^{-1}$, whose pH was adjusted to 6.0 by the addition of Na_2HCO_3, to allow the formation of a monolayer. All handling of NK 2684 such as the preparation of mono- and multilayers containing the dye was conducted at 20 °C under the dim red light in order to prevent the possible photo-induced chemical degradation of it.[3] The replica method seems to be a powerful tool for the micro-structural analysis of the extremly small and ultra-thin samples such as LB-film systems and biomaterials with high resolution (up to 0.6 nm[4]) and without introduction of any artifact such as shadowing and staining.[2,4,5] A replica film of an LB-film on a glass plate was prepared under the same conditions as used in our previous report.[2] Each replica film was examined with a JEM 100 S or 1200 EX electron microscope (JEOL).

Figure 1 shows a transmission electron micrograph of a replica film prepared from a single monolayer-coated glass plate. In Fig. 1, the deposition of a monolayer was carried out at a surface pressure of 25 mN/m with deposition ratio of unity. As seen herein, however, numerous pond-like micro-pores and bank-like lines were visualized.

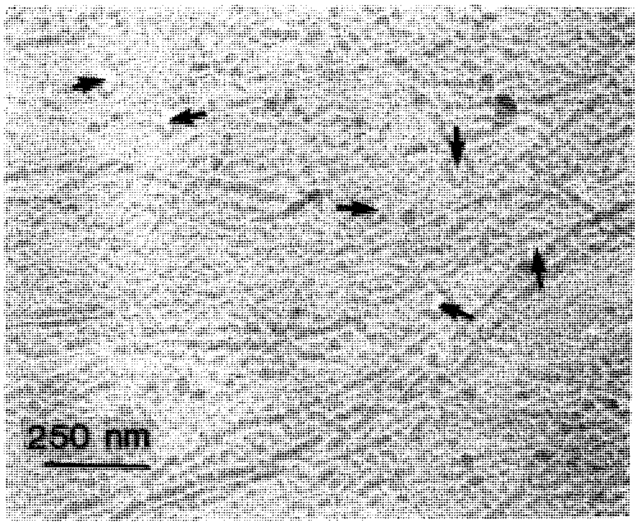

Fig. 1. The typical replica image of an LB-film.

We aimed to make the LB-film surface smooth. However, we were unable to prepare any LB-film systems without any structural defects as visualized in Fig. 1. In our previous report,[3] the LB-film of NK-2684 without cadmium arachidate (CdA) was used as a dye sensitizer to SnO_2 optically transparent electrode. Therefore, the plausible presence of structural defects in the dye LB-film system might not produce any significant errouneous result. Nevertheless, we aimed to elucidate the origin of structural defects such as micro-pores and lines appeared in Fig. 1 in order to obtain some significant informations for the preparation of an LB-film system for practical use. Two monolayers were deposited onto a glass plate under the same conditions used in Fig. 1 and the third monolayer was successively deposited on it under a surface pressure of 0 mN/m just before the surface-pressure generation through a Wilhelmy plate by aid of the experimental set-up schematically illustrated in Fig. 2. Two monolayers-deposited glass plate was carefully placed to be parallel to the air-water interface as shown in Fig. 2 and a monolayer was then prepared on it at a surface pressure of 0 mN/m. Spontaneous evaporation of water from the aqueous subphase could permit the lowering of the subphase level to contact between the monolayer and the glass plate. The monolayer on the aqueous subphase was removed. The typical replica image of the LB-film thus prepared is shown in Fig. 3. As shown in Fig. 3, the presence of two-dimensional island-like domains in the thirdly deposited monolayer were apparently visualized. As partly visualized in Fig. 3, the secondly deposited monolayer had any remarkable structural defects in its replica image on the same electron microscopic scale as used in Fig. 3. One of the domains visualized in Fig. 3 was electron micrographed after the scale expansion of the replica image in order to visualize a micro-structure of the LB-film surface. The expanded replica image is shown in Fig. 4. The pattern shown in Fig. 4 seems to be resemble to that of marbling with chinese ink. As shown in Fig. 4, numerous pond-like areas were electron microscopically visualized. This observation seems to suggest that numerous pond-like micro-pores apparently in Figs. 1 and 4 might be formed during the course of monolayer preparation on the aqueous subphase before the deposition. On the basis of the informations

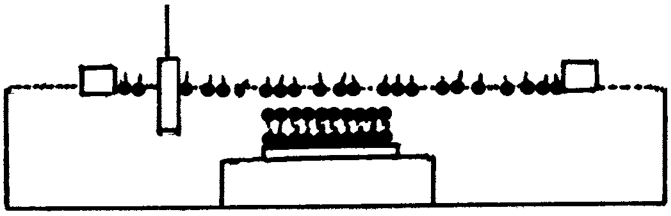

Fig. 2. A schematic illustration of experimental set-up for the deposition of a monolayer onto a solid substrate.

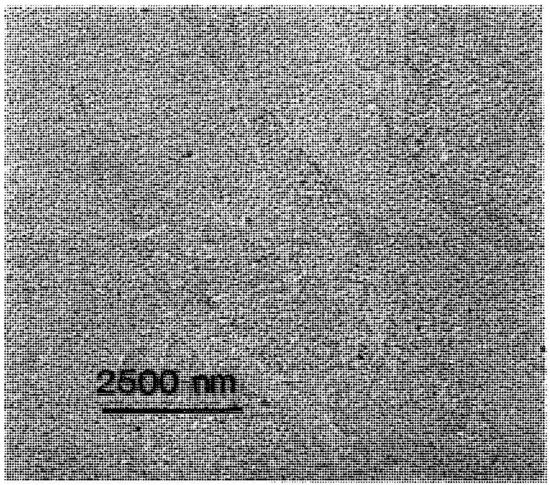

Fig. 3. The typical replica image of an LB-film. For explanations, see the text.

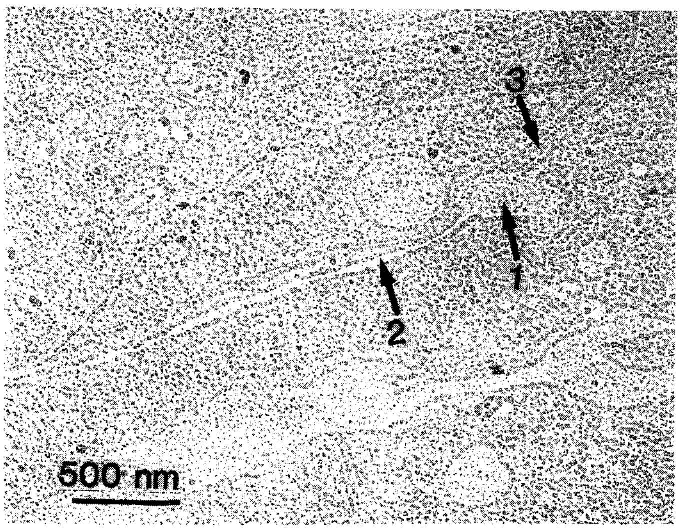

Fig. 4. A replica image of an LB-film. For further explanations, see the text.

obtained from Fig. 4, we speculate the origin of micro-pores and bank-like lines in the LB-film system. As pointed out by arrow 1 in Fig. 4, a lagoon-like area was able to be visualized. Two bank-like lines along with a canal-like area (see the direction of arrow 2) were able to be visualized and the canal-like area seems to connect to the lagoon-like area. If a surface pressure given to the thirdly deposited monolayer might be higher than 0 mN/m (e.g., 25 mN/m), the canal-like area should be narrowed to form lines similar to the lines pointed out by arrow 3 and the lagoon-like area should become a pond-like area. The observed numerous micro-pores and lines in the LB-film system seems to be formed during the course of monolayer preparation on the aqueous subphase. On the basis of the information obtained from Fig. 4, we aimed to optimize a procedure for the preparation of an LB-film without any micro-pores and lines on the electorn microscopic scale and have been able to prepare it.[6] Kajiyama et al.[7] used the so-called shadowing technique to visualize the surface structure of an LB-film system and posturated that the formation of amorphous or crystalline monolayers of fatty acids mainly might depend on the magnitude of T_{sp} (temperature of an aqueous subphase) and T_m (melting point of a monolayer). The replica method allows to visualize the LB-film surface micro-structure without introduction of any artifact such as shadowing.[2,4,5] Most recently, Inoue et al.[8] have succeeded in the direct observation of lattice images of CdA in LB-films. These electron microscopic techniques seem to help the evolution of an LB-film system for the future application in micro-electronic devices such as Josephson junction.[9]

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