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# Local Collapse of a Monolayer on an Aqueous Subphase at a Fairly High Surface Pressure Lower than Its Collapsing Pressure Visualized by Electron Microscopy

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Local collapse of a monolayer on an aqueous subphase at a high surface pressure below its collapsing pressure could be apparently visualized on the electron microscopic scale.

An old saying, "Seeing is Believing", seems to be still valid in Science. As pointed out by Miyano,$^{1)}$ however, although the results of microscopic experiments will be stressed, experimental techniques for probing interfaces selectively are still extremely limited and are mostly macroscopic in nature. Electron microscopists have developed a number of techniques to identify, localize, quantify and understand the dynamics of sample component(s) at the ultra-structural level or at the molecular level.$^{2)}$ Inoue et al.$^{3)}$ succeeded in the direct observation of Langmuir-Blodgett (LB) films by use of a liquid helium-cooled cryo-microscope. We also added a replica technique for transmission electron microscopic observation of LB-film systems without introducing any significant artifacts such as shadowing and fixing.$^{4)}$ Numerous efforts have been paid for preparing an LB-film system of high quality.$^{5-7)}$ Recently, we could obtain an electron microscopic evidence$^{8)}$ that an LB-film system without any structural defect might be able to be prepared under the appropriate conditions. In this letter, we demonstrate the plausible local collapse of a monolayer on the electron microscopic scale in order to provide a crucial information for preparing an LB-film system of high quality.

All the experiments were conducted at 20 ± 1 °C, unless otherwise stated. A cadmium arachidate (CdA) monolayer-deposited glass plate was prepared according to the same surface chemical conditions employed in our previous report.$^{9)}$ Briefly, an aliquot of a spreading solution of arachidic acid (AA) in chloroform was delivered onto an aqueous subphase containing $CdCl_2$ (pH 6.0) to form a CdA monolayer. A replica film of a monolayer-deposited glass plate was prepared according to the same procedure described elsewhere.[4] Each replica film was examined in a JEM 100 S or EX 1200 electron microscope (JEOL).

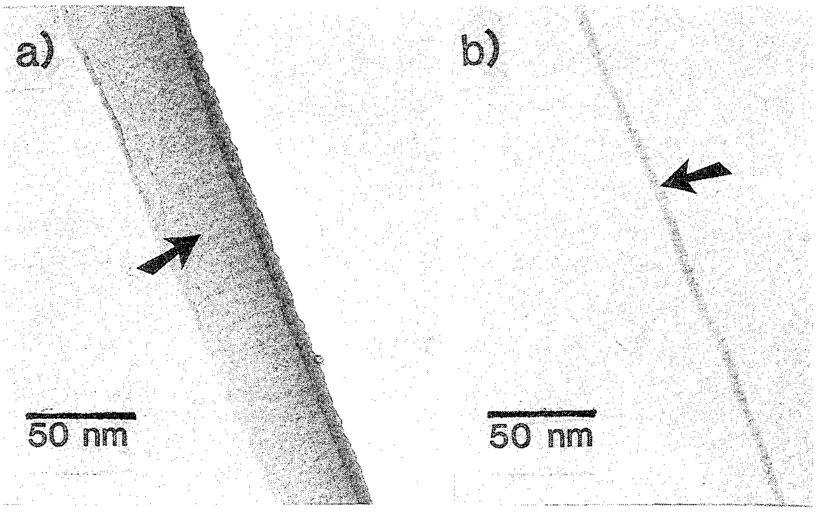

Fig. 1. The typical replica images of a partially collapsed CdA monolayer deposited onto a glass plate under a surface pressure controlled at 30.0 mN/m below the collapsing pressure.

When the spreading solution was delivered onto the aqueous subphase and the CdA molecule-floating area was then gradually decreased to form a condensed monolayer, numerous irregular pattern could be visually observed in it at a high surface pressure below its collapsing pressure (around 65 mN/m). Nevertheless, its surface pressure-area (F-A) curve could keep the linear relationship until the collapsing point. Figure 1 shows the typical replica images of the CdA monolayer deposited onto a glass plate at a surface pressure of 30.0 mN/m, when numerous irregular pattern could be visually observed in its film structure on the aqueous subphase. As partly visualized in Fig. 1, numerous structural defects might be introduced in a monolayer at a surface pressure even lower than its collapsing pressure. This finding seems to suggest that although the formation of a condensed monolayer on an aqueous subphase has generally been recognized by its F-A curve measurements, the linear relashionship in an F-A curve might not always be able to assure the formation of a condensed monomolecular layer without any structural defects.

As shown in Fig. 2, occasionally, a CdA monolayer of high quality on a glass plate could be also prepared under the same surface chemical conditions as used in Fig. 1. The discrepancy between the replica images in Figs. 1 and 2 is assumed to be due to the uncontrollable micro-environmental changes in a common thermostated dust-free room. In this study, a sample (a plasma polymerized film/a CdA monolayer/a glass plate) was softly cut onto its film-coated side by a cutter with a diamond before its

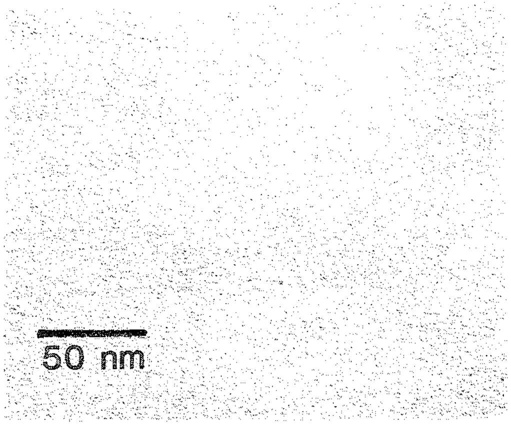

Fig. 2.. A replica image of a CdA monolayer of a high quality.

immersion into a 5% hydrofluoric acid solution for the preparation of its replica film. Therefore, the size of each relica film fragment for the electron microscopic observation was approx. 2 mm x 2 mm. We could find any structural defect in the replica-film fragment, whose electron microscopic image is partly shown in Fig. 2. The resolution of the replica technique coupled with transmission electron microscopy was estimated to be ca. 2 nm.8)

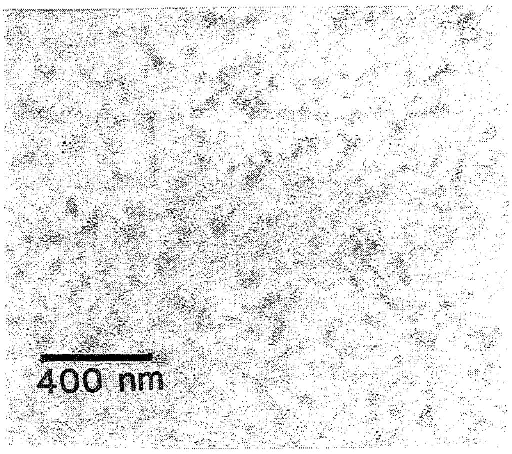

Fig. 3. A replica image of a CdA monolayer adsorbed onto a glass plate at a surface pressure of 0 mN/m.

Figure 3 shows a typical replica image of a CdA monolayer adsorbed onto a glass plate at 0 mN/m just before the initial raise of a surface pressure. In Fig. 3, a glass plate was carefully placed to be parallel to the air-water interface and a monolayer was then prepared. Spontaneous evaporation of water from the 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 to pick up the monolayer-covered glass plate. Further decrease of the monolayer-covering area could allow to form a condensed monolayer, whose replica image was generally found to be similar to that shown in Fig. 2. For some cases, the monolayer might be locally collapsed during its compression below its collapsing pressure.

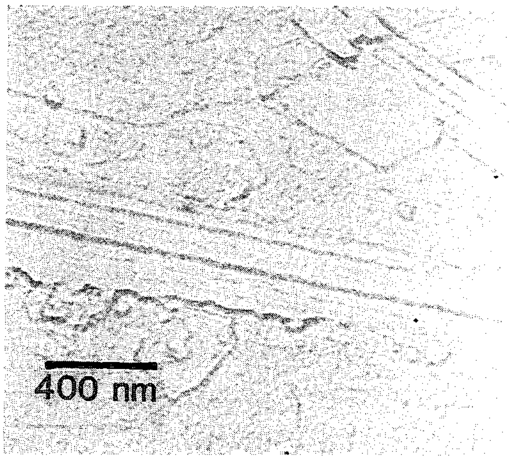

Fig. 4. A typical replica image of a stearic acid monolayer.

Ries10) proposed a mechanism of monolayer collapse on the basis of his electron microscopic images of stable ridges in a collapsing monolayer of 2-hydroxytetracosanic acid. Ries10) divided into at least four processes for monolayer collapse: (a) weakening; (b) folding; (c) bending; (d) collapsed. We assume that the partial collapsing process during the course of monolayer compression below the collapsing point might be also divided into the same as those by Ries.10) A broad bank-like area by arrow in Fig. 1 (a) might be considered as the collapsed one, whereas a narrow line pointed out by arrow in Fig. 1 (b) might be considered as the weakening monolayer area. Figure 4 shows a replica image of a stearic acid (SA) monolayer deposited onto a glass plate from a surface of the distilled water (pH 5.8) at a surface pressure of 30.0

mN/m. As shown in Fig. 4, numerous closely packed two-dimensional crystal-like domains were apparently visualized. When an SA monolayer was deposited onto a glass plate near its collapsing pressure (around 59 mN/m), its replica image was found to be close to the electron micrographs shown by Ries.[10] CdA molecules seem to form a relatively fluid monolayer, whereas SA molecules seem to form their rigid monolayer. The replica images demonstrated in this paper may visualize the difference of the film-rigidity between a CdA monolayer and an SA monolayer.

As demonstrated in this paper, the local collapse in a monolayer during the compression of it below its collapsing pressure should be taken much care in order to prepare an LB-film system, in which molecular arrangement and orientation might be purposely well-regulated. The so-called F-A curve measurements as well as the macroscopic observations can provide some macro-structural informations for an organic thin-film prepared on an aqueous subphase. The replica technique coupled with transmission electron microscopy can provide some significant informations on the electron microscopic scale, as partly demonstrated in this paper. Thus, the replica technique may be able to assist the evolution of an LB-film system, for example, for its application into the so-called micro-electronic device, not into the macro-electronic device.

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