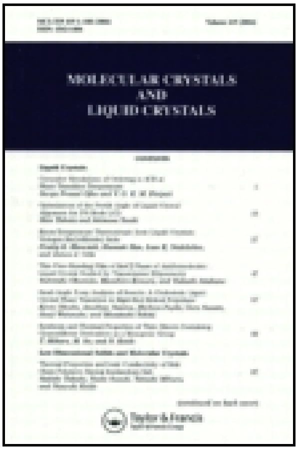

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# Unusual Two-Step Phase Transitions in Spread Monolayers of Chloro(Dimethyl)(Octadecyl)Silane at the Water Surface Observed with Brewster Angle Microscopy (BAM)

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# UNUSUAL TWO-STEP PHASE TRANSITIONS IN SPREAD MONOLAYERS OF CHLORO(DIMETHYL)(OCTADECYL)SILANE AT THE WATER SURFACE OBSERVED WITH BREWSTER ANGLE MICROSCOPY (BAM)

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Abstract Unusual two-step phase transitions of spread monolayers of chloro-(dimethyl)(octadecyl)silane were studied by π-A isotherm measurements and Brewster angle microscopic observation, with varying temperature and times of observation. It is found that the two-step phase transitions appear in a very narrow temperature range around 20 ℃. The compression-expansion cycles of the monolayers demonstrated that the transitions are rather reversible ones.

## INTRODUCTION

Recently, the organized ultra thin films have attracted growing attention. [1] Langmuir-Blodgett (LB) film is the representative one of such films, and a precursor of LB film is a spread monolayer at air/water interface. Therefore, the phase transition behavior of the monolayers has been studied extensively for fundamental understanding of monolayer properties to fabricate the desired film structures. [2] Monolayer properties are usually characterized by π-A isotherms at constant temperatures where the monolayers at the air/water interface undergo various two-dimensional states as the monolayer density is increased with compression. It has been found that the monolayer behavior strongly depends on both temperature and time of observation ($t_{ob}$).[3]

We have reported previously that π-A isotherms of the monolayer of chloro-(dimethyl)(octadecyl)silane (CDMOS) measured at 20℃ show unique two-step phase transitions. [4] In this paper, the effects of changing experimental parameters such as temperature and $t_{ob}$ on this phase transition behavior were studied by π-A isotherms and the BAM observation during compression and re-expansion.

## EXPERIMENTAL

CDMOS (Tokyo Chemical Industry) was used as received. Solutions of CDMOS in spectrograde hexane (Dojin Chemicals) were spread on the freshly prepared ultrapure water from the Elgastat (UHQ-PS) system, and allowed for 30 min before starting compression. π-A isotherms were measured under the constant strain rate compression (constant time of observation). Both Langmuir trough and BAM were constructed in our laboratory, and details of these instruments were described elsewhere. [5,6)]

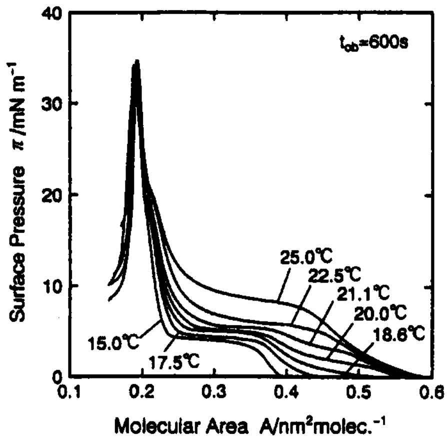



FIGURE 1 Temperature-dependence of π-A isotherms of CDMOS monolayers measured under $t_{ob}$ of 600 s.

## RESULTS AND DISCUSSION

Figure 1 shows temperature-dependence of the π-A isotherms of CDMOS monolayers measured under $t_{ob}$ of 600 s. As described in our previous paper, CDMOS is hydrolyzed rapidly after spreading at the water surface. [4)]

It is apparent that the two-step phase transitions appear only at very narrow temperature region around 20 ℃. At both higher and lower temperature, the monolayers show the isotherms with only one-step phase transition. However, the so-called solid film regions coincide well each other. The BAM images always revealed that the three dimensional partial collapse structures have already started to grow in this region.

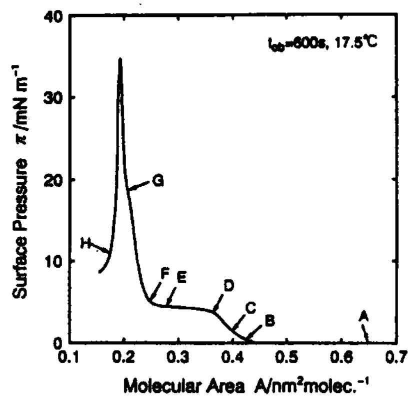
Fig. 2(a) presents the π-A isotherm of the CDMOS monolayer measured at 17.5 ℃ under $t_{ob}$ of 600 s, and Fig. 2(b) shows BAM images observed *in situ* during compression. The points of BAM observation are marked on the isotherm. The isotherm exhibits only one phase transition at this temperature, but we can observe the separated growing of two kinds of dense domains. As shown in the image A, a number of circular domains around a hundred μm diameter ($L_2$ phase), surrounded by rather expanded phase (G phase), were already observed before starting compression. The $L_2$ domains are gathered and deformed to fuse with compression as shown in the image B and C. Once the monolayer becomes almost uniform at point D, nucleation and growth of the second kind of domains ($L_3$ phase) follow as seen in the image E and F. After the completion of the second phase transition, the monolayer looks uniform again at point G, from where two-dimensional solid state starts. The image H shows the collapsed structure.

In Fig. 1, the isotherm at 20 ℃ exhibits two successive phase transitions that start at about 0.52 and 0.37 nm$^2$molec.$^{-1}$, respectively. Images are not shown here, but the BAM observation reveals successive growth of the $L_2$ and $L_3$ phase domains in the first and second transition region, respectively, and the overlapping structure that the $L_3$ phase domains begin to appear in the $L_2$ phase domains before the completion of the first step transition. This means that nucleation of the $L_3$ phase is limited in the $L_2$ domains at 20 °C.

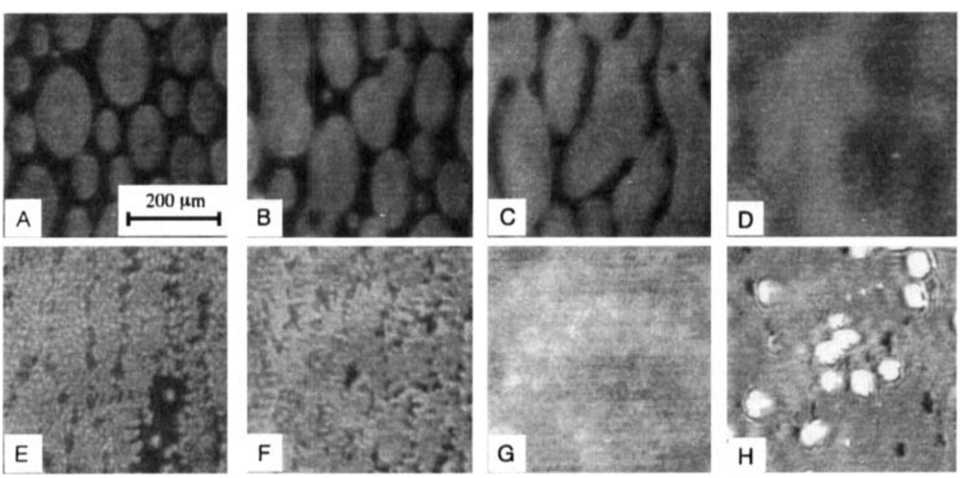
At 25.0 °C, the monolayer shows the one-step transition from the $L_1$ phase to the $L_3$ phase where the almost circular $L_3$ phase domains are uniformly distributed to grow in the $L_1$ phase. However, the average size of a single $L_3$ domain is much larger than that at 17.5 °C, reflecting the difference in degree of supersaturation between the $L_2$ and $L_1$ phase.

Since the change of times of observation will affect the shape of the π-A isotherm considerably, we varied $t_{ob}$ from 600 s to 12000 s to understand the monolayer behavior at 20 °C. The extension of $t_{ob}$ led to the disappearance of the so-called solid film region, but it is not effective for separating the overlapped two-step phase transitions into two clearly distinct transitions.

To examine the reversibility of the phase transitions, compression-expansion cycles of the CDMOS monolayer were carried out at 20.0 °C. The monolayer was compressed up to 7 $mNm^{-1}$ at $t_{ob}$ of 600 s, and then expanded at the same strain rate, and this cycle was repeated four times. After each of the cycle, the monolayer were allowed to stand for 10 min before starting next compression. While there were hystereses between the compression and expansion isotherms, the isotherms in every compression agree well




(a)




(b)

FIGURE 2 (a) π-A isotherm of the CDMOS monolayer measured at 17.5 °C under $t_{ob}$ of 600 s. (b) BAM images of the monolayer observed *in-situ* during compression. (See Color Plate V).

with each other. These facts indicate that the two-step transitions are rather reversible, and therefore chemical reactions such as condensation among hydroxyl groups do not occur during the measurements of the isotherms under our experimental conditions.

## CONCLUSIONS

We have presented the phenomenological results on the very unusual phase transition behavior of the CDMOS monolayers using the $\pi$-A isotherms and BAM observation. It is found that the two-step phase transition is very sensitive to temperature, and it appears at very a narrow temperature range around 20 ℃. According to BAM observations during the systematic measurements of the isotherms shown in Fig. 1, it becomes clear that the two-step phase transitions correspond to growth of the $L_2$ phase domains from the $L_1$ phase, and that of the $L_3$ phase from the $L_2$ phase, respectively. The compression-expansion cycles demonstrated the reversible character of the two-step transitions.

It is very difficult to explain quantitatively the molecular processes occurring in the phase transitions by the present techniques. However, we are now developing an instrument combined with BAM and a micro-ellipsometer, which can measure the change of the thickness and the refractive index of a small area of the monolayer during compression. This will make it possible to explain physical measuring of the transitions. This is the next subject of the study.

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