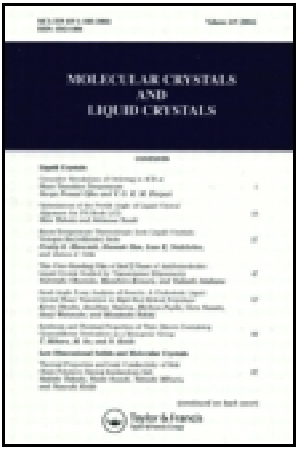

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Pressure-Induced Structural Change of the Langmuir-Blodgett Films of Squarylium Dye and Arachidic Acid

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By changing the surface pressure a drastic change of morphology was induced in monolayers of a surface-active squarylium dye and arachidic acid at the air-water interface. After transfer on solid supports, the films were investigated by atomic force microscopy. The presence of three-dimensional cones was associated with the squeezing-out of dye molecules from the planar film as the surface pressure grew.

Keywords: monolayer; Langmuir-Blodgett film; squarylium dye; squeezing-out; supermonomolecular layer; AFM

INTRODUCTION

Molecular layers of organic molecules can provide new functions to solid devices and their controlled arrangement is the key to many applications.

Langmuir-Blodgett (LB) technique is a versatile way of assembling surface-active molecules in two dimensions (2D). Recently, 3D structures have been found in a number of LB films[1,2]. The selective pressure-induced squeezing-out process of the dye component from mixed monolayers of squarylium dye and arachidic acid has been reported, suggesting the 3D nature of the supermonomolecular layers[3,4]. In this study, the structure of the LB films will be investigated using atomic force microscopy.

EXPERIMENTAL

The structure of the squarylium dye (SQ) is shown in Figure 1. Mixed layers of SQ and arachidic acid (C20) were formed on aqueous subphases containing 4.0×10^{-4} M of $CdCl_2$ and 5.0×10^{-5} M of $KHCO_3$ at 289 K (compression speed: 2 cm/min). Single-layer LB films were transferred on mica by vertical withdrawal with a transfer ratio of 1.0. The AFM images were taken on a Seiko SPA300 with an SPI 3700 probe station using noncontact mode at ca. 145 kHz.

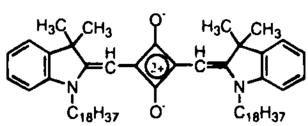

FIGURE 1 Chemical structure of SQ.

RESULTS AND DISCUSSION

The surface pressure-area isotherms of mixed layers of SQ and C20 are shown in Figure 2 for several mixing ratios. At around 20 mN m^{-1}, plateau regions appear in the mixed layers, which is explained by a type of phase transition from a conventional mixed monolayer to a 3D surpermonomolecular layer[3,4].

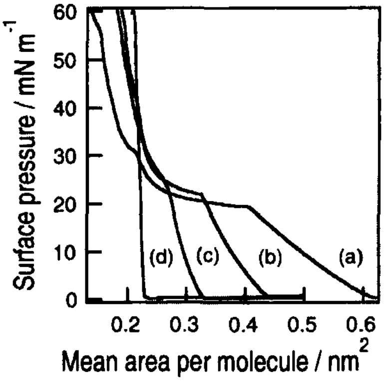

FIGURE 2 Surface pressure-area isotherms of SQ and C20 at molar mixing ratio r . (a): r=1/2, (b): r=1/5, (c): r=1/10, (d): r=0.

Figure 3 shows the AFM images of LB films transferred below and above the transition pressure for mixing ratios 1/10 and 1/2. At lower surface

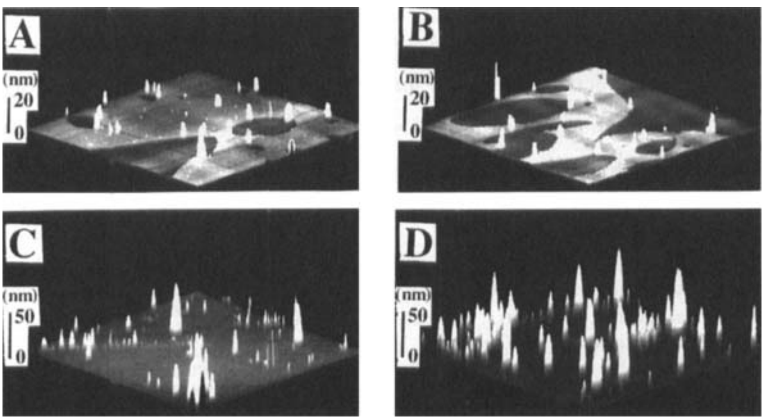

FIGURE 3 AFM images of the LB films transferred at lower pressures with r=1/10 (A) and r=1/2 (B), and those at higher pressures with r=1/10 (C) and r=1/2 (D). Scanned area is 10μm × 10μm each.
(See Color Plate II at the back of this issue)

pressures, two phases are seen. The lower phase is attributed to a monolayer of SQ since the area fraction of the lower phase increases with increasing mixing ratio of SQ. This is supported by the fact that the height difference of the two phases is only ca. 1.5 nm. This suggests that SQ molecules adopt a tilted conformation. Small 3D structures are seen at the border of the domains.

LB films transferred at higher pressures clearly have a large number of cones, whose height can be larger than 100 nm for r=1/2. This indicates that an increase in surface pressure gives rise to a conversion of 2D film structures into 3D structures. This is consistent with the previously proposed model of partial squeezing-out of SQ molecules during the transition[3,4]. The 3D structures account for ca. 2.5 and 8.5 % of the total volume for r=1/10 and 1/2, respectively.

CONCLUSIONS

This study shows that AFM is a powerful tool in characterizing molecular films especially when a phase transition with a large morphological change is involved. It is demonstrated that the pressure-induced squeezing-out of SQ molecules from monolayers brings about the conversion of 2D layers into 3D supermonomolecular layers.

References

[1] M. Matsumoto, H. Tachibana, F. Sato, and S. Terrettaz, *J. Phys. Chem. B,* **101,** 702(1997).

[2] M. Matsumoto, D. Miyazaki, M. Tanaka, R. Azumi, E. Manda, Y. Kondo, N. Yoshino, and H. Tachibana. *J. Am. Chem. Soc.*, **120,** 1479(1998).

[3] Y. Kawabata, T. Sekiguchi, M. Tanaka, T. Nakamura, H. Komizu, K. Honda, E. Manda, M. Saito, M. Sugi, and S. Iizima, *J. Am. Chem. Soc.*, **107**, 5270(1985).

[4] M. Matsumoto, T. Nakamura, M. Tanaka, T. Sekiguchi, H. Komizu, S. Y. Matsuzaki, E. Manda, Y. Kawabata, M. Saito, S. Iizima, and M. Sugi, *Bull. Chem. Soc. Jpn.*, **60,** 2737(1987).