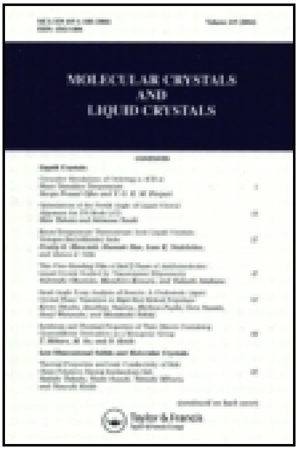

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J-Aggregate Formation and Morphological Change on UV Irradiation of the Langmuir-Blodgett Films of Spiropyran

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J-Aggregate Formation and Morphological Change on UV Irradiation of the Langmuir-Blodgett Films of Spiropyran

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Photochemical reactions of an amphiphilic spiropyran (SP) have been investigated in single-layer LB films. The SP LB films were prepared from a pure water subphase at 30°C. When these LB films were irradiated with UV light at room temperature, SP was converted into photomerocyanine (PMC), followed by the formation of J-aggregate of PMC. In situ AFM observations revealed the presence of large circular domains with diameters of 10–20 μm and height of 4–5 nm before irradiation. Irregularly-shaped structures were evident in the center of most of the domains. On irradiation with UV light, dendritic structures spread radially from the irregularly-shaped structures and developed within the domains. The morphological change was not observed in the domains without the irregularly-shaped structures.

Keywords: spiropyran: Langmuir-Blodgett films; in-situ AFM; J-aggregate

INTRODUCTION

Among photochromic compounds, spiropyran derivatives have been extensively investigated[1], because they can form J-aggregates in the solution, the interlayers of layered compounds, bilayer membranes dispersed in water, and thin films when isomerized to photomerocyanines on irradiation with UV light. Langmuir-Blodgett (LB) method has been utilized for the fabrication of thin films with structures defined at the molecular level. J-aggregate formation of photomerocyanine and dyes has been reported in the LB films. Recently, we have found that J-aggregate formation is induced by utilizing cis-trans photoisomerization of azobenzene as a photochemical trigger in the mixed LB films of cyanines[2,3] and spiropyran[4]. Drastic morphological changes accompanied the J-aggregate formation. Further, J-aggregate formation of photomerocyanine has been reported in the LB films mixed with ocatdecane on the UV irradiation at temperatures more than 35℃[5]. In this paper, we will report on the formation of J aggregate in single-component LB films of an amphiphilic spiropyran on irradiation of UV light at room temperature. The morphological changes accompanied by the J-aggregate formation were monitored by in situ AFM.

EXPERIMENTAL

Monolayer measurements and LB film fabrication were carried out using a Lauda film balance. Chloroform solution of 1', 3'-dihydro-3', 3'-dimethyl-6-nitro-1'-octadecyl-8-docosanoyloxymethylspiro[2H-1-benzopyran-2, 2'-[2H]indol (SP) was spread on pure water at 30℃. After compression, a single monolayer was transferred using the vertical dipping method at 10 mNm^{-1}. Monochromatic light at 334 nm from a high-pressure mercury lamp was used as the UV light source for the photoreactions of SP. A Seiko SPA-300 AFM, operating in non-contact mode, was employed to image the LB films. In situ AFM images were observed as well as usual ex situ AFM images. In the in situ AFM measurements, the LB films were held on the scanner even during the UV irradiation in order to monitor the morphological change of the films locally. All measurements were made in air at room temperature (23℃).

RESULTS AND DISCUSSION

Monolayer formation of SP at the air-water interface was investigated.

Figure 1 shows a surface pressure-area (π-A) isotherm on pure water. This isotherm is considerably different in several aspects from the one reported for SP measured on a buffer at 18℃[5]. In the present study, we observed the onset of surface pressure at a larger area per molecule and, in addition, a plateau region at around 7.5 mN m^{-1}. Further, the monolayer was stable up to 25 mNm^{-1} whereas it was reported that the monolayer was not very stable on the buffer at 18℃[5].

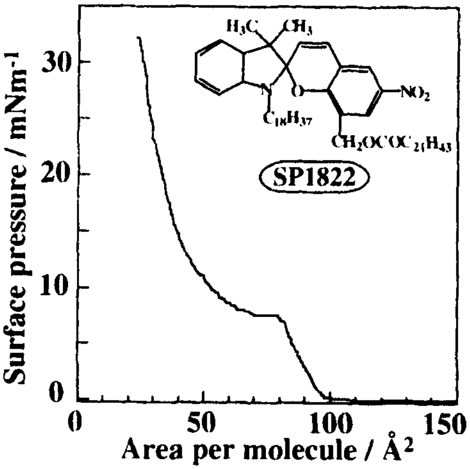

FIGURE 1 Surface pressure-area (π-A) isotherm of SP on pure water at 30℃. The chemical structure of SP is also shown.

Figure 2 shows the change in the UV-visible absorption spectrum of a single-layer SP LB film on irradiation with UV light. In the initial regime, SP isomerized to open

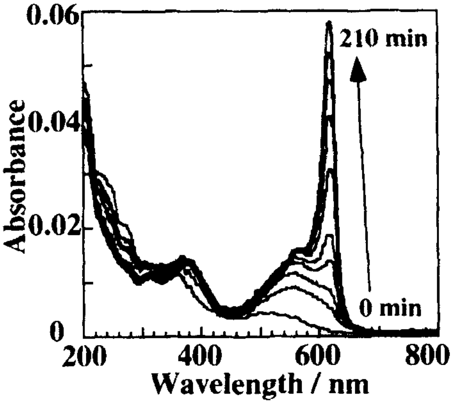

FIGURE 2 Change in UV-visible absorption spectrum of a single-layer LB film of SP as a function of UV irradiation time.

colored photomerocyanine (PMC) in the monomeric form on irradiation. A broad absorption band was observed ranging from 500 to 650 nm. On prolonged irradiation, a relatively narrow absorption band developed at ca. 620 nm, increasing its intensity with the irradiation. This indicates the formation of J-aggregate of PMC, which is surprising because J-aggregate of PMC has been previously formed in mixed LB films with the aid of other external stimuli. Ando et al. reported the J-aggregate formation of PMC in the LB films mixed with ocatdecane at temperatures more than 35℃ on UV irradiation[5]. Further, we have found that the formation of J-aggregate of PMC was induced by the photoisomerization of azobenzene in the LB films and that no J-aggregates were formed when the mixed LB films of SP and octadecane were illuminated with UV light at room temperature[4]. In the present study, the subphase temperature was 30℃, much higher than those employed in the previous studies. That should be the reason for the difference in the LB film structures in terms of the J-aggregate formation of PMC.

Figure 3 represents the AFM image of a single-layer SP LB film on mica before irradiation. Large circular domains with diameters of 10-20 μm are seen in the image. The circular domains did not cover the entire surface of mica. Small domains and bare mica surface were evident between the large domains when

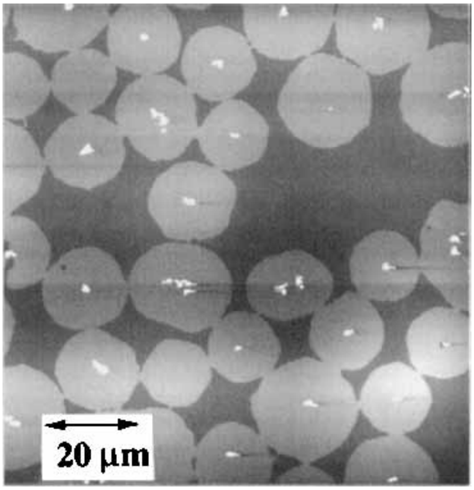

FIGURE 3 AFM image (100 μm×100 μm) of a single-layer SP LB film before irradiation.

the film was imaged under higher magnification. The large domains were 4-5 nm in height, which shows that these domains probably have bilayer structures. Irregularly-shaped structures are evident in the center of most of the circular domains. The size of the circular domains depended on the subphase temperature and the solvent, probably due to the difference in the evaporation speed of the solvent.

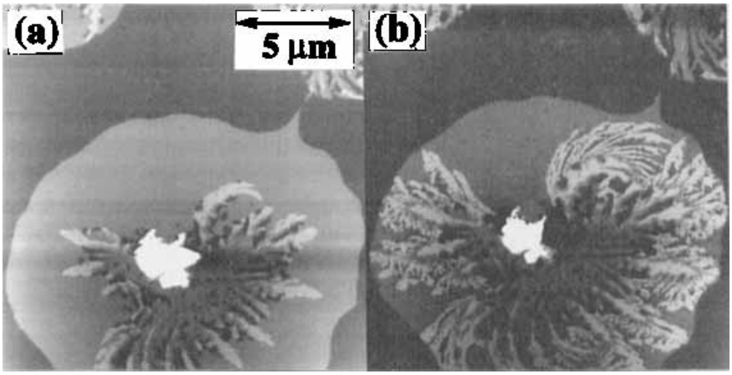

FIGURE 4 In-situ AFM images (20 µm×20 µm) of a single-layer SP LB film after irradiation with UV light. The irradiation time was (a) 5 min and (b) 120 min.

Next, the morphological change of the LB films on UV irradiation was investigated by in situ AFM measurements. Figure 4 shows the in situ AFM images of a single-layer SP LB film after irradiation with UV light. Drastic morphological changes are evident. Dendritic three-dimensional structures spread radially from the irregularly-shaped structures in the center of the circular domains (Figure 4(a)). This suggests that the irregularly-shaped structures serve as the nucleation centers of the morphological changes. This is supported by the finding that the morphological change was not observed in the domains without the irregularly-shaped structures. On prolonged irradiation (Figure 4(b)), the morphological changes proceeded further until nearly the entire part of the affected domains had dendritic structures. The dendrites extended toward the domain boundaries, by removing the material between the branches and transporting them to the boundary region where branches were higher than the unaffected region. The dendrites were confined within the domains probably due to the absence or insufficient concentration of PMC outside the domains. It should be noted that the dendritic structures observed in the present study have essentially the same morphology with those observed when the J-aggregate formation of PMC was triggered by the photoisomerization of azobenzene[4]. These results indicate that the morphological changes were related with the development of J-aggregate of PMC.

In summary, J-aggregate of PMC was formed by the UV irradiation of single-layer SP LB films at room temperature, which has not previously been reported. In situ AFM images revealed that the morphology of the LB films changed drastically with the J-aggregate formation in a manner similar to the one reported in the previous paper[4]. This study demonstrates that a change in the preparation conditions of the LB films gives rise to a significant difference in the film structure. The results further suggest that LB films can be modified to give structures suitable for specific functions by optimizing preparation conditions.

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