

## Structures and Photoreactions of Mixed Langmuir-Blodgett Films of Spiropyran and Arachidic Acid

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The structures and photoreactions of mixed Langmuir-Blodgett (LB) films of SP and C20 were investigated. In the low-temperature regime, the films consisted of multilayer domains of undefined shape embedded in a monolayer of C20 in contrast to a continuous trilayer structure of the LB film of pure SP in the same temperature range. In the high-temperature regime, SP molecules were squeezed out of a C20 monolayer during the phase transition to form multilayer domains, resulting in the structures of LB films similar to those formed in the low-temperature regime. The structures were different from those of the LB film of pure SP in which circular trilayer domains were positioned sparsely on the substrate because the monolayer region failed to be transferred on the substrates. Only the photoisomerization of SP to MC proceeded in the LB films fabricated at 7°C. On the other hand, light-induced J-aggregation occurred in the LB films fabricated at 30°C.

Key words: Langmuir film, LB film, spiropyran, merocyanine, J-aggregate, isomerization

### 1. INTRODUCTION

Langmuir-Blodgett (LB) films have been attracting considerable attention because LB films have many characteristics such as the structures defined at the molecular level, the structures with low dimensions, the thickness at the molecular level, and the easiness with which to fabricate superstructures. Many researches have been conducted to understand the physical and chemical properties of the films and to fabricate nanostructured material with relevance to molecular devices and other functionalized materials [1-4].

The incorporation of photoactive moieties in the Langmuir and LB films is particularly interesting because of the well-defined structures and the low-dimensionality of the films. Photoreactions can serve as triggers to control the functions of the films as in biological systems in which photoisomerization of chromophores promotes the structural changes of the proteins that surround the chromophores, resulting in the biological activities [5]. Well-defined structures with very smooth surface and thickness at the molecular level permit the detection of subtle changes in the film structures accompanied by the photoreactions using scanning probe microscopy.

Aggregation of dye molecules strongly affects the properties of the molecules. The structures and optical properties of J-aggregates of dye molecules have attracted much attention from the viewpoint of applications in photography, opto-electronics and solar cells [6-31]. Molecules in J-aggregates are arranged one-dimensionally or as in a brick-stone work. J-aggregation gives rise to a sharp absorption band (J-band), which is positioned at longer wavelengths with respect to the monomer band. J-aggregates confined in two-dimensional molecular assemblies such as Langmuir and LB films are of considerable interest because of the well-defined film structures with low-dimensional nature. Two types of J-aggregation

caused by photoisomerization have been reported. One is "light-induced J-aggregation" [9,11,19-23,25-27,31] and the other is "triggered J-aggregation" [15,16]. In the former process, dye molecules photoisomerize and then form J-aggregates, while in the latter process the photoisomerization of dye molecules triggers the formation of J-aggregates of different chemical species. Light-induced J-aggregation and triggered J-aggregation of dye molecules allow for the patterning of material with J-aggregates, enabling to modify the optical and physical properties of local areas selectively [25].

Ando et al. reported the first observation of light-induced J-aggregation [9]. They fabricated multilayer mixed LB films of spiropyran (SP in Fig. 1) and octadecane.

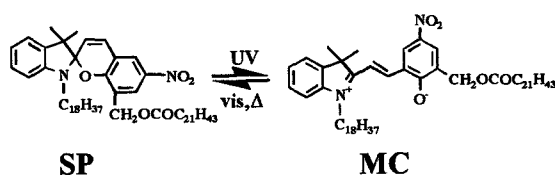


Figure 1. Structure of SP and photoisomerization to MC.

When the films were irradiated with UV light at room temperature, photoisomerization of SP to merocyanine (MC) proceeded. On the other hand, UV irradiation of the films at high temperatures, temperatures higher than 35°C, gave rise to photoisomerization followed by J-aggregation of MC. Unuma and Miyata fabricated multilayer mixed LB films of SP and stearic acid [11]. They also observed similar results: only the photoisomerization when irradiated with UV light at room temperature and J-aggregation when irradiated at temperatures higher than 40°C. The reason why the matrix molecules were used in the above studies was that the Langmuir films of pure SP were difficult to

transfer onto solid substrates.

We have investigated the structures and photoreactions of the Langmuir films of SP. At first we did not use matrix molecules for simplicity's sake. The structures of the Langmuir films were studied on the basis of the surface pressure-area isotherms and Brewster angle microscopic (BAM) observations [26]. The Langmuir films of SP were divided into three regimes: a low-temperature regime at 7-13°C, a medium-temperature regime at 23-30°C and a high-temperature regime at 40°C. In the low-temperature regime, the isotherm was of condensed type and the surface pressure rose at 0.4-0.5 nm<sup>2</sup>. BAM observations showed that the plate-like domains were gradually fused together to form a continuous trilayer film around the onset of the surface pressure. In the medium-temperature regime, the surface pressure rose at a larger area per molecule than in the low-temperature regime, followed by a phase transition at ca. 5 mN m<sup>-1</sup>. Circular trilayer domains were formed in a continuous monolayer during the phase transition. The characteristic features of the high-temperature regime were similar to the ones of the medium-temperature regime except for the absence of a steep rise in surface pressure after the phase transition and the absence of the circular trilayer domains. UV illumination of the Langmuir films led to the formation of J-aggregates of MC only when the circular trilayer domains were present.

We have found that the Langmuir film of SP was successfully transferred onto solid substrates at a subphase temperature of 30°C [19]. The transfer ratio was significantly smaller than unity at lower temperatures. AFM observations of single-layer LB films of SP revealed that the films consisted of multilayer domains without the monolayer region. These structures should be the same ones that were present in the trilayer domains in the Langmuir films. UV illumination of a single-layer LB film of SP at 23°C gave rise to J-aggregation of MC. With J-aggregation of MC, dendritic structures developed from the three-dimensional structures on the domains. These dendritic structures were assigned to the J-aggregates of MC [22].

In this study, the structures and photoreactions of the mixed LB films of SP and arachidic acid (C20) are investigated on the basis of AFM observations and spectroscopic measurements. The results are compared with those of the LB films of pure SP and those of the mixed LB films of SP and C20.

## 2. EXPERIMENTAL SECTION

All the monolayer measurements were done using a NIMA 632D1D2 trough equipped with two moving barriers. Chloroform was used as a spreading solvent. Mixing ratio of SP to C20 was 1 to 2 for all the measurements. Mixed solution at an SP concentration of 1.0 × 10<sup>-4</sup> M was spread on an aqueous subphase purified using a Barnstead NANOpure Diamond (> 18 MΩ cm). The molecules were compressed at a speed of 3.3 × 10<sup>-2</sup> nm<sup>2</sup> (SP molecule)<sup>-1</sup> min<sup>-1</sup> after 5 min of evaporation time.

The Langmuir film was transferred using the vertical dipping method at a withdrawal speed of 4 mm min<sup>-1</sup> onto quartz plates for spectroscopic measurements and

onto freshly cleaved mica for AFM observations. UV/vis absorption spectra of single-layer LB films were recorded on a JASCO V-560 spectrophotometer. UV illumination of the LB films was carried out at normal incidence using a Xenon lamp at room temperature. AFM observations were made using a Seiko SPA300 microscope in a non-contact mode using a silicon tip with a resonant frequency of 28 kHz and a spring constant of 1.8 N m<sup>-1</sup>.

## 3. RESULTS AND DISCUSSION

### 3.1 Surface pressure-area isotherms

Figure 2 shows surface pressure-area isotherms of SP and C20 in the subphase temperature range of 8-30°C. The isotherms depend strongly on the subphase temperature and can be divided into two regimes: a low-temperature regime at 8-13°C and a high-temperature regime at 23-30°C. There is an intermediate region between the two regimes. In the low-temperature regime, the isotherms are of condensed type and the onset points of the surface pressures are ca. 1 nm<sup>2</sup>. In the high-temperature regime, the surface pressure rises at ca. 2 nm<sup>2</sup> and a phase transition occurs at ca. 5 mN m<sup>-1</sup>. These features are similar to those observed in the isotherms of pure SP in the same temperature range except for the large area per SP molecule due to the addition of C20 molecules [26].

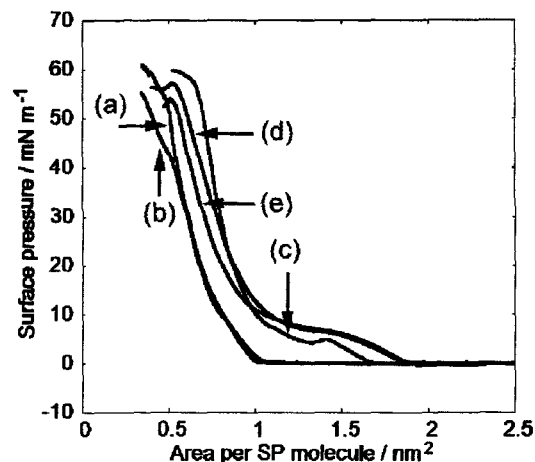


Figure 2 Surface pressure-area isotherms of SP and C20 at the subphase temperatures of (a) 8°C, (b) 13°C, (c) 17°C, (d) 23°C and (e) 30°C.

On the other hand, the addition of n-alkane changes the isotherms considerably [27]. Below the melting point of n-alkane, continuous mixed monolayers of SP and n-alkane are formed whereas n-alkane is squeezed out of the SP Langmuir films above the melting point. The completely different behaviors of C20 and n-alkane should be attributed to the fact that C20 is amphiphilic whereas n-alkane is nonamphiphilic (hydrophobic). In usual cases, each C20 molecule is expected to occupy ca. 0.2 nm<sup>2</sup> in the condensed phase in the mixed Langmuir films whereas n-alkane will reside in the hydrophobic region of the films and will not contribute to the area significantly.

### 3.2 Photoreactions of mixed LB films of SP and C20

UV/vis absorption spectrum of a mixed LB film of SP and C20 fabricated at 7°C and that of the LB film after UV irradiation at room temperature are shown in Fig. 3. Photoisomerization of SP to MC is confirmed by the development of a broad band centered at ca. 550 nm. However, the J-aggregation does not proceed in the film. This cannot be compared directly to the absence of J-aggregation in the Langmuir film of pure SP at 7°C [26] or to the absence of J-aggregation in the LB films of pure SP fabricated at 30°C followed by UV irradiation at 7°C [22] because of the difference in the UV irradiation temperature.

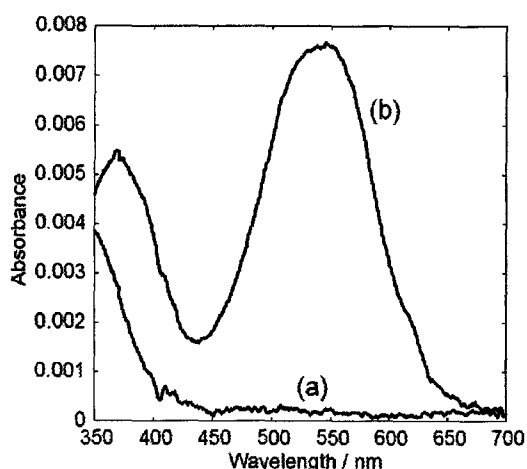


Figure 3 UV/vis absorption spectrum of a mixed LB film of SP and C20 fabricated at  $10 \text{ mN m}^{-1}$  at 7°C; (a) as-deposited film and (b) after UV irradiation at room temperature for 60 min.

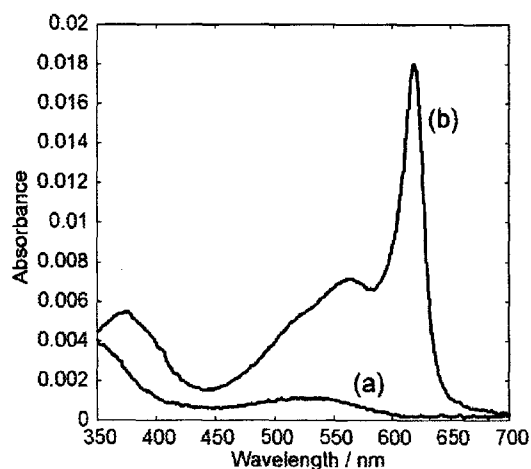


Figure 4 UV/vis absorption spectrum of a mixed LB film of SP and C20 fabricated at  $10 \text{ mN m}^{-1}$  at 23°C; (a) as-deposited film and (b) after UV irradiation at room temperature for 60 min.

UV/vis absorption spectrum of a mixed LB film of SP and C20 fabricated at 23°C and that of the LB film after UV irradiation at room temperature are shown in Fig. 4. In this case, UV irradiation gives rise to isomerization of SP to MC followed by J-aggregation of MC. This should

be relevant to the fact that light-induced J-aggregation proceeds in the LB films of pure SP fabricated at 30°C [22]. This shows that the presence of C20 does not inhibit the light-induced J-aggregation in the mixed LB films. The photoreactions that depend strongly on the fabrication temperature are not understood at present.

### 3.3 AFM observations of mixed LB films of SP and C20

AFM has been used to monitor morphological changes of LB films accompanied by photoreactions [15-17,19,21-23,27]. The smooth surface of the LB films allows for the detection of subtle changes of the morphology of the films.

*As-deposited LB films:* AFM images were obtained of as-deposited LB films of SP and C20 fabricated at 30°C. The LB films were not typical monolayers. Multilayer domains of ill-defined shape were buried in monolayers. This feature was different from that of the LB films of pure SP in which circular trilayer domains of the size of several tens of micrometers were embedded in monolayers of SP. The films consisted of several regions. The lowest region should be a monolayer of C20. This region was positioned ca. 1 to 2 nm above the mica substrate on the basis of the sectional analysis. The medium layer was 4 to 5 nm higher than the monolayer of C20. This region can be trilayer domains consisting of SP as observed in the LB films of pure SP. It was not clear if the bottom layer of the trilayer domains was a monolayer of SP or that of C20. The highest region consisted of cone-shaped domains with curved surfaces. The height was several tens of nanometers. This region may not have a layer structure because the surface of this region was not flat. When the transfer was conducted at 7°C, the structure of the LB film was similar to that of the film fabricated at 30°C except for the absence of the highest regions.

*LB films after UV irradiation:* LB films fabricated at 30°C were irradiated with UV light. The AFM observations revealed the development of structures of fractal shape mainly on the medium region. These newly created structures should be attributed to J-aggregates of MC. On the other hand, when LB films fabricated at 7°C were irradiated with UV light, no significant change was observed in the AFM images.

### 3.4 Structural model of the mixed films

On the basis of the surface pressure-area isotherms and AFM observations, we suggest that, in the high-temperature regime, a mixed monolayer of SP and C20 is transformed during the phase transition into a complex structure in which SP molecules are squeezed out of a C20 monolayer, resulting in the formation of trilayer domains of SP. The Langmuir films are transferred onto solid substrates without large reorganization of the structures in contrast to the case of the films of pure SP whose monolayer region fails to be transferred onto solid substrates, resulting in the LB film structures with circular trilayer domains located sparsely [22]. In the low-temperature regime, the films have complex structures similar to those formed after the phase transition in the high-temperature regime.

## 4. CONCLUSIONS

This study shows the structures and photoreactions of

mixed LB films of SP and C20. The addition of C20 causes large differences on the structures of the films. In the low-temperature regime, the films consist of multilayer domains of undefined shape embedded in a monolayer of C20 in contrast to a continuous trilayer structure of the LB film of pure SP in the same temperature range. In the high-temperature regime, SP molecules are squeezed out of a C20 monolayer during the phase transition to form trilayer domains in contrast to the LB film of pure SP with circular trilayer domains positioned sparsely on the substrate. Photoreactions of the LB films depend strongly on the fabrication temperature. Only the photoisomerization of SP to MC proceeds in the LB films fabricated at 7°C. On the other hand, light-induced J-aggregation occurs in the LB films fabricated at 30°C. These results indicate that the addition of C20 affects the structures and photoreactions of the LB films in a manner very different from the case of adding n-alkane. Studies are under progress to clarify the reason why the photoreactions depend strongly on the fabrication temperature.

#### 5. ACKNOWLEDGMENT

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