A Morphological Study on the Changes in Texture of the Merocyaninecontaining LB Films Induced by Hydrothermal Treatments

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Change in morphology of merocyanine – Cd arachidate mixed Langmuir-Blodgett (LB) films has been studied before and after the hydrothermal treatments (HTT) of 100% humidity at temperatures ranging from 30°C to 90°C using a polarized light photomicroscope. By applying HTT, the J-band with an in-plane anisotropy in the as-deposited LB films is reorganized into an isotropic phase characterized with a narrowing of the peak. Correspondingly, the microscopic image, initially anisotropic and featureless under polarized light, changes to be isotropic and filled with round-shaped domains as large as 0.1 mm or more in diameter. Observation of four types of LB samples with different monolayer stacks indicates that each domain is confined to one single monolayer.

Key words: Langmuir-Blodgett films, Merocyanine chromophores, Control of J-aggregate, Formation of supestructures, Hydrothermal treatments

1. INTRODUCTION

Langmuir-Blodgett (LB) films are attracting a continued attention as a designable molecular assembly system [1]. They are fabricated using a technique known as the LB method which is based on the preparation of monolayers at the air-water interface followed by the transfer of them one after another onto a solid substrate by dipping and raising it traversing the interface. Thus prepared LB film is associated with a one-dimensional (1D) sequence of monolayers in accordance with the plan along the direction normal to the substrate plane: a variety of 1D sequences, e.g., ABAB..., AABB..., ABBABB..., and so forth can be constructed using only two different monolayer species A and B.

The in-plane molecular organization is however not a direct consequence of the LB technique, and additional means have therefore been introduced for developing it. A vast literature is dedicated to the modification of aggregation state in the LB films. In this respect, mixed LB films of a surface-active merocyanine and arachidic acid (MS and C₂₀ in Figs. 1 (a) and (b), respectively) have drawn attention as a model system to examine the effects of various secondary treatments, i.e., the acid treatment (AT) and the basic treatment (BT) in both gas- and liquid-phases, and the heat treatment (HT) in gas phase [2-9]. AT dissociates the J-band, BT restores it, and HT dissociates it at higher temperatures (90°C, typically) [3] but reorganizes it at lower temperatures ("mild" HT at 60°C ~ 70°C) to form a new phase with spectra further red-shifted and sharper in shape than those before the treatment [5, 6]. Recently, we have found that the reorganization of J-band is induced in a similar manner for a wider temperature range, 30°C ~ 90°C, by applying hydrothermal treatments (HTT) under 100% relative humidity as exemplified in Fig. 2 [7-9], and that the reorganization process is associated with changes in the film texture observed by a photomicroscope [8]. Superstructures with round-shaped domains of approximate diameters as large as up to 0.1 mm or more appear after HTT [8].

For a better understanding of HTT, the changes in texture of the $MS-C_{20}$ LB system have been further



CH₃(CH₂)₁₈COOH (b)

Fig. 1 Chemical structures of film-forming materials. (a) Merocyanine (MS), and (b) arachidic acid (C_{20}).



Fig. 2 Typical UV-visible absorbance spectra A_{\parallel} and A_{\perp} before HTT of a 10-layered MS-C₂₀ LB film shown by the solid and dashed lines, respectively. The thick line refers to the spectra after HTT at 90°C for 15 min, respectively, where the A_{\parallel} and A_{\perp} spectra are identical with each other.

studied for varying heating temperature $T_{\rm H}$ and heating time $t_{\rm H}$ employing LB samples with different monolayer stacks. The results are shown in the present paper.

2. EXPERIMENTAL

MS and C_{20} from Hayashibara Biochemical Lab. Inc. and Fluka AG, respectively, were used without further purification. They were dissolved in optical-grade chloroform from Tokyo Kasei with a molar mixing ratio of [MS] : $[C_{20}]=1:2$. The monolayers were prepared on a Cd²⁺-containing subphase water and successively



Fig. 3 Photomicrographs of 10-layered MS-C₂₀ mixed LB films deposited on the C₂₀-hydrophobized substrates after HTT for a fixed heating time of $t_{\rm H}$ =60 min. (a), (b), (c) and (d) refer to $T_{\rm H}$ =40, 60, 80 and 90°C, respectively.



Fig. 4 Average size d_{appr} for 60-min-HTT plotted as a function of $T_{\rm H}$. The deviations are given by bars.

deposited onto one side of a substrate using the standard vertical dipping technique as described in the previous

papers [2-4]. The substrates, each 1/4 of ordinary slide glass, were hydrophobized by coating them with five monolayers of C₂₀ [6-8]. The monolayers, either of MS-C₂₀ or pure C₂₀, were then successively deposited, where they were transferred with a deposition ratio of approximately unity for both upward and downward strokes irrespective of the monolayer compositions, resulting in the Y-type LB films. We prepared four different types: (a) 10-layered, (b) 4-layered films, (c) 2-layered, and (d) 1-layered, each deposited on a C₂₀-hydrophobized substrate. Types (a)-(c) consist of homogeneous Y-type bilayer unit cells, while a type-(d) sample involves a heterogeneous unit cell composed of a $MS-C_{20}$ monolayer and a pure C_{20} one picked up by upward and downward strokes, respectively. An aluminum tube (ca. 20 mm in diameter and 150 mm long) with a screw lid at one end was used for HTT [8]. A small amount of pure water (2 cm² or less) was first introduced into the tube to realize the condition of 100% relative humidity, a spacer was then settled at the bottom to avoid the direct contact between the water and the sample that was finally placed in the tube [8]. The tube was immersed for a given heating time in a water bath kept at a constant temperature and then pulled off from the bath to cool down to room temperature. The photomicrographs were recorded using an Olympus BH-2 photomicroscope with a CCD camera. UV-visible absorption spectra A_{\parallel} and A_{\perp} for 400-700 nm were measured using a Shimadzu UV-2100 spectrophotometer, where A_{\parallel} and A_{\perp} refer to absorbances taken using linearly polarized light incidents with the electric vector parallel and perpendicular to the dipping direction in the deposition process, respectively.

3. RESULTS AND DISCUSSION

3.1 HTT-induced change in the absorbance spectra

Figure 2 exemplifies typical UV-visible absorbance spectra A_{\parallel} and A_{\perp} of a 10-layered MS-C₂₀ LB film in the as-deposited state and after HTT at a heating temperature $T_{\rm H}$ =90°C for a heating time $t_{\rm H}$ =15 min. The as-deposited spectra show an in-plane anisotropy with a dichroic ratio $R=A_{\parallel}/A_{\perp}>1$ (R=1.22 for this sample), each associated with a J-band centered around 590 nm which is redshifted by ca. 70 nm from the 530-nm band observed in MS solution in CHCl₃. A new phase of J-band with further redshift appears after



Fig. 5 Photomicrographs of 10-layered MS-C₂₀ mixed LB films deposited on the C₂₀-hydrophobized substrates after HTT at a fixed heating temperature $T_{\rm H}$ =90°C. (a) and (b) refer to $t_{\rm H}$ =15 and 45 min, respectively (see also Fig. 3 (d) for $t_{\rm H}$ =60 min).

the 90°C-HTT for $t_{\rm H}=15$ min, and the band is fully developed with respect to its position, height and sharpness. The anisotropy is no more to be seen between the both spectra. The above remarks are consistent with those reported so far and the detailed analysis to be dealt with in a separate paper.

3.2 Morphology of the HTT-induced superstructures

The photomicroscope images of as-deposited films are featureless within the resolution although they are associated with vague local inhomogeneities as outlined in a preliminary report [8]. The brightness of the field under polarized light incident varies with a π -periodicity when the sample is rotated on the stage in accordance with the anisotropy in absorbance.

After HTT at temperatures $T_{\rm H}$ =30-90°C, there appear superstructures, round-shaped and as large as up to 100 µm or more in the approximate diameter, in the images as preliminarily reported [8]. The occurrence of these round-shaped domains is found to depend on both temperature $T_{\rm H}$ and time $t_{\rm H}$. In the following, further details are shown using the microscopic images.

3.2.1 Dependence on $T_{\rm H}$

Figures 3 (a)-(d) show the images from 10-layered LB films after 60-min HTT at $T_{\rm H}$ =40, 60, 80 and 90°C, respectively, where all samples belong to the same batch. Two different types of round-shaped domains are



Fig. 6 Average size d_{appr} for 90°C-HTT plotted as a function of $t_{\rm H}$. The deviations are given by bars.

recognized: those surrounded by bright lines and those by dark lines, which will be hereafter referred to as the B- and the D-types, respectively.

The image for the 40°C-HTT in Fig. 3(a) represents an initial stage of the growing process of the round-shaped domains. The domains are of B-type and smaller in size than those seen in the later stages where the new phase of J-band is fully developed. It is noted that the remaining in-plane anisotropy is often observed in this stage as the anisotropic spectra with R>1 and the variation of field brightness with the π -periodicity under polarized light incident giving the maximum brightness when the dipping direction is parallel or anti-parallel to the polarization direction.

From $T_{\rm H}$ =60°C on, D-type domains appear in the field as seen in Figs. 3 (b)-(d). The B-type domains are occasionally stacked one on another in a random manner, while the D-type are located above the B-type. Stacks up to four-fold are so far recognized as reported in the previous paper. Both B-type and D-type domains tend to grow in size with increasing $T_{\rm H}$. This suggests that the B- and D-type domains are bound to the inner and the outer monolayers, respectively. Here, the difference in color between the B-type and D-type rims may originate from the different dielectric environments surrounding the domains: an inner monolayer is sandwiched between the adjacent monolayers while an outer monolayer is faced to air on one side.

The average value of the approximate domain diameter d_{appr} for $t_{\rm H}$ =60 min is given as a function of $T_{\rm H}$ in Fig. 4, where each point involves data from ~100 or more domains seen in randomly chosen fields. The d_{appr} -value remains in a range of 20-30 μ m below $T_{\rm H}$ =70°C, increases up to its maximum at $T_{\rm H}$ =80°C and then tends to decrease down to ca. 70 μ m at $T_{\rm H}$ =90°C. The larger deviations of d_{appr} at $T_{\rm H}$ =80 and 90°C are due to the increased contribution from D-type domains whose sizes occasionally exceed 150 μ m.

3.2.2 Dependence on $t_{\rm H}$

Figures 5 (a) and (b) show the images from 10layered LB films at $T_{\rm H}$ =90°C for $t_{\rm H}$ =15 and 45 min, respectively. Here, Fig. 4 (d) is referred to as the case of $t_{\rm H}$ =60 min.

The image for $t_{\rm H}=15$ is filled with B-type domains alone as seen in Fig. 5 (a) as is the case with Fig. 3 (a) of $T_{\rm H}=40^{\circ}$ C and $t_{\rm H}=60$ min. The new phase of J-band is however fully developed at $T_{\rm H}=90^{\circ}$ C within 15 min as shown in Fig. 2. It is therefore indicated that the process of domain growth has a delay compared to the



Fig. 7 Photomicrographs of $MS-C_{20}$ mixed LB films deposited on the C_{20} -hydrophobized substrates after 80°C-HTT for 60 min. (a), (b) and (c) refer to 4-, 2- and 1-layer films, respectively (see also Fig. 3 (c) for the 10-layer case).

J-band reorganization process.

The image for $t_{\rm H}$ =45 min in Fig. 5 (a) shares common features with Fig. 4 (d) for $t_{\rm H}$ =60 min except for the larger domain sizes in the latter, showing that the domain growth is still under way. Both B-type and D-type domains coexist in the field with occasional stackings among them.

Figure 6 shows the dependence of d_{appr} on $t_{\rm H}$ at $T_{\rm H}=90^{\circ}{\rm C}$ based on samples belonging to one single batch. Up to $t_{\rm H}=30$ min it remains in a range of 20-30 $\mu{\rm m}$, and then it increases up to $d_{appr}=ca.$ 80 $\mu{\rm m}$ at $t_{\rm H}=60$ min, which is by ca. 10 $\mu{\rm m}$ larger than that from a sample of another batch given in Fig. 4. This

difference may involve the batch dependence of the sample properties, the experimental errors and also the statistical fluctuations in small-scale sampling.

3.2.3 Dependence on the film thickness

We have prepared samples with reduced number of $MS-C_{20}$ mixed monolayers to evaluate the thickness of the round-shaped domains. Figures 7 (a)-(c) show the images of the 4-, 2- and 1-layered $MS-C_{20}$ LB films after 80°C-HTT for 60 min, respectively. The 4- and the 2-layer cases are discriminated from the 10-layer case (Fig. 3 (c)) by their relative predominance of the D-type over the B-type, while the 1-layer case is characterized by the absence of the D-type. These observations lead to a picture that D-type and B-type domains represent those in the outermost monolayer and the inner ones, respectively, and that each is one monolayer thick or even less since it is confined to one single monolayer. It is noted that the above scheme is consistent with the tentative interpretation given in the previous paper [8].

4 CONCLUDING REMARKS

We have examined the change in morphology of MS - Cd arachidate mixed LB films before and after HTT at $T_{\rm H}$ =30°~ 90°C for $t_{\rm H}$ up 60 min by means of a polarized light photomicroscope. By applying HTT, the as-deposited J-band with an in-plane anisotropy is reorganized into a new phase of J-band characterized with a sharp peak. The microscopic image, initially anisotropic and featureless under polarized light, tends to be isotropic and filled with either or both types of round-shaped domains as large as 0.1 mm or more in diameter. The growth process of the domains is found to have a delay compared to that of the peak height of the reorganized J-band, indicating that it is continued after the spectral change is saturated. Observation of four types of LB samples with different monolayer stacks indicates that each domain is confined to one single monolayer.

Acknowledgements

The authors wish to thank Dr. S. Morita and Mr. J. Miyata for their helpful discussions and comments in the early stages of the present work.

REFERENCES

[1] H. Kuhn: Naturwissenschaften 54, 429 (1967).

[2] M. Sugi and S. Iizima, *Thin Solid Films* 68, 199 (1980).

[3] M. Sugi, M. Saito, T. Fukui and S. Iizima, *Thin Solid Films* **129**, 15 (1985).

[4] Y. Hirano, T. M. Okada, Y. F. Miura, M. Sugi and T. Ishii: J. Appl. Phys. 88, 5194 (2000).

[5] J. Miyata, S. Morita, Y. F. Miura and M. Sugi, Jpn. J. Appl. Phys. 44, 8110 (2005).

[6] J. Miyata, S. Morita, Y. F. Miura and M. Sugi: Colloids and Surfaces A 284-285, 509 (2006).

[7] S. Mouri, J. Miyata, S. Morita, Y. F. Miura and M. Sugi: Jpn. J. Appl. Phys. 45, 7925 (2006).

[8] S. Mouri, H. Moshino, S. Hasegawa, Y. F. Miura and M. Sugi: Jpn. J. Appl. Phys. 46, 1650 (2007).

[9] H. Moshino, S. Hasegawa, S. Mouri, Y. F. Miura and M. Sugi: *Trans. Mater. Res. Soc. Jpn.* accepted for publication.