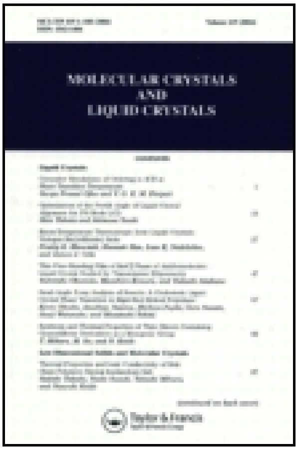

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A Study on the Micro-Phase Separation in Two-Component Monolayers

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A Study on the Micro-Phase Separation in Two-Component Monolayers

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Some experiments for fundamental understanding of micro-phase separated structures formed in mixed monolayers of *n*-alkyltrichlorosilanes and a partially fluorinated amphiphile are presented. The surface morphology of the mixed monolayers is varied by changing some parameters, such as chain length of alkyltrichlorosilanes, temperature of the water surface, and solvents of spreading solutions. It is demonstrated that the surface structures are mainly governed by the dynamic molecular process during spreading. The most likely mechanism of the micro-phase separation is proposed.

Keywords: trichloro(long-alkyl)silanes; spread monolayers; Langmuir-Blodgett (LB) films; micro-domains; two-dimensional micro-phase separation; Atomic Force Microscope (AFM).

INTRODUCTION

In recent years, Langmuir-Blodgett (LB) techniques have attracted growing attention in the field of molecular photonics and electronics, since they are regarded as having technological potential to fabricate functionalized surfaces.[1]

We have reported the micro-phase separated structures in mixed monolayers of trichloro(octadecyl)silane (TCOS) and a partially fluorinated silazane derivative (FS) using AFM topographic and friction force observations.[2] When the monolayers were spread from mixtures of TCOS/FS, the surfaces made up of condensed phase micro-domains of TCOS surrounded by continuous fluorocarbon phase of FS were formed. Morphology of the mixed monolayers was varied by changing molar fraction of the components; at low TCOS mixing ratios almost circular TCOS micro-domains of 0.1 to 1 μm in diameter were formed, while at higher ratios they were locally fused to form larger domains of a lateral size of a few μm.

In this paper, we will report further detailed examination for fundamental understanding of the micro-phase separation in mixed monolayers by changing some experimental parameters such as temperature of the water surface, alkyl chain length of the film molecules, and the spreading solvents.

EXPERIMENTAL

Trichloro(octadecyl)silane (TCOS), trichloro(eicosyl)silane (TCES), trichloro-(docosyl)silane (TCDS) and Bis[6,9-bis(trifluoromethyl) 6,8,8,9,11,11,12,12,13,13,13-undecafluoro-4,7,10-trioxatridecyl dimethyl-silyl]amine (FS) were used as film materials. Pentane, hexane, heptane and octane were employed as the spreading solvents. Concentration of the spreading solutions was around 2.5×10^{-3} M. The mixing molar ratios of alkyltrichlorosilanes and FS was kept constant at 2 : 8 throughout this study. The subphase in all experiments was the ultrapure water from the Elgastat UHQ-PS system. A computer-controlled Langmuir trough developed in our laboratory was used.[3] Compression of the monolayers started at 30 min after spreading unless otherwise stated. All π-A isotherms were measured at a constant time of observation (t_{ob}) of 600 s.[4] 1-layer LB films were transferred onto cover glass of optical microscope with the horizontal scooping up method.[5] AFM observations were performed by Nanoscope III (Digital Instrument Inc.) with the tapping mode. Surface roughness of the cover glass was less than 0.3 nm.

RESULTS

TCOS monolayers exhibit fully condensed isotherms where the surface pressure starts to increase at an area around the cross-section area of an alkyl chain.[2] It is found that limiting molecular areas of TCOS monolayers were not changed by temperature change so much, as compared with those of FS monolayers. Temperature dependency of π-A isotherms of TCOS/FS mixed monolayers is shown in Fig. 1(a); only part of the isotherms to the first-step collapse are shown here. One

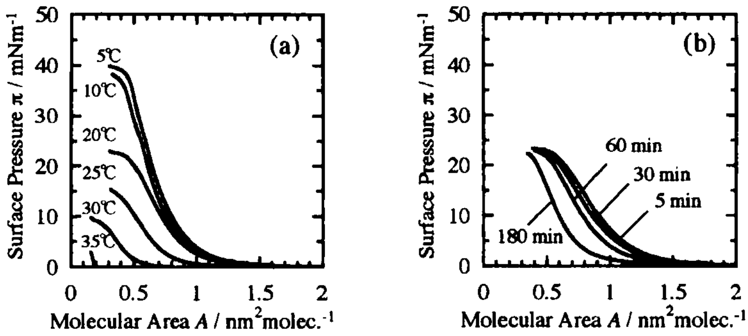

FIGURE 1 (a) Temperature dependency of π-A isotherms of TCOS/FS mixed monolayers. (b) Temporal change of π-A isotherms of FS monolayers at 20 ℃. The monolayers were allowed to stand for 5 to 180 min before starting compression.

should remind that the regions of the isotherms in Fig. 1(a) are governed dominantly by FS component, and after the collapse of FS component features of monolayers of TCOS component will appear.[2] This figure indicates that the isotherms of TCOS/FS mixed monolayers shift to smaller molecular area with increasing temperature. As shown in Fig. 1(b), the decrease of the molecular area is due to the dissolution of FS component into the subphase.

Figure 2 shows temperature dependency of the surface morphology of TCOS/FS mixed monolayers transferred at 0.85 nm^{2}molec.$^{-1}$. The circular micro-domains of TCOS are dispersed in a continuous FS phase at 20 ℃. At 5 ℃, we can see some locally fused, irregularly shaped domains. With increasing temperature, there is a tendency that beaded micro-domains appear. To examine the effect of dissolution of the FS component at higher temperatures, AFM observation was performed on the sample prepared at 5 min after spreading at 35 ℃. The observed structure was almost the same as that shown in image (d), indicating that the beaded micro-domain structure was preferentially formed at an early stage of the monolayer formation.

Figure 3 presents AFM images of TCES/FS and TCDS/FS mixed monolayers. The image (a) reveals that even at 20 ℃ the shape of the micro-domains in TCES/FS mixed monolayer deviates from circular as well as that at 5 ℃ (image is not shown). The primary micro-domains at 30 ℃, however, are almost circular but many are beaded (image (b)). TCDS/FS mixed monolayers show the considerably fused, irregularly shaped domains at any temperature from 5 to 30 ℃. At 5 ℃, we could observe a characteristic surface structure as shown in Fig. 3(c) and 4.

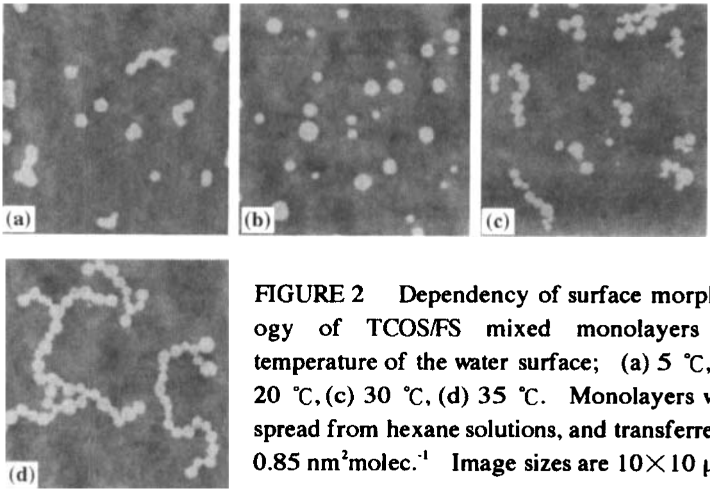

FIGURE 2 Dependency of surface morphology of TCOS/FS mixed monolayers on temperature of the water surface; (a) 5 ℃, (b) 20 ℃, (c) 30 ℃, (d) 35 ℃. Monolayers were spread from hexane solutions, and transferred at 0.85 nm^{2}molec.$^{-1}$ Image sizes are 10×10 μm^2.

Dependency of the surface morphology of TCOS/FS mixed monolayers at 20 ℃ on the spreading solvents is shown in Fig. 5. The images indicate that almost circular isolated micro-domains are formed in these conditions, but the size of them becomes smaller with decreasing chain length of the solvents.

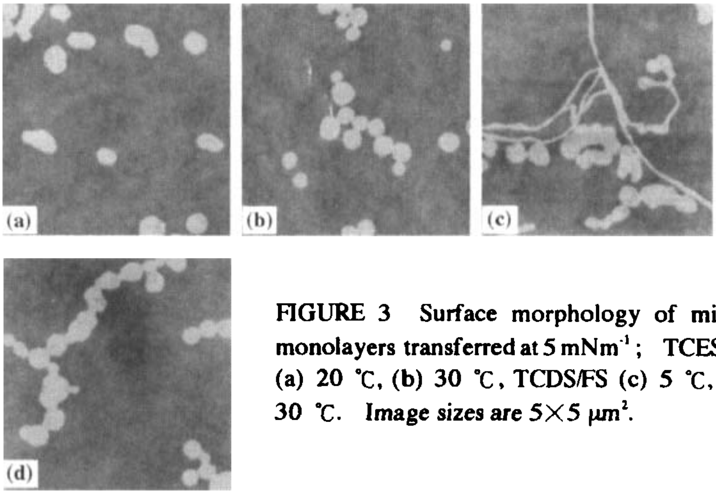

FIGURE 3 Surface morphology of mixed monolayers transferred at 5 mNm^{-1} ; TCES/FS (a) 20 ℃, (b) 30 ℃, TCDS/FS (c) 5 ℃, (d) 30 ℃. Image sizes are 5×5 µm^2.

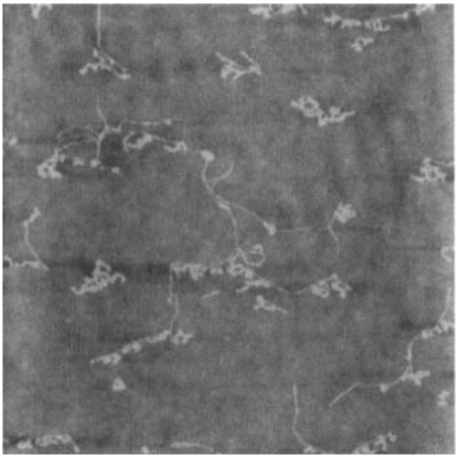

FIGURE 4 Surface morphology of TCDS/FS mixed monolayers transferred at 5 mNm^{-1}, 5 ℃ (30×30 µm^2).

DISCUSSION

It has been well known that the most fundamental driving force to determine the shape of two-dimensional domains at equilibrium is the line tension at the two-phase boundary. If the line tension is large enough, the shape of the domain becomes circular. It is apparent, however, that the results mentioned above cannot be explained only by the line tension. We have reported that the surface morphology of insoluble monolayers should be determined by the molecular processes during spreading.[2,6] In the spread monolayer systems, the

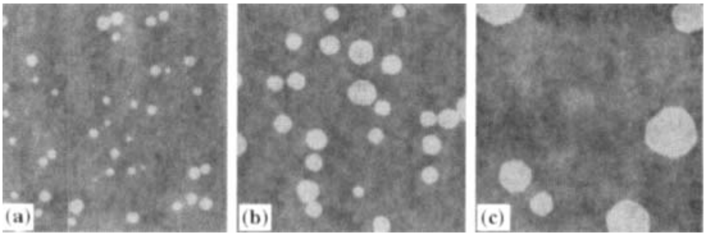

FIGURE 5 Dependency of surface morphology of TCOS/FS mixed monolayers on the spreading solvents used; (a) pentane, (b) heptane, (c) octane. Monolayers were transferred at 5mNm^{-1},20 ℃. Image sizes are 10×10 μm^2. Refer Fig. 2(b) for the monolayer prepared from hexane solution.

most important factors may be the speed of solvent evaporation and the mobility of the film molecules on the water surface during spreading.

It seems reasonable to assume that the film molecules which form condensed monolayers can move rapidly on the water surface only while they are fully solvated by the spreading solvent, on the contrary the movement will be almost stopped after completing evaporation of the solvent. The speed of solvent evaporation is affected not only by the spreading temperature but also by the affinity between the film material and the solvent. The degree of solvation will be related to the solubility parameter (δ) of them.[7] If the δ values of the film material and the solvent are close to each other, the speed of solvent evaporation becomes relatively slow. Slow evaporation of the solvent allows the micro-domains to grow circular and large. At lower temperatures, since the movement of silane molecules in the micro-domains on the water surface should be suppressed severely although the speed of solvent evaporation is relatively slow, the structures will be frozen prior to completion of the formation of the circular-shaped micro-domains. On the other hand, at higher temperatures active movement of solvated film molecules will lead the shape of the primary micro-domains to circular one. But if the evaporation is too fast, the structures of the micro-domains will be frozen to form a shape like strings of beads. For the same solvent, the large difference of the δ between the film material and the solvent is expected for the silane having longer alkyl-chain. As the result, the speed of solvent evaporation will be accelerated and the shape of the micro-domains is considerably deformed from circular to irregular.

A series of the results cited above give an idea to explain the formation mechanism of the micro-phase separated structures. The most likely mechanism is the two-dimensional spinodal decomposition during spreading.[6] Spinodal decomposition is well known in the field of two-component polymer systems or two-component metal alloys to form some characteristic regular structures such as the bicontinuous phases by changing temperature rapidly or by rapid evaporation of the co-solvent of two components. In the two-component monolayer systems, the two-dimensional bicontinuous structure of hydrocarbon and fluorocarbon phases should be formed during the rapid evaporation of the spreading solvent. Each component of the alkylsilane and FS on the water surface starts to condense and to expand, respectively, just after formation of the two-dimensional bicontinuous phase. So, the monolayers form the structure like that shown in Fig. 4 during the spreading process. If enough mobility of the silane molecules is assured at this stage, elongated domains will be broken to pieces by line tension. This is the result of two-dimensional version of the capillary instability. The pieces become circular by line tension and they scatter almost uniformly by the Brownian movement if the temperature is relatively high.

In summary, it becomes apparent that the surface morphology of the spread monolayers is determined mainly by the balance among some molecular processes during spreading rather than by the process in equilibrium. Thus, the surface morphology of mixed monolayers of long-alkyl silanes and FS as shown in Figs. 2-4 are the frozen-in structures at the every stage of spreading processes by the balance of evaporation speed of spreading solvent, condensation energy among the long alkyl-chains of silanes and the spreading temperature. The surface composed of the isolated, circular micro-domains is formed under the very narrow conditions where all parameters are suitably balanced.

Acknowledgments

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