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Compression Dependency of Micro-Phase Separated Structures in Binary Mixed Monolayers of n-Alkyl Fatty Acids and a Perfluoropolyether Acid

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Condensed-phase micro-domains of n-alkyl fatty acid (Cn) in binary mixed Langmuir monolayers of Cn and a perfluoropolyether amphiphile (PFPE) take various shapes depending on experimental parameters such as surface temperature and alkyl chain length of fatty acid. In this work, the shape of the domains was evaluated by fractal dimension (D) as a function of molecular area. It becomes apparent that values of D are constant irrespective of molecular area under a constant temperature, meaning the shape is unchanged by compression. Distance between domains (L) was also estimated and compared for the compression direction and the transverse direction. The L for two directions nearly coincides, which demonstrates that the compression-induced anisotropy is negligible at least around the center of the rectangular trough with two symmetrically movable barriers although the molecules were compressed in one direction.

Key words: Langmuir Monolayer, Micro-Phase Separation, Atomic Force Microscopy, Fractal Dimension

1. INTRODUCTION

Langmuir and Langmuir-Blodgett films have been studied actively in recent years aiming at development of devices and biomimetic systems [1-3]. Two-dimensional micro-phase separation in binary mixed Langmuir monolayers is of great interest in surface engineering as template for fabrication of functionalized surfaces applicable to complex biosensors, micro-reactors, electric circuits, and so on.

In our previous work, a mixed monolayer of *n*-alkyltrichlorosilane and perfluorosilazane form interesting mesoscopic phase-separated structures, in which the shape of condensed domains changes from circular to linear with decreasing surface temperature and increasing chain-length of *n*-alktltrichlorosilane [4]. Similar change was observed for mixed monolayers composed of the most widely used film material forming condensed phase, n-alkyl fatty acids (Cns), and a perfluoropolyether acid (PFPE) forming expanded phase [5,6]. AFM image analysis indicated the monolayer morphology could be divided into three temperature regions; circular-shaped domains of Cn formed for shorter alkyl-chain Cn at high temperatures, branching domains with narrow lines for longer Cn at low temperatures, and irregular-shaped domains at intermediate conditions. Careful consideration of experimental results indicated that the branching domains change to circular ones via irregularly-shaped ones with increasing mobility of Cn molecules determined by the alkyl chain length and the subphase temperature.

In our experiment, Langmuir monolayer is compressed with two movable barriers sliding on a rectangular trough. Under such circumstance, one might wonder if monolayers are compressed anisotropically in one direction. Malcolm and co-workers demonstrated anisotropic strain of condensed monolayers by the method painting grid on water surface with sulfur fine powders, and described the effect of anisotropic compression on the quality of Langmuir and Langmuir-Blodgett (LB) monolayers [7-10]. In order to resolve the anisotropic problem, Matsumoto and co-workers developed a Langmuir trough with a diaphragm barrier which compresses monolayers radially [11]. Miyano and co-workers developed a Langmuir trough with four movable barriers, which allow isotropic compression by compression of two orthogonal directions [12].

In this paper, we examined the effect of anisotropic compression on the micro-phase separated structures in Cn/PFPE monolayers. Average distances (L) of the condensed-phase domains are compared in compression direction and transverse direction. The domain shape was

evaluated by fractal dimension (*D*).

2. EXPERENTAL

n-Alkyl fatty acids (Cn: n = the number of carbon atoms) (> 99.9%) were obtained from Research Institute of Biological Materials Japan. A carboxyl terminated perfluoropolyether, perfluoro-2,5,8-trimethyl-3,6,9-trioxadodecanoic acid (PFPE) (>97%) was purchased from PCR. Spreading solvent was spectro-grade chloroform purchased from Dojin Chemicals. All materials were used without further purification. Cn and PFPE were mixed in spreading solution. The mixing molar ratio of Cn/PFPE was 2/8 and a total concentration in the spreading solution was 2.5 mM. The monolayers were spread onto the temperature-controlled aqueous subphase surface to give molecular area of 2.2 nm^2/molecule and allowed to stand for 30 min before compression at a constant strain rate of 10 %/min. The subphase was 0.5 mM aqueous solution of cadmium acetate dihydrate (>98 %, Wako chemicals) adjusted to pH 7.0 with potassium hydrogen carbonate (special grade, Kanto Chemicals). Monolayer deposition was carried out by the scooping-up method on highly polished silicon wafers at almost the center of our rectangular Langmuir trough. Prior to deposition, the substrate was cleaned by RCA method and then stored in ultrapure water until use.

A microcomputer-controlled Langmuir trough was constructed in our laboratory. Two barriers confining monolayers were driven symmetrically under constant strain rate mode of compression. Temperature of the subphase surface was controlled using a large number of integrated Peltier element modules attached to the back of a base plate of the trough, and was detected precisely by platinum wire resistance temperature sensors. AFM observation was made under an ambient atmosphere with a Nanoscope III (Digital Instruments) in tapping mode with 512×512 pixels.

3. RESULTS and DISCUSSION

Figure 1 shows dependency of Cn/PFPE phase-separated structures on compression at 20℃. Mixing ratio is fixed at 2/8 for all cases. Bright

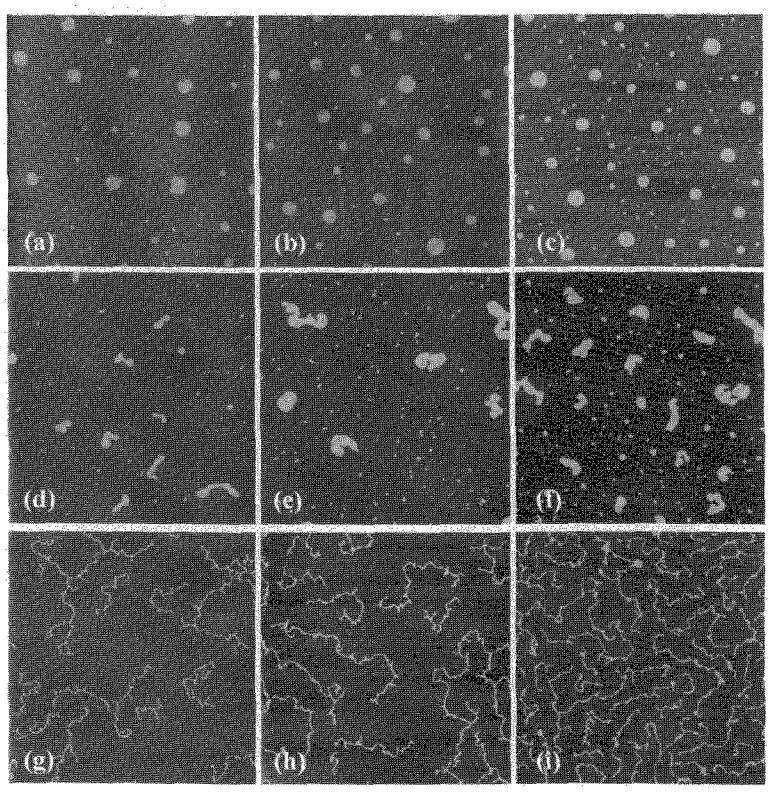

Fig.1 AFM images of Cns/PFPE (2/8) mixed monolayers at 20℃ transferred on silicon wafers: C20/PFPE at (a) 1.0, (b) 0.8, (c) 0.6 nm^2/molecule, C22/PFPE at (d) 1.0, (e) 0.8, (f) 0.5 nm^2/molecule, C24/PFPE at (g) 1.0, (h) 0.7, (i) 0.4 nm^2/molecule. The image sizes are 40×40 μm^2 for (a), (b), (d), (e), (g), and 30×30 μm^2 for (c) (f), (h), (i).

micro-domains correspond to the condensed phase of Cn while dark part is the expanded phase of PFPE. The condensed domains take circular shape for C18/PFPE, irregular shape for C22/PFPE, and branching linear shape for C24/PFPE. As seen from the images, the shape of condensed domain seems to be unchanged by compression. This is due to that the Cn molecules are closely packed in the domains although there is a slight difference in the molecular packing density depending on the chain length which causes change in the domain shape. In order to evaluate the domain shape quantitatively, fractal dimension (D) of the condensed-phase domains is estimated according to the image analysis procedure reported previously [5]. Values of D are (a) 1.07, (b) 1.04, (c) 1.05 for C18/PFPE, (d) 1.37, (e) 1.33, (f) 1.34 for C22/PFPE, and (g) 1.91, (h) 1.87, (i) 1.84 for C24/PFPE. Since the fractal dimension is a measure of complexity of domain shape, the constant fractal dimension for each monolayer demonstrates once-formed condensed domains are unchanged by compression at a constant temperature in our mixed monolayer system.

Compression of the mixed monolayers was carried out symmetrically by two barriers only from one direction on our Langmuir trough. This does not change the domain shape as seen from the D values mentioned above, but may give the anisotropic effect on distribution of the condensed domains. The compression anisotropy was examined by comparing distances (L) between the condensed-phase domains for parallel and transverse directions with respect to the compression direction at several molecular areas.

Figure 2 presents a set of examples of AFM image analysis for determination of the domain distances. It should be noted that the L is the average distances between edges of the domains along the pixel lines. In Figure 3, correlation between Lc and Lt, which are the domain distances for the compression direction and the transverse direction respectively, are plotted with the standard deviation. Each point represents the average obtained from more than ten AFM images observed for at least two different samples. It is found from Fig. 3 that the L values tend to be slightly larger for the compression direction than for the transverse one. This might be the effect of compression for one direction. Nevertheless, it also can be seen that the difference between Lc and Lt is surprisingly small; two distances seem to be in agreement within experimental errors even when the monolayers were compressed to about 1/4 to 1/5 of the initial molecular area. This experimental fact demonstrates that the compression-induced morphological disorder can

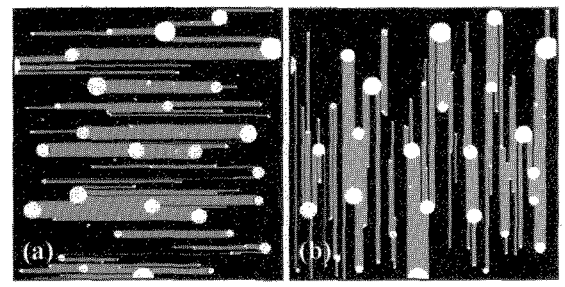

Fig.2 Examples schematically explaining average domain distance (L) for (a) parallel and (b) transverse directions with respect to the compression direction. Observed AFM images are binarized to black and white ones, and lines were drawn between the Cn-phase domains along the pixel lines. The L corresponds to the average length of the lines between domains.

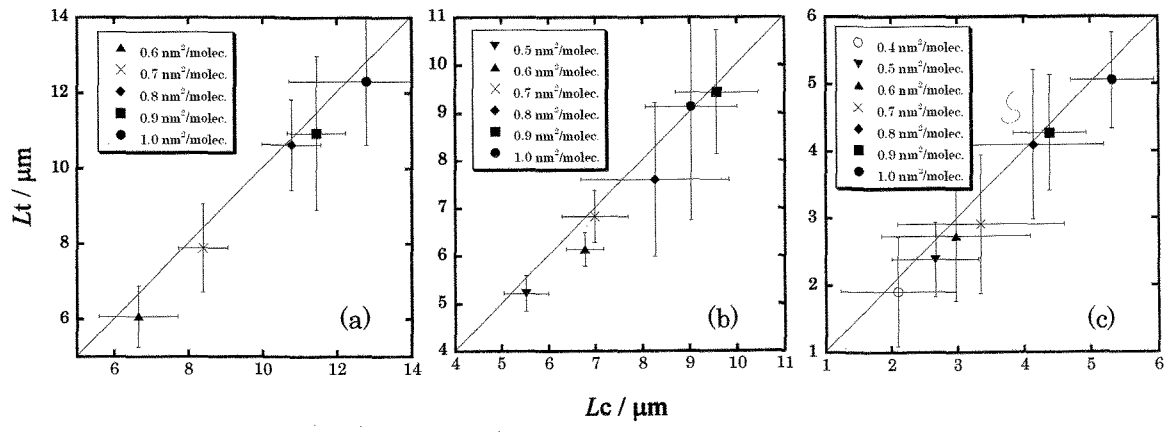

Fig.3 Domain distances along the compression direction (Lc) and the transverse direction (Lt) for phase-separated monolayers of (a) C18/PFPE (2/8), (b) C22/PFPE (2/8), and (c) C24/PFPE (2/8) at 20℃.

be avoided as long as the monolayer is compressed with two barriers and deposited at the center of the rectangular Langmuir trough.

4. CONCLUSIONS

We examined the effect of compression on the morphology of the micro-phase separated monolayers of Cn/PFPE (2/8) at 20℃. It was demonstrated experimentally that the effect is small in terms of Cn-phase domain distance and shape. The unchanged shape of the domains indicates that the condensed-phase domains behave as rigid bodies in the mixed monolayers due to the tight molecular packing in the domains and to the fluidic character of the expanded phase of PFPE. The isotropic arrangement of the condensed domains is realized as long as deposition is made at the center of Langmuir trough for monolayers symmetrically compressed with two barriers.

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