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Temperature-Dependent Change of Packing Structure of Condensed-Phase in a Micro-Phase Separated Langmuir Monolayer Studied by Grazing-Incidence X-ray Diffraction

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Abstract. Packing structure of condensed-phase in a binary mixed Langmuir monolayer of behenic acid (C22) and perfluoro-2,5,8-trimethyl-3,6,9-trioxadodecanoic acid (PFPE) on a cadmium acetate aqueous solution was studied by grazing incidence X-ray diffraction (GIXD) as a function of the subphase temperature. The measurements were made during temperature scan at a fixed molecular area to explain the morphological change of the condensed-phase domains due to a thermal treatment reported previously [1]. Analysis of GIXD data implies that the condensed-phase domains are composed of only the C22 molecules perpendicularly oriented and very closely packed in a centered rectangular unit cell with orthorhombic distortion at low temperatures. As the temperature increases the area occupied by molecule increases, and above 25 °C the lattice becomes disordered, which would allow morphological transformation of the condensed-phase domains. The process of packing structure change is almost reversible except for non-equilibrium phases observed for the monolayer spread at a low temperature, 5.5 °C.

1. Introduction
A continuous interest has been attracted to micro-phase separation in mixed Langmuir monolayers at the air/water interface for fundamental and applied sciences. In the monolayers, various morphological patterns are formed depending not only on film molecules but also on experimental parameters. Although a phenomenological understanding on the phase separation and resultant structures has progressed owing to advanced observation techniques such as Brewster angle microscopy for the air/water interface and atomic force microscopy for the solid surface, there are still many unknowns in the mechanisms for morphology formation at the molecular level, which would be because of a lack of quantitative information on molecular arrangement/packing in the phase-separated ultrathin films.

In our previous works [1-3], systematic investigations were performed for micro-phase separation in binary mixed Langmuir monolayers of cadmium salts of Cn (CH3(CH2)n-2COOH, n=18, 20, 22, 24) and PFPE. According to average molecular area-mixing ratio plots for the monolayers at the air/water interface and AFM observation for the monolayers deposited on a silicon wafer substrate, Cn and PFPE completely phase-separate into condensed-phase micro-domains of Cn and a surrounding matrix of PFPE in the mixed monolayers. Morphology of the condensed-phase domains changed depending on the surface temperature and on the alkyl chain length of Cn. AFM image analysis indicated that the
morphology is classified into three regimes: branched, long and narrow domains are dominantly formed as longer Cns are spread at lower temperatures (Regime I), circular-shaped domains are formed when shorter alkyl-chain Cns are spread at higher temperatures (Regime III), and irregular-shaped domains are formed at intermediate conditions (Regime II). The domain morphology formed in the regime I is thermodynamically non-equilibrium, because the branched narrow domains formed at 5°C changed to the circular one after a thermal treatment (spreading at 5°C and heating up to 30°C, then cooling to 5°C).

In the present work, a grazing incidence X-ray diffraction (GIXD) measurement was applied to the phase-separated Langmuir monolayer of C22/PFPE (1:1) on the Cd²⁺ subphase in order to evaluate the packing structure change upon the heating and cooling between about 5°C and 30°C. Results obtained give a better understanding of principles and fundamental reasons for the morphology change at the molecular level during the thermal treatment.

2. Experimental

2.1. Materials and Monolayer Preparation
Behenic acid (C22) (> 99.9%) was obtained from Research Institute of Biological Materials Japan. A perfluoro polyether acid, perfluoro-2,5,8-trimethyl-3,6,9-trioxadodecanoic acid (PFPE) (> 97%) was purchased from PCR. Spectro-grade chloroform (Dojin Chemicals) was used as a solvent of spreading solution. All materials were used without further purification. C22 and PFPE were mixed in chloroform at 1:1 molar ratio to give a total concentration of 2.5 mM. 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). The monolayers were spread onto the subphase water at 5.5°C. After about 30 min from the spreading, the monolayer was compressed to 70 Å/molec., and the first GIXD measurement was started. Then, the subphase temperature was increased to about 30°C, and then decreased to about 5°C. During the thermal treatment, GIXD measurements were repeated.

2.2. GIXD Experiment
A synchrotron GIXD experiment for the monolayer was carried out using the liquid surface diffractometer on the undulator beamline BW1 in HASYLAB at DESY (Hamburg, Germany) [4]. The monochromatic X-ray beam with the wavelength of 1.30 Å, obtained by Bragg reflection from a beryllium crystal, was irradiated to the air-water interface under a total reflection condition. The diffracted X-ray was passed through a Soller collimator and detected by a position-sensitive detector (PSD). The scattering signal was scanned over a range of the in-plane scattering vector \( Q_{xy} \) from 1.74 to 1.38 Å⁻¹. The PSD covered a range of the out-of-plane scattering vector \( Q_z \) of 0 - 1.2 Å⁻¹. The in-plane and the out-of-plane peaks obtained were least-square fitted by the Lorentzian and the Gaussian function respectively.

3. Results and Discussion
Table 1 presents water surface temperatures and GIXD peak positions in the horizontal plane. The GIXD scans were continuously repeated during the thermal treatment, so that the subphase temperature changed within a few degrees during each scan. Consequently, lattice parameters obtained in this work would be different in details from ones at defined temperatures, but give information on overall structural change during the thermal treatment. Hereafter, the water temperature is represented by a middle temperature that corresponds to the average temperature during the scan.

Figure 1 shows, as examples, GIXD contour plots for the C22/PFPE monolayer spread and compressed at (a) 5.5 °C, and on heating at (b) 15.7 °C and (c) 30.3 °C. Since C22 forms the condensed-phase whereas PFPE is in the fluid state on the aqueous solution surface, the diffractions are expected to arise from ordered hydrocarbon chains of C22. Typical diffraction patterns are seen at 15.7 °C, at which two intense peaks appear at \( Q_{xy} = 1.68 \) Å⁻¹ and 1.51 Å⁻¹, attributed to the non-
degenerate (0,2) reflection and the degenerate (1,1) + (1,1) reflections, respectively, in the centered rectangular unit cell with distortion to the nearest-neighbor (NN) direction. The intensity profiles of the Bragg rods corresponding to these reflections are peaked at $Q_z = 0 \, \text{Å}^{-1}$, indicating an untilted orientation of the hydrocarbon chains on the water surface. At 5.5 °C, however, diffraction patterns are very complicated. We found at least four peaks at $(Q_{xy}, Q_z) = (1.680 \, \text{Å}^{-1}, 0 \, \text{Å}^{-1})$, $(1.624 \, \text{Å}^{-1}, 0.147 \, \text{Å}^{-1})$, $(1.519 \, \text{Å}^{-1}, 0 \, \text{Å}^{-1})$, and $(1.501 \, \text{Å}^{-1}, 0.243 \, \text{Å}^{-1})$. This feature of diffraction pattern, which is also observed for the pure C22 monolayer prepared at the same subphase condition (the data are not shown here), implies coexistence of some lattices of tilted and non-tilted chains in a quenched state.

Aggregation tendency of C22 molecules is considerably enhanced not only by cadmium salt formation but also by lowering temperature, and thus the molecular motion in the condensed-phase to arrange into the most stable lattice is highly restricted. Based on a series of diffraction patterns obtained during the thermal treatment shown in the next section (see Fig.3), two peaks at $Q_{xy} = 1.680 \, \text{Å}^{-1}$ and $1.519 \, \text{Å}^{-1}$, indicated by inverted triangles in Figure 2, come from a stable lattice and others are from non-equilibrium, quenched ones. At 30.3 °C, the highest mid-temperature in the present work, the condensed phase still possesses two diffraction peaks at $(Q_{xy}, Q_z) = (1.623 \, \text{Å}^{-1}, 0 \, \text{Å}^{-1})$ and $(1.506 \, \text{Å}^{-1}, 0 \, \text{Å}^{-1})$, suggesting the lattice is basically the centered rectangular packing of untilted molecules. However, one might notice that the former peak is much less intense relative to the latter. This means that the molecular alignment producing the former reflection is rather disordered.

Temperature-dependent development of X-ray diffraction profiles in the horizontal plane is shown in Figure 3. Upon heating, the two equilibrium peaks shift to lower $Q_{xy}$ values. Above about 25 °C, the peaks get broader and the degree of shift is accelerated for the (0,2) reflection. As the temperature decreases, on the other hand, a reversed change occurs and finally the peak positions almost return to the initial ones at 5.9 °C. It should be emphasized here that the two peaks observed at $Q_{xy} = 1.624 \, \text{Å}^{-1}$ and $1.501 \, \text{Å}^{-1}$ at the spreading temperature (5.5 °C) disappear after the thermal treatment at 5.9 °C, implying the non-equilibrium characteristics of the lattice(s) causing these peaks. The packing structure change during the thermal treatment can be better understood from Figure 4, in which the peak positions, lattice spacings for the centered rectangular unit cell, and the molecular area are plotted as a function of the mid-temperature. One can confirm that the structural change of the condensed-phase of C22 in the mixed monolayer is almost reversible. At lower temperatures, the C22 molecules are packed in the unit cell with dimensions of $a = ca. 5.0 \, \text{Å}$ and $b = ca. 7.5 \, \text{Å}$, and the molecular area estimated is below 19 Å²/molec., being in good agreement with the so-called herring-

Table 1. Subphase water temperatures at which GIXD measurements started (S Temp) and ended (E Temp), and their middle temperatures (M Temp), and in-plane diffraction peak positions.

| S Temp /°C | E Temp /°C | M Temp /°C | $Q_{xy}$ (n) / Å⁻¹ | $Q_{xy}$ (d) / Å⁻¹ |
|------------|------------|------------|-------------------|-------------------|
| 5.50       | 5.50       | 5.5        | 1.680             | 1.519             |
| 8.50       | 13.65      | 11.1       | 1.682             | 1.512             |
| 14.03      | 17.39      | 15.7       | 1.681             | 1.507             |
| 18.61      | 21.96      | 20.3       | 1.670             | 1.506             |
| 23.48      | 26.32      | 24.9       | 1.667             | 1.505             |
| 27.18      | 29.60      | 28.4       | 1.637             | 1.505             |
| 30.18      | 30.36      | 30.3       | 1.623             | 1.506             |
| 28.04      | 24.53      | 26.3       | 1.639             | 1.504             |
| 21.10      | 15.06      | 18.1       | 1.655             | 1.505             |
| 12.98      | 8.97       | 11.0       | 1.672             | 1.515             |
| 6.17       | 5.69       | 5.9        | 1.673             | 1.515             |
Figure 1. Contours of equal intensity vs the in-plane and out-of-plane scattering vector components for the phase-separated monolayer of C22/PFPE (1:1) on a cadmium acetate aqueous solution; (a) 5.5 °C at which the monolayer was spread and compressed, (b) 15.7 °C and (c) 30.3 °C during the thermal treatment.

Figure 2. A X-ray diffraction profile in the horizontal plane integrated over Qz for the monolayer at 5.5 °C.

bone packing of hydrocarbon chains with the smallest molecular area [5]. This finding indicates that C22 forms its pure condensed-phase without incorporation of PFPE, which supports our previous conclusion that C22 and PFPE are completely phase-separated in their mixed monolayer [1]. At higher temperatures above 25 °C, one can again recognize the larger decrease of peak position for the (0, 2) reflection, which causes the larger separation between the lattice spacings and the slightly rapid increase of the molecular area. The temperature-dependent behavior of packing structures observed in this work is consistent with that reported for henicosanoic acid monolayers [6].

As conclusion, the GIXD experiments reveal the temperature-dependent change of packing structure of condensed-phase in the C22/PFPE (1:1) monolayer on the cadmium acetate aqueous solution. The NN-distorted centered rectangular unit cell of well aligned, very closely packed hydrocarbon chains at low temperatures changed to the relatively loosely packed, less ordered lattice above 25 °C. The morphology change for the C22 domains could be interpreted in terms of different rigidity of the lattices. In the low-temperature lattice, mobility of the C22 molecules should be highly restricted due to the strong intermolecular interaction leading to the almost closest packing. Therefore, the morphology of branched narrow lines of the condensed-phase domains cannot transform spontaneously to the circular shape to minimize the line energy along the domain circumference. However, in the high-temperature lattice, the C22 molecules should be rather mobile so that the non-circular domains can change its shape to circular one. Then, the once formed stable shape is maintained even when the temperature decreases to 5 °C, as observed in Ref.[1].
Figure 3. In-plane GIXD diffraction profiles for the C22/PFPE (1:1) monolayer at different mid-temperatures during the thermal treatment.

Figure 4. In-plane peak positions ($Q_{xy}$), lattice spacings of the centered rectangular unit cell ($a$, $b$), and area per molecule (A) as a function of the mid-temperature; ● on heating, × on cooling.

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