

Phase Separation in Hybrid Langmuir–Blodgett Films of Perfluorinated and Hydrogenated Amphiphiles. Examination by Atomic Force Microscopy

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Received February 25, 1999. In Final Form: August 17, 1999

Atomic force microscopic (AFM) observations were carried out for monolayer Langmuir–Blodgett (LB) films of two-component hybrids consisting of eicosanoic acid ($C_{19}H_{39}COOH$), perfluorooctadecanoic acid ($C_{17}F_{35}COOH$), perfluorotetradecanoic acid ($C_{13}F_{27}COOH$), and [2-(perfluorodecyl)-ethyl]dimorpholinophosphate ($C_{10}F_{21}C_2H_4OP(O)[N(C_2H_4)_2O]_2$, F10C2DMP). There were two domains with the height difference of 4 Å on AFM photographs of the hybrid LB films of $C_{17}F_{35}COOH/C_{19}H_{39}COOH$, indicating phase separation. This phase separation was also observed for $C_{13}F_{27}COOH/C_{19}H_{39}COOH$ and $C_{13}F_{27}COOH/C_{17}F_{35}COOH$ hybrids. At low surface pressures, the isolated domains, which were $C_{19}H_{39}COOH$ rich and $C_{17}F_{35}COOH$ rich, respectively, were segregated by the continuous $C_{13}F_{27}COOH$ -rich region. $C_{13}F_{27}COOH$ molecules were piled up on the monolayers at high surface pressures. $C_{13}F_{27}COOH$ was miscible with F10C2DMP, and the hybrid film displayed a fractal texture. The surface pressure–area isotherms of Langmuir films were discussed in relation to the phase separation and miscibility.

Introduction

The C–F bond has a high bond energy owing to the ionic bond as well as the covalent bond, since fluorine atoms exhibit the greatest electric negativity. Therefore, fluorocarbon derivatives have characteristic properties of being heat proof, immune to most chemicals, and nontoxic. Moreover, since the van der Waals attraction of the fluorocarbon chain is very weak, perfluorinated amphiphiles possess strong air/water surface activity^{1–3} and, therefore, display strong moistening or penetrating characteristics. On the other hand, the weak attraction of fluorocarbons causes the lipophobicity of perfluorinated amphiphiles besides their hydrophobicity. This results in low oil/water interface activity. To supply this rather unfavorable characteristic, inter- or intramolecular hybrid amphiphiles consisting of perfluorinated and hydrogenated alkyl chains are constructed and investigated with a view to industrial and medical applications.⁴ The formation of supramolecular assemblies by such hybrids has been investigated in solutions^{1,5–13} and for ultrathin films or two-dimensionally-organized systems.^{14,15}

Generally, two scenarios are possible when mixing two kinds of amphiphiles. The first is that an amphiphile is mixed in the assembly constructed by another amphiphile. The second is that two amphiphiles form the isolated phases or assemblies. Mori and Imae¹⁶ have reported the miscibility of eicosanoic acid ($C_{19}H_{39}COOH$) and octadecyldimethylamine oxide in the two-dimensionally-organized Langmuir–Blodgett (LB) films, while $C_{19}H_{39}COOH$ and azodye amphiphile were phase separated in the LB film.¹⁷ On the other hand, Mayer et al.¹⁴ have investigated the miscibility of perfluorinated amphiphile and hydrogenated fatty acids in the LB films. The isolated regions of $C_{19}H_{39}COOH$ were segregated by a continuous region of perfluorinated amphiphiles. Moreover, the texture of isolated regions varied with changing hydrocarbon chain lengths of hydrogenated fatty acids.

In this work, for perfluorinated fatty acids mixed with $C_{19}H_{39}COOH$, Langmuir (L) films on water subphase and LB films on mica substrate were investigated by surface pressure–surface area (π – A) isotherm examination and atomic force microscopy. The miscibility of perfluorinated and hydrogenated amphiphiles with the same hydrophilic headgroup and the dependence on the alkyl chain length of perfluorinated fatty acid were discussed in relation to the characteristic properties of fluorocarbon chains. The results were compared with those of mixtures of two perfluorinated amphiphiles with different hydrophilic groups.

Experimental Section

Perfluorooctadecanoic acid ($C_{17}F_{35}COOH$) and perfluorotetradecanoic acid ($C_{13}F_{27}COOH$) were purchased from Fluorochem Ltd. $C_{19}H_{39}COOH$ was a product from Wako Pure Chemical Ind.,

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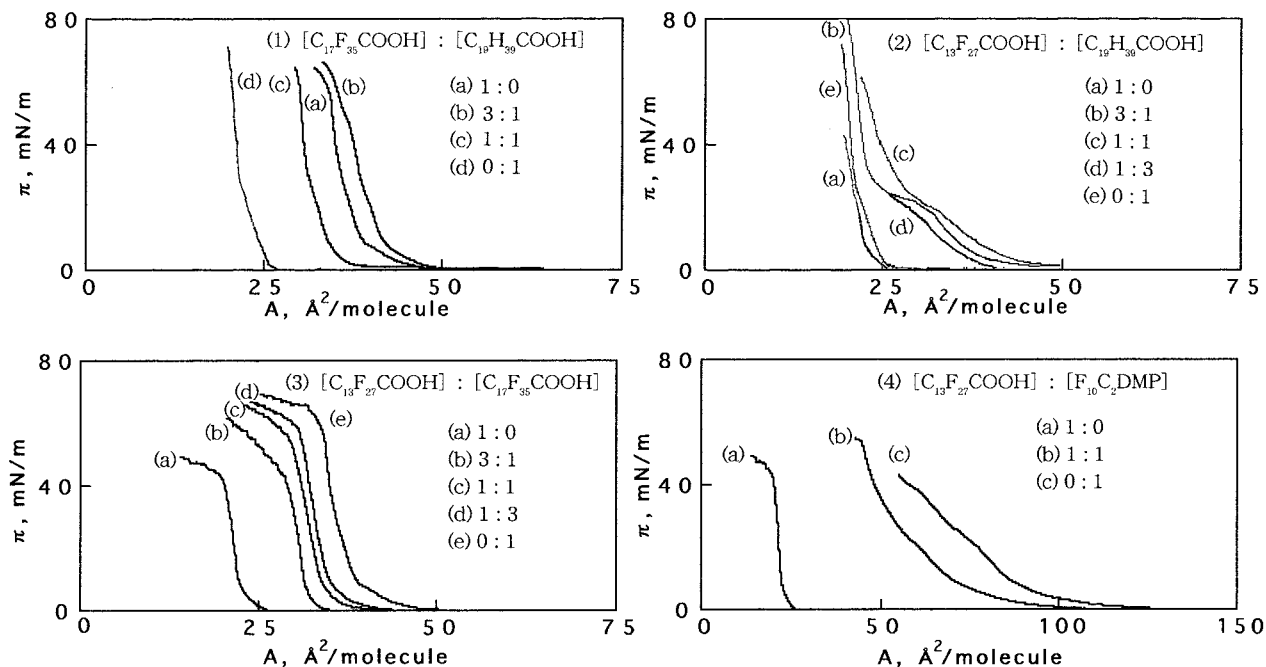


Figure 1. π - A isotherm curves for L films of perfluorinated and hydrogenated amphiphiles and their hybrids.

Ltd. [2-(Perfluorodecyl)ethyl]dimorpholinophosphate ($C_{10}F_{21}C_2H_4$ -OP(O)[N(C_2H_4) $_2$ O] $_2$, F10C2DMP) was donated by Dr. M.-P. Krafft. Organic solvents and the aqueous HCl solution were commercial products. Water was redistilled from alkaline $KMnO_4$.

Surface pressure measurements and LB film preparation were carried out on a LB film deposition apparatus (Nippon Laser & Electronics Lab.). Amphiphiles and their hybrids were dissolved in chloroform at a concentration of 1.4 mg/cm 3 , except that $C_{17}F_{35}$ -COOH was dissolved in hexane/ethanol (9/1 v/v). A small quantity (10–30 mm 3) of the solution was spread on a water subphase at 25 °C. An acidic, aqueous subphase at pH 1–1.5 was used for preparing $C_{13}F_{27}$ COOH L film. After allowing 10–30 min for the solvent to evaporate, the surface area in a 5 × 35 cm 2 trough was compressed at a constant rate of 10 mm/min. The L films at various surface pressures were transferred onto freshly cleaved mica substrates by the upstroke mode of the vertical dipping method. The monolayer LB films prepared were dried in vacuo for more than 8 h.

Atomic force microscopy (AFM) observations were performed at room temperature by an AFM Nanoscope III (Digital Instruments, Inc.) in air. A crystalline silicon tip on a cantilever was used. The vertical distance and surface roughness of LB films were measured by section analysis.

Results

$C_{17}F_{35}COOH$ and the Hybrids with $C_{19}H_{39}COOH$.

Figure 1(1) shows π - A isotherm curves for L films of $C_{17}F_{35}COOH$, $C_{19}H_{39}COOH$, and their hybrids. For all systems, the solid film was formed through the expanded and condensed liquid states as the surface area was compressed. The collapse pressure π_{col} and the transition pressure π_{l-s} from liquid film to solid film are listed in Table 1. Both values were obtained at 47–70 and 27–40 mN/m. Table 1 includes values of the occupied area A_{iso} per molecule obtained from the π - A curve. The occupied area per molecule was maximum at the mixing ratio of $[C_{17}F_{35}COOH]:[C_{19}H_{39}COOH] = 3:1$.

An AFM photograph of monolayer LB film of $C_{17}F_{35}COOH$ prepared at 20 mN/m is shown in Figure 2. Many nearly circular islands were formed even at 1 mN/m. They were coalesced at 40 mN/m, which was the liquid–solid transition pressure. The height difference, 15–18 Å, between the isolated islands and the continuous region segregating them was obtained from the sectional analysis. The surface of islands exhibited the 6–8 Å roughness.

Table 1. Characteristics of π - A Isotherm Curves of Perfluorinated and Hydrogenated Amphiphiles and Their Hybrids

	π_{col} , mN/m	π_{l-s} , mN/m	A_{iso} , Å 2 /molecule
(1) $[C_{17}F_{35}COOH]:[C_{19}H_{39}COOH]$			
1:0	56	40	37
3:1	47	29	42
1:1	59	36	32
0:1	70	27	20
(2) $[C_{13}F_{27}COOH]:[C_{19}H_{39}COOH]$			
1:0	44	11	22
3:1	82	~25 ^a	24
1:1	61	~30 ^a	29
1:3	62	~22 ^a	25
(3) $[C_{13}F_{27}COOH]:[C_{17}F_{35}COOH]$			
3:1	42	12	32
1:1	53	15	34
1:3	57	21	35
(4) $[C_{13}F_{27}COOH]:[F10C2DMP]$			
1:1	54		55
0:1	44		84

^a The inflection pressure.

The AFM texture of $C_{19}H_{39}COOH$ LB films¹⁶ was different from that of $C_{17}F_{35}COOH$. A smooth surface was uniformly formed over the whole region on monolayer LB film of $C_{19}H_{39}COOH$ already at 20 mN/m, which was slightly lower than the liquid–solid transition pressure. There were some holes on the surface with depths comparable to their molecular lengths (28 Å).

Similar surfaces with holes (<18 Å depth) were also observed on the LB films of $C_{17}F_{35}COOH/C_{19}H_{39}COOH$ (3:1 and 1:1) hybrids at 25 mN/m, as shown in Figure 2. However, for the hybrids, the smoother and higher regions were separated from the rougher and lower regions, although the height difference between the two regions was only less than 4 Å.

Figure 3 shows AFM photographs, on a smaller scale, of the LB film of $C_{19}H_{39}COOH$ and of the smoother and higher region in the LB film of $C_{17}F_{35}COOH/C_{19}H_{39}COOH$ (1:1) hybrid at 25 mN/m. Surfactant molecules displayed a rough ordering in the smoother and higher region of the hybrid LB film, in contrast to the ordered arrangement in the $C_{19}H_{39}COOH$ LB film. The ordering was not

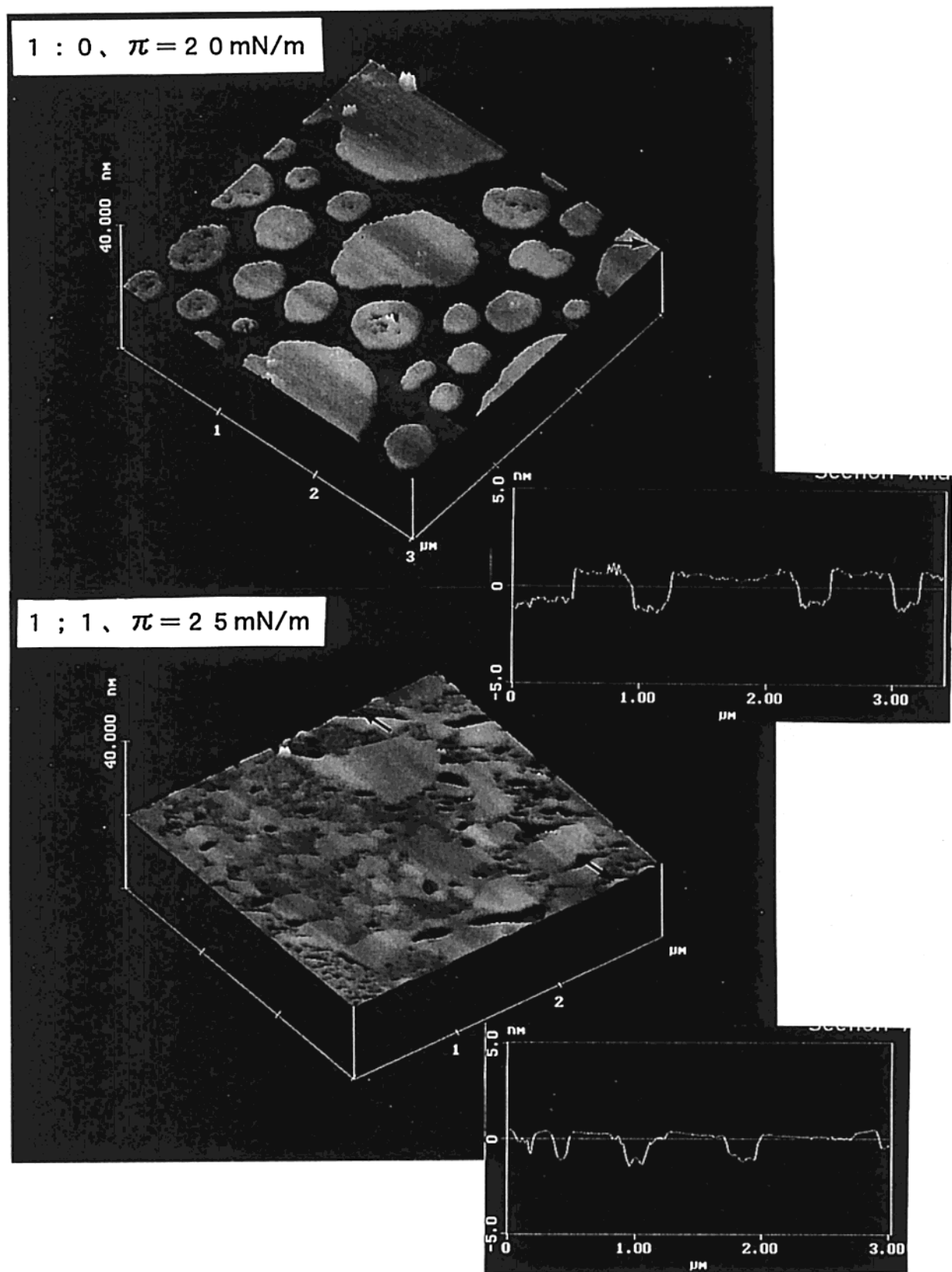


Figure 2. AFM photographs of monolayer LB films of $C_{17}F_{35}COOH$ and the hybrid (1:1) with $C_{19}H_{39}COOH$. The surface pressure is 20 mN/m for $C_{17}F_{35}COOH$ and 25 mN/m for the hybrid. The inserts are the sectional analyses between arrows.

observed for the rougher and lower region in the LB film of the $C_{17}F_{35}COOH/C_{19}H_{39}COOH$ (1:1) hybrid.

$C_{13}F_{27}COOH$ and the Hybrids with $C_{19}H_{39}COOH$. As seen in the π - A curves of Figure 1(2) and the numerical values of Table 1, the occupied area of the $C_{13}F_{27}COOH$ L film was $22 \text{ \AA}^2/\text{molecule}$, which was smaller than the

value for $C_{17}F_{35}COOH$, an analogue with a longer alkyl chain. The π - A curves for $C_{13}F_{27}COOH/C_{19}H_{39}COOH$ hybrids at the mixing ratios of 3:1, 1:1, and 1:3 were expanded in comparison with those for homogeneous $C_{13}F_{27}COOH$ or $C_{19}H_{39}COOH$ and were inflected at 22–30 mN/m. The collapse pressures (>60 mN/m) for hybrid

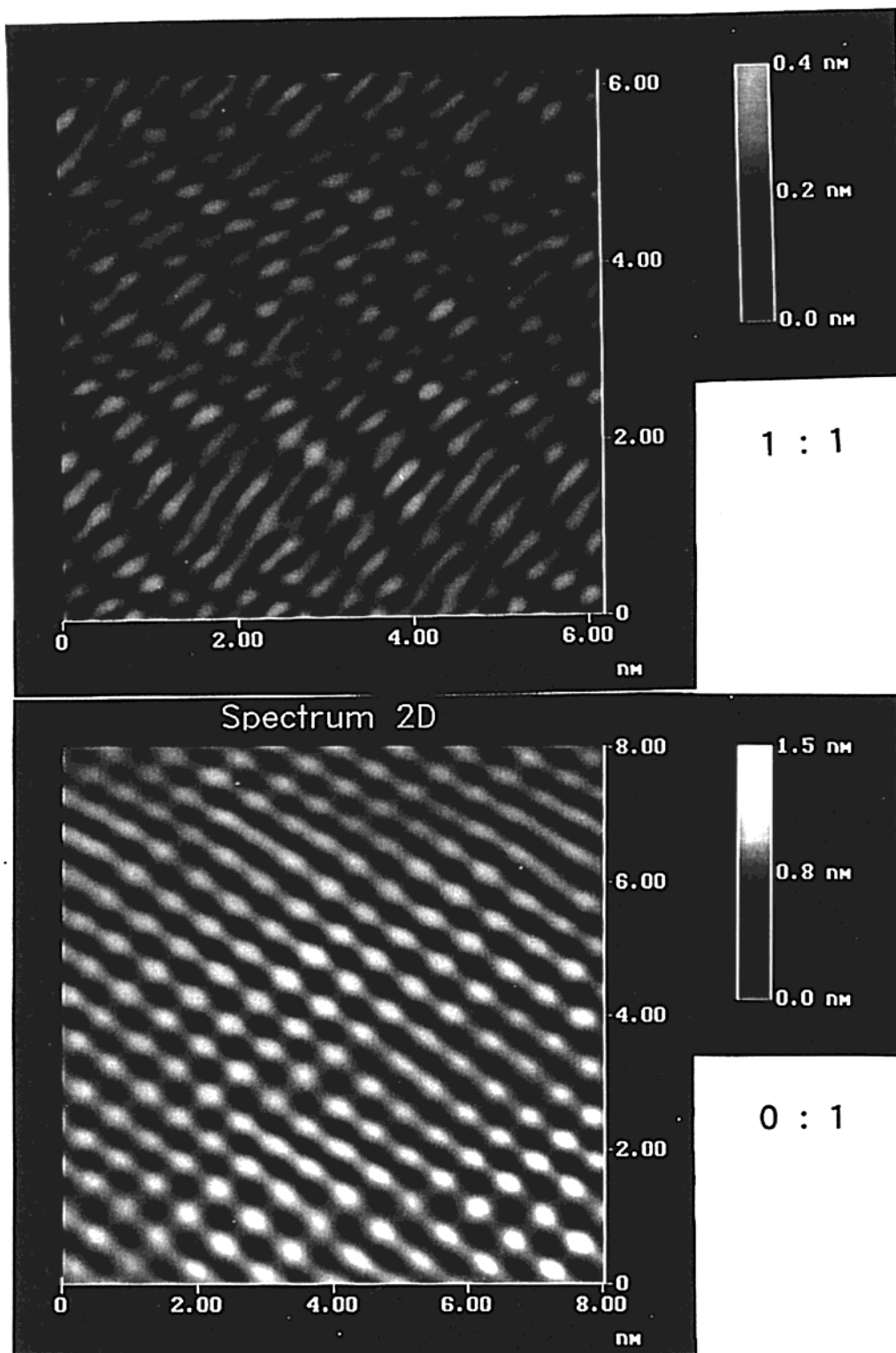


Figure 3. AFM photographs, in the smaller scale, of monolayer LB film of $C_{19}H_{39}COOH$ (lower) and of the smoother and higher region in the LB film of $C_{17}F_{35}COOH/C_{19}H_{39}COOH$ (1:1) hybrid (upper) at 25 mN/m.

L films were higher than those of homogeneous $C_{13}F_{27}COOH$ L film but equivalent to those of homogeneous $C_{19}H_{39}COOH$ L film. However, the occupied areas (24–29 $\text{\AA}^2/\text{molecule}$) for hybrid L films were rather close to those of homogeneous $C_{13}F_{27}COOH$ L film.

Figure 4 shows AFM photographs of monolayer LB films of $C_{13}F_{27}COOH$ and $C_{13}F_{27}COOH/C_{19}H_{39}COOH$ hybrids prepared at 10 mN/m. The $C_{13}F_{27}COOH$ LB film consisted of a surface with a roughness of less than 40 \AA . The surface roughness increased at 20 mN/m. For a hybrid film at a

mixing ratio of 3:1, some islands with smoother surfaces coexisted with rough continuous regions at a surface pressure of 10 mN/m, which is below the inflection pressure. The smoother regions widened with increasing amounts of $C_{19}H_{39}COOH$, although the roughness of the continuous region was unchanged. For 3:1 and 1:1 hybrids at $\pi = 20$ mN/m, the smoother regions were no longer observed and a uniformly rough surface was observed as well as for homogeneous $C_{13}F_{27}COOH$ LB film. However, in the AFM photographs for the 1:3 hybrid, even at $\pi =$

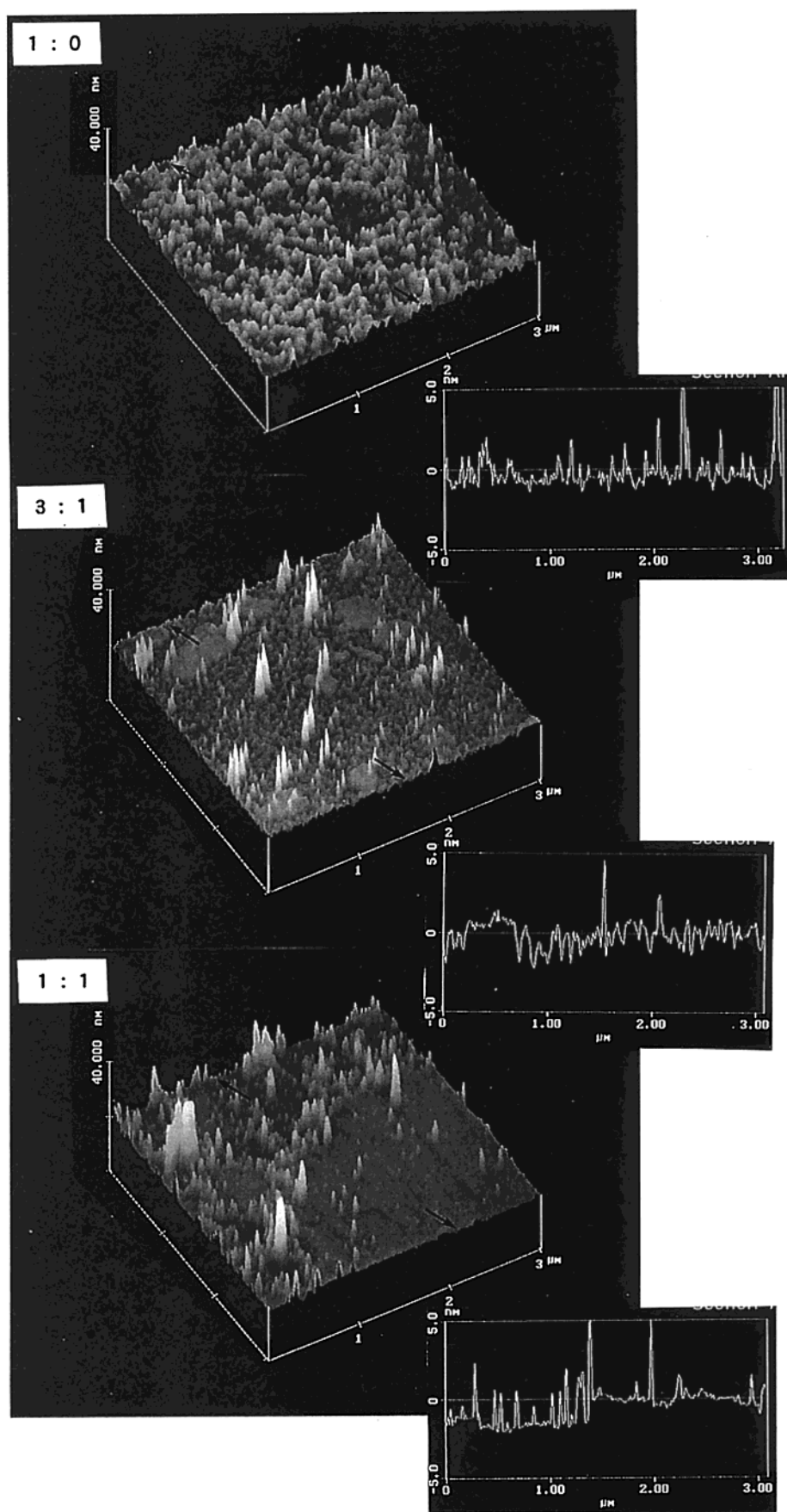


Figure 4. AFM photographs of monolayer LB films of $C_{13}F_{27}COOH$ and the hybrids (3:1 and 1:1) with $C_{19}H_{39}COOH$. The surface pressure is 10 mN/m. The inserts are the sectional analyses between arrows.

20 mN/m, the smoother regions were still distinguishable from the rough continuous region.

Hybrids of $C_{13}F_{27}COOH$ and $C_{17}F_{35}COOH$. The π - A isotherms of $C_{13}F_{27}COOH/C_{17}F_{35}COOH$ hybrids are given

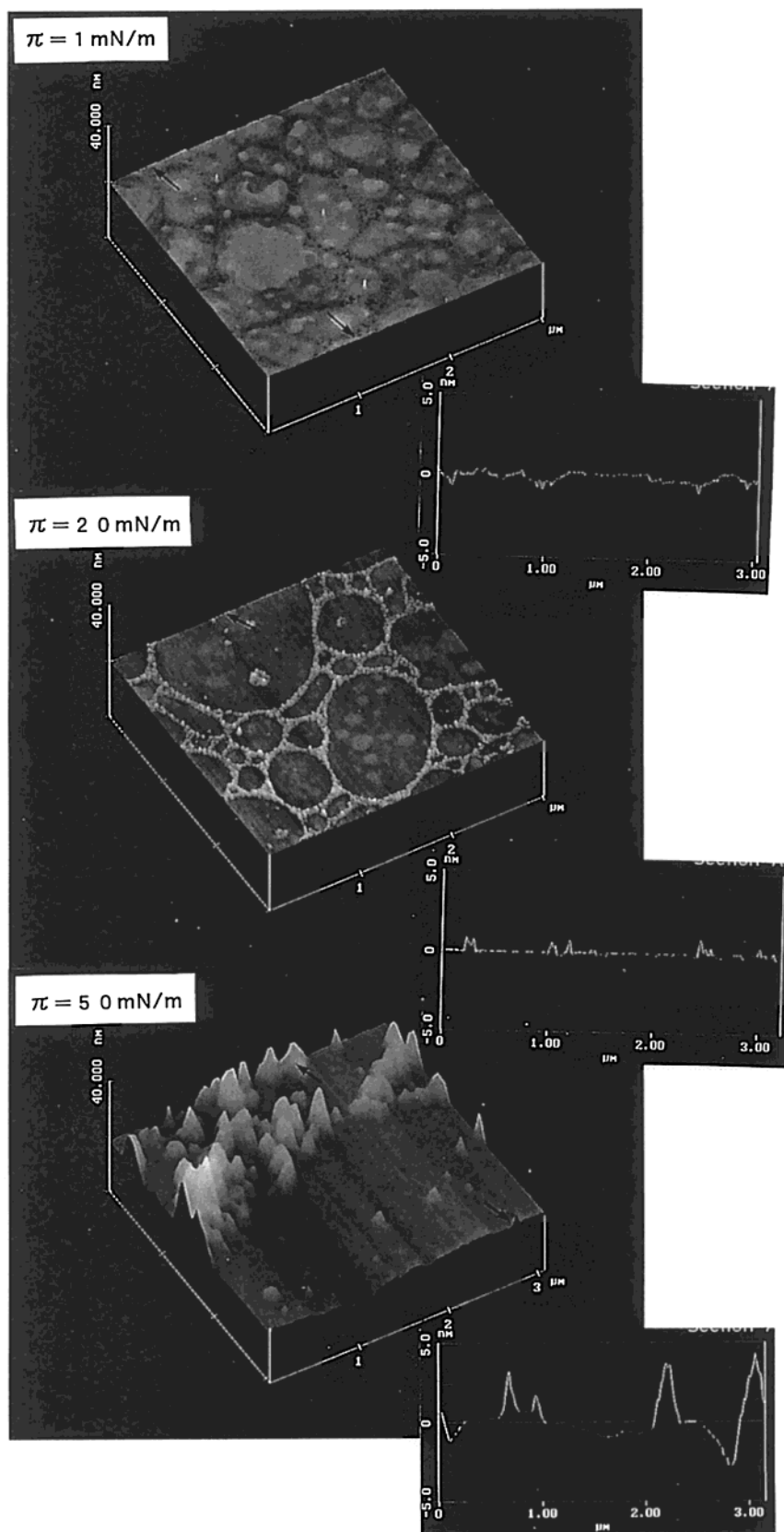


Figure 5. AFM photographs of monolayer LB films of the hybrid (1:1) of $C_{13}F_{27}COOH$ and $C_{17}F_{35}COOH$. The surface pressures are 1, 20, and 50 mN/m. The inserts are the sectional analyses between arrows.

in Figure 1(3). The hybrid L films varied from a liquid to solid state at low surface pressure. This is different from homogeneous $C_{17}F_{35}COOH$ film with expanded and condensed liquid states but similar to homogeneous $C_{13}F_{27}COOH$ film. The isotherms changed in proportion to the

mixing ratio variation of 1:0 to 0:1. As seen in Table 1, the occupied areas per molecule were close to those of homogeneous $C_{17}F_{35}COOH$, while the liquid–solid transition pressures were near to those of homogeneous $C_{13}F_{27}COOH$.

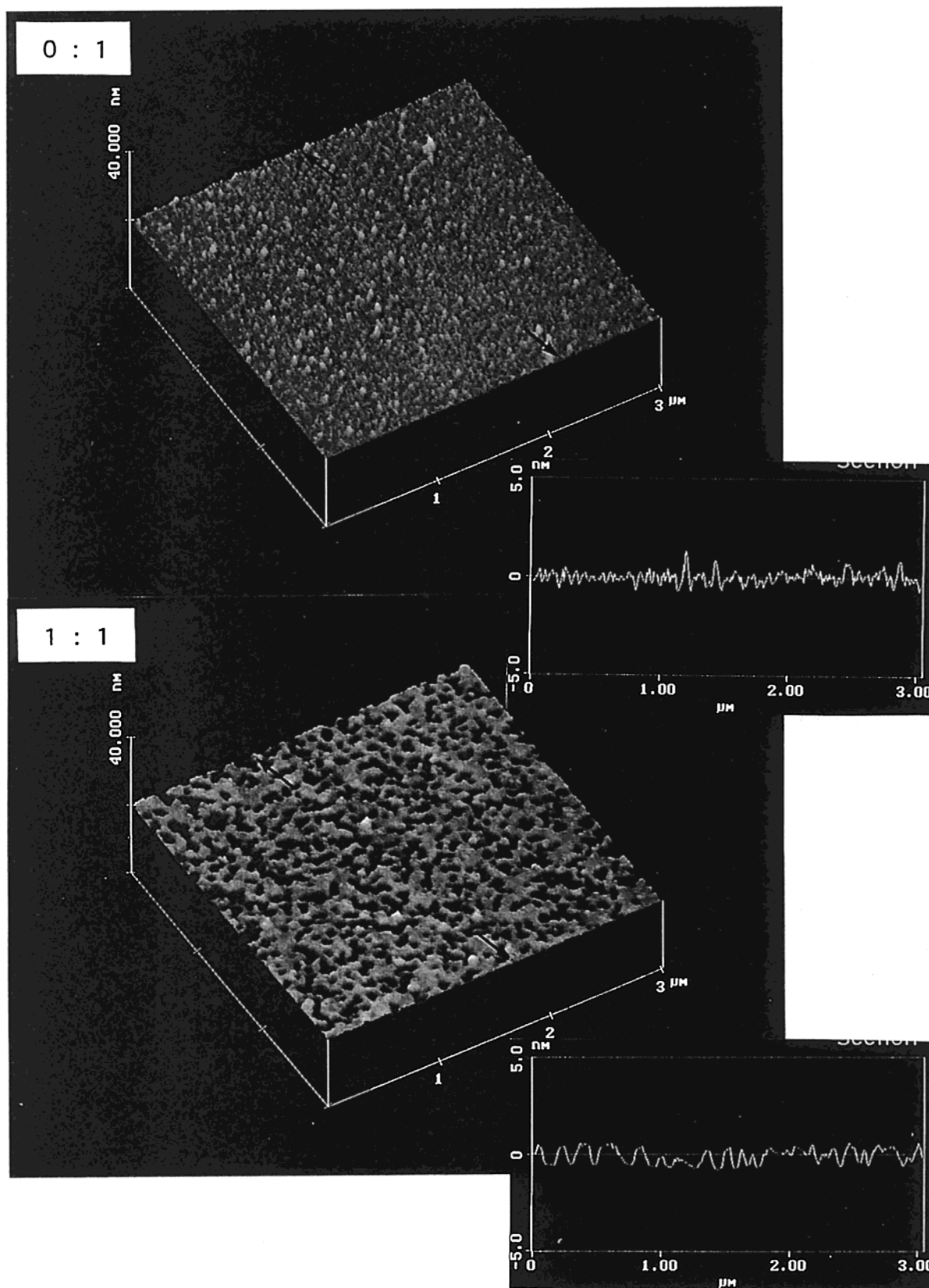


Figure 6. AFM photographs of monolayer LB films of F10C2DMP and the hybrid (1:1) with $C_{13}F_{27}COOH$. The surface pressure is 20 mN/m. The inserts are the sectional analyses between arrows.

Figure 5 shows AFM photographs of LB films of 1:1 hybrids prepared at different surface pressures. At 1 mN/m, molecules formed isolated regions consisting of hills and terraces. The surface of the hills was smoother than that of terraces, although their height differences from

the deepest position were only 11 and 6 Å at maximum, respectively. On the other hand, the roughness of the continuous region segregating the isolated regions was less than 5 Å. At 20 mN/m in the solid state, the isolated regions, which were islands at 1 mN/m, were lower than

the continuous region segregating them. The height from the isolated regions to the embankment was less than 11 Å. Within the isolated regions, there were smaller circular hills with the height difference of 2–3 Å. At 50 mN/m close to the collapse pressure, a continuous surface with bumps less than 40 Å in height was observed. The surface profile, where the isolated regions were segregated by continuous embankment, was also observed for the 3:1 and 1:3 hybrids at 20 mN/m.

C10C2DMP and the Hybrid with C₁₃F₂₇COOH. Figure 1(4) shows the π - A curves of F10C2DMP and the hybrid with C₁₃F₂₇COOH. The π - A curve of homogeneous F10C2DMP did not display the distinct liquid–solid transition in contrast to that of homogeneous C_{*n*}H_{2*n*+1}-COOH or C_{*n*}F_{2*n*+1}COOH. The apparent occupied area of 84 Å²/molecule was larger than that of homogeneous C_{*n*}H_{2*n*+1}COOH or C_{*n*}F_{2*n*+1}COOH. The π - A curve of the C₁₃F₂₇COOH/F10C2DMP (1:1) hybrid was the intermediate curve of homogeneous amphiphiles, as elucidated from the medium occupied area (55 Å²/molecule), although the collapse pressure was slightly higher than those of homogeneous C₁₃F₂₇COOH and F10C2DMP. The numerical values of the occupied area and the collapse pressure are listed in Table 1.}}}}

The AFM photographs of monolayer LB films of F10C2DMP and the C₁₃F₂₇COOH/F10C2DMP (1:1) hybrid prepared at 20 mN/m are shown in Figure 6. The surface of the F10C2DMP LB film was a collection of bumps with height differences of 11 Å on average. On the other hand, the surface of the C₁₃F₂₇COOH/F10C2DMP (1:1) hybrid film consisted of a fractal texture which was drawn by the smooth region with a height less than 14 Å.

Discussion

Molecular Arrangement in Langmuir–Blodgett Films of Homogeneous Amphiphiles. The molecular arrangement in L film on an air/water surface can be estimated on the basis of the molecular structure, the π - A isotherm, and the AFM observation of LB films. It is known that C₁₉H₃₉COOH, a hydrogenated fatty acid with a long alkyl chain, forms L film in a solid state.¹⁶ C₁₉H₃₉COOH molecules are oriented with their molecular axes perpendicular to the water subphase. Perfluorinated alkyl chains are more rigid and thicker than hydrogenated alkyl chains owing to the larger fluorine atom. Therefore, perfluorinated fatty acids may construct L films with a larger occupied area per molecule than hydrogenated fatty acids do. As expected, the occupied area (37 Å²/molecule) per molecule in the solid L film of C₁₇F₃₅COOH is larger than that (20 Å²/molecule) of C₁₉H₃₉COOH, although that (22 Å²/molecule) of C₁₃F₂₇COOH is smaller than that of C₁₇F₃₅COOH. Different occupied areas were also obtained for other perfluorinated amphiphiles. Barton et al.¹⁸ have reported π - A curves for C₁₀F₂₁CH₂COOH and C₈F₁₇(CH₂)₄-COOH with occupied areas of 28 and 38 Å²/molecule, respectively. On the other hand, the occupied area of C₁₀F₂₁(CH₂)₂OCOCH₂CH(NH₃⁺)COO⁻ reported by Jacquemain et al.¹⁹ was 28.5 Å²/molecule.

The alkyl chain length dependence on the π - A isotherms of perfluorinated fatty acids (C_{*n*}F_{2*n*+1}COOH) is different from that of hydrogenated fatty acids (C_{*n*}H_{2*n*+1}-COOH). C₁₉H₃₉COOH molecules display the π - A curve characteristic of the solid state, while the C₁₃H₂₇COOH}}

film is in the expanded liquid state.²⁰ This is in contrast with perfluorinated analogues. On the other hand, the collapse pressure (70 mN/m) of C₁₉H₃₉COOH film is higher than that of C₁₃H₂₇COOH film. This tendency is the same as that of perfluorinated fatty acids: The collapse pressure (56 mN/m) of C₁₇F₃₅COOH film is higher than that (44 mN/m) of C₁₃F₂₇COOH. It is suggested that hydrogenated fatty acids with longer alkyl chains construct more compactly packed monolayer L films. However, this does not seem to be the case for perfluorinated fatty acids.

When results from the π - A isotherms are compared with those from the AFM observation, the difference between behaviors of hydrogenated and perfluorinated fatty acids and their alkyl chain length dependence can be further elucidated. It has been confirmed on the basis of AFM photographs that C₁₉H₃₉COOH molecules construct a monolayer film in a solid state with a two-dimensionally/organized array, although the molecular ordering of C₁₉H₃₉COOH is slightly disarranged in the presence of C₁₇F₃₅COOH, as seen in Figure 3.

As seen in AFM photographs, C₁₇F₃₅COOH also forms LB film with smoother surfaces at high surface pressures. C₁₇F₃₅COOH molecules form monolayer islands at low surface pressures. The height difference (15–18 Å) between islands and the continuous region is shorter than the molecular length (25 Å) of C₁₇F₃₅COOH, indicating the existence of tilted molecules in the continuous region. Then the tilt angles of molecular axes are 65–75° from the normal direction.

In contrast with C₁₇F₃₅COOH, the surface of C₁₃F₂₇COOH LB film is rather rough. This roughness results from the formation of bumps where C₁₃F₂₇COOH molecules are piled up on the monolayer, since the height of bumps is at most 40 Å, which is equal to twice the molecular length (19 Å). Since perfluoroalkyl chains have not only hydrophobic but also lipophobic characteristics, C₁₃F₂₇COOH molecules tend to form bumps as well as monolayers. Such bump formation is promoted with increasing surface pressure. It should be noted that the apparent occupied area per C₁₃F₂₇COOH molecule is smaller than that of C₁₇F₃₅COOH, because of the piling-up behavior of C₁₃F₂₇COOH. C₁₇F₃₅COOH molecules tend favor the monolayer arrangement rather than piling up, due to the stronger hydrophobic interaction between longer alkyl chains. If C₁₃F₂₇COOH molecules have an occupied area of 37 Å²/molecule as well as C₁₇F₃₅COOH, it can be estimated from the apparent occupied area of the 25 Å²/molecule that about 30% of C₁₃F₂₇COOH molecules form bumps. It can be concluded that the molecular arrangement in Langmuir–Blodgett films of homogeneous perfluorinated surfactants is determined by the competition of hydrophobic interactions between perfluorinated chains and the lipophobic character of perfluorinated chains. This originates from the characteristic property of fluorocarbon chains.

It may be insisted that the smaller occupied area of C₁₃F₂₇COOH molecules does not occur by reason of dissolution or collapse. The surface area is not decreased with time, when the surface pressure is kept constant, and the π - A isotherm is not changed by changing compression speed. The gradual or nothing change of surface pressure, characteristic of collapse, after steep increase happens above 44 mN/m with decreasing molecular area, and the reproducibility of the π - A curve is high. Those facts do not support the dissolution or collapse.

Phase-Separation in Langmuir–Blodgett Films of Amphiphile Hybrids. On the hybrid LB films of C₁₇F₃₅-

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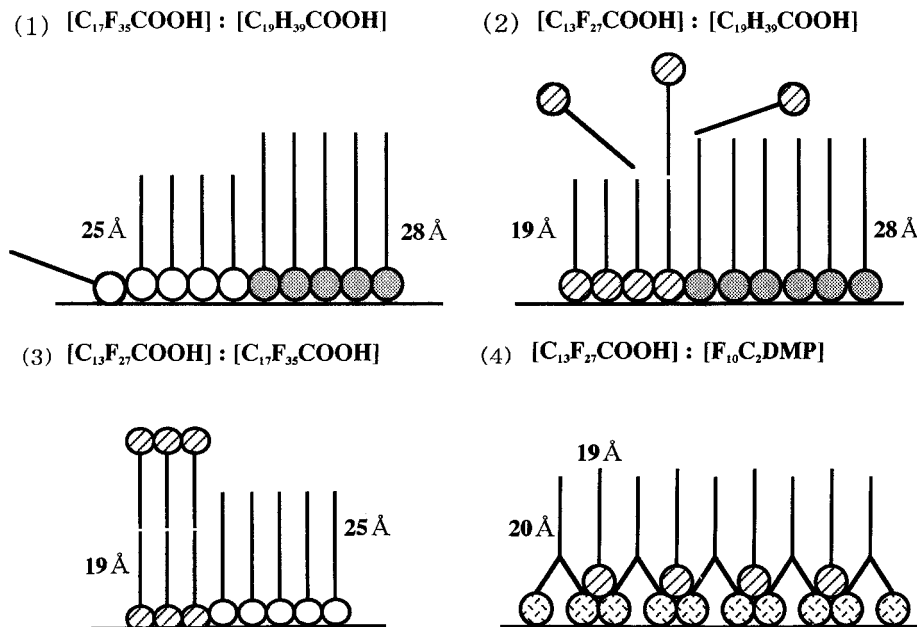


Figure 7. Schematic presentation of molecular arrangements in L and LB films ($\pi = 10\text{--}25$ mN/m) of the equimolar hybrids of perfluorinated and hydrogenated amphiphiles.

COOH with $C_{19}H_{39}COOH$, there are two surface regions which are smoother and rougher. Since the height difference (4 Å) between the two regions corresponds to the difference between molecular lengths of $C_{19}H_{39}COOH$ and $C_{17}F_{35}COOH$ (28 and 25 Å, respectively), the smoother region may be $C_{19}H_{39}COOH$ rich and the other $C_{17}F_{35}COOH$ rich. Surface roughness is observed even on the surface of islands in monolayer LB film of homogeneous $C_{17}F_{35}COOH$. The regular molecular array is not observed in the rougher region of the $C_{17}F_{35}COOH/C_{19}H_{39}COOH$ hybrid LB film, although the formation of the array is obvious in the smoother region of the hybrid and in the LB film of homogeneous $C_{19}H_{39}COOH$, as seen in Figure 3. Those indicate the lesser ordering of $C_{17}F_{35}COOH$ than those of $C_{19}H_{39}COOH$ in the LB film, originating from the weak attraction of fluorocarbons.

In the $C_{13}F_{27}COOH/C_{19}H_{39}COOH$ hybrid film, islands with a smoother surface coexist with rough continuous regions. The islands widen with $C_{19}H_{39}COOH$ content, while the continuous region is similar to the surface of homogeneous $C_{13}F_{27}COOH$ LB film. Therefore, the islands must be the $C_{19}H_{39}COOH$ -rich region and the continuous region is $C_{13}F_{27}COOH$ rich. The $C_{19}H_{39}COOH$ -rich islands are not detected at higher surface pressures for the hybrids with low $C_{19}H_{39}COOH$ content, because of the piling up of $C_{13}F_{27}COOH$ on the $C_{19}H_{39}COOH$ monolayer as well as on the $C_{13}F_{27}COOH$ monolayer. Then the inflection at $\pi = 22\text{--}30$ mN/m in the $\pi\text{--}A$ isotherm of hybrids is interpreted as a transition from a monolayer in the expanded liquid state to piling-up, but not from a liquid to solid state in a monolayer.

The AFM texture for $C_{13}F_{27}COOH/C_{17}F_{35}COOH$ hybrids is rather complicated. At 1 mN/m, the height difference (5 Å) between terraces and hills in isolated regions is close to the difference (6 Å) between molecular lengths of $C_{13}F_{27}COOH$ and $C_{17}F_{35}COOH$. The terraces and the hills can then be attributed to $C_{13}F_{27}COOH$ -rich and $C_{17}F_{35}COOH$ -rich regions, respectively. The continuous region segregating isolated regions consists of $C_{13}F_{27}COOH$ molecules which are normal or tilted on the substrate, because the highest level of the rough continuous regions is close to the level of the terrace. The embankments constructed at 20 mN/m have the height difference of 11 Å from the

surface of isolated regions. This value is equivalent to the difference between heights of the $C_{13}F_{27}COOH$ bilayer and $C_{17}F_{35}COOH$ monolayer. This means that, with compressing the L film, $C_{13}F_{27}COOH$ molecules in the terrace and the continuous region are rearranged into bilayers to form the embankment. Since the height of bumps on the LB surface at 50 mN/m is 40 Å, it is assumed that $C_{13}F_{27}COOH$ bilayers are piled up on the $C_{17}F_{35}COOH$ monolayers.

The molecular lengths of $C_{13}F_{27}COOH$ and $F_{10}C_2DMP$ are almost the same (20 and 19 Å). Nevertheless, the apparent occupied area (84 Å²/molecule) per $F_{10}C_2DMP$ molecule is larger than that of $C_{13}F_{27}COOH$, since $F_{10}C_2DMP$ has a bulky hydrophilic headgroup. Moreover, the occupied area of $F_{10}C_2DMP$ is larger than the headgroup surface area (ca. 42 Å²/molecule), which is evaluated from the Gibbs film studies for $F_{10}C_2DMP$, a homology with different fluorocarbon and hydrocarbon components.²¹ This indicates the formation of the liquid-state film by $F_{10}C_2DMP$.

As expected from the L film in the liquid state, the surface of the $F_{10}C_2DMP$ LB film is rough. However, it must be noted that the $C_{13}F_{27}COOH/F_{10}C_2DMP$ hybrid displays smoother regions with a fractal texture. $C_{13}F_{27}COOH$ molecules are stuck in the expanded two-dimensional array of $F_{10}C_2DMP$, without resulting in piling up. This implies the preferable miscibility of $C_{13}F_{27}COOH$ and $F_{10}C_2DMP$, in contrast to the phase separation for the three hybrid systems described above, although the $\pi\text{--}A$ isotherms of $C_{13}F_{27}COOH/C_{17}F_{35}COOH$ hybrids seem to behave ideally as well as those of the $C_{13}F_{27}COOH/F_{10}C_2DMP$ hybrid. The molecular arrangements in L and LB films of the hybrids of perfluorinated and hydrogenated amphiphiles discussed above are schematically represented in Figure 7.

The formation of smooth regions segregated from rough regions is found on the hybrids between hydrogenated and perfluorinated fatty acids or between perfluorinated fatty acids of different alkyl chain lengths, with the exception of the hybrid between perfluorinated am-

(21) Sadtler, V. M.; Giulieri, F.; Krafft, M.-P.; Riess, J. G. *Chem. Eur. J.* **1998**, *4*, 1952.

phiphiles with different headgroups. This implies the phase separation of hydrogenated or perfluorinated fatty acids. A similar phase separation has been reported for the mixed LB film of $C_{19}H_{39}COOH$ and partly fluorinated carboxylic ether acid ($C_9F_{19}C_2H_4OC_2H_4COOH$).¹⁴ On investigation with friction force microscopy, the phase separation manifests as circular domains for a mixture of equimolar ratio. By shortening the alkyl chain length in the fatty acid, the phase-separation regions increase the disorder and take on a two-dimensional fractal geometry.

It is suggested that the attractive hydrophobic interaction forces dominate between long alkyl chains of $C_{19}H_{39}COOH$ in the L and LB films, minimizing the boundary length and the surface energy, while the entropic effects become more important for molecules with shorter alkyl chains in the films. On the other hand, the higher cohesive energy between the fluorocarbon chains stabilizes the two-dimensional solid of perfluorinated amphiphiles such as $C_{17}F_{35}COOH$. However, the intrinsic lipophobicity of

perfluorinated fatty acids with shorter chains overcomes the lateral cohesion and demands bump formation. In other words, although the ability of bump formation is the intrinsic property of perfluorinated amphiphiles, it becomes remarkable as the alkyl chain lengths shorten. Thus, the phase separation or miscibility in Langmuir and Langmuir–Blodgett films of perfluorinated amphiphile hybrids with different perfluorinated amphiphiles or hydrogenated amphiphiles depends on the combination of amphiphiles owing to the complicated interaction forces between amphiphiles.

Acknowledgment. This work was supported by the Izumi Science and Technology Foundation. We are grateful to Dr. M.-P. Krafft for her kind supply of F10C2DMP and to Mr. Y. Ikeda for his assistance with AFM measurements.

LA9902237