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The Synthesis and Langmuir-Blodgett Film Formation of Branched Fatty Acids with Two Long Alkyl Chains

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Three kinds of branched fatty acids with two long alkyl chains were synthesized: 2-octadecyleicosanoic acid (I), 3-heptadecyleicosanoic acid (II), and 3,5-dioctadecyloxybenzoic acid (III). The structure assignments were confirmed by IR, ^{1}H-NMR and elemental analysis. The monomolecular film properties of the fatty acids at an air/water interface were investigated. II and III gave stable monomolecular films at a surface pressure of 25 dyn/cm, while I did not. Multilayer films of II and III were grown on silicon substrates, and analyzed by X-ray diffraction.

Keywords: branched fatty acid, dialkyl fatty acid, Langmuir-Blodgett films, monomolecular films

INTRODUCTION

Linear fatty acids such as stearic acid and arachidic acid have been investigated as standard molecules for Langmuir-Blodgett film (LB film) formation by many workers.[1] In LB film formation, the balance between the hydrophobic and hydrophilic nature of the molecule is thought to be important. Stearic acid gives a relatively stable LB film, while methyl stearate LB films are apt to crystallize. Long alkyl ammonium salts give expanded monomolecular films at an air/water interface and cannot give LB films. Branched fatty acids, which have two long alkyl chains and a carboxyl group, are of interest from the viewpoint of attaining this desired balance.

In order to prepare a multilayer film on a solid substrate, a corresponding monomolecular film at an air/water interface has to be stable and closely packed under high surface pressures.[2] Fatty acids with nonlinear structures, such as oleic acid (cis-9-octadecenoic acid),[3] isostearic acid (16-methyl-heptadecanoic acid)[4] and octadecyl malonic acid (2-carboxyl-eicosanoic acid),[5] do not give stable and condensed monomolecular films under high surface pressures. Other acids with branched structures can also be considered and we have synthesized three kinds via different synthetic routes.

In this paper, the synthesis details of the branched fatty acids and the relationship between the molecular structures and the condensed monomolecular film stabilities on a water surface will be discussed. Preliminary results of multilayer film formation will also be shown.

RESULTS AND DISCUSSION

Synthesis

The synthetic schemes of three branched fatty acids are shown in Figure 1.

2-Octadecyleicosanoic acid (I) was synthesized through malonic ester synthesis. Although 2-hexadecyloctadecanoic acid has been obtained in this manner,[6] we

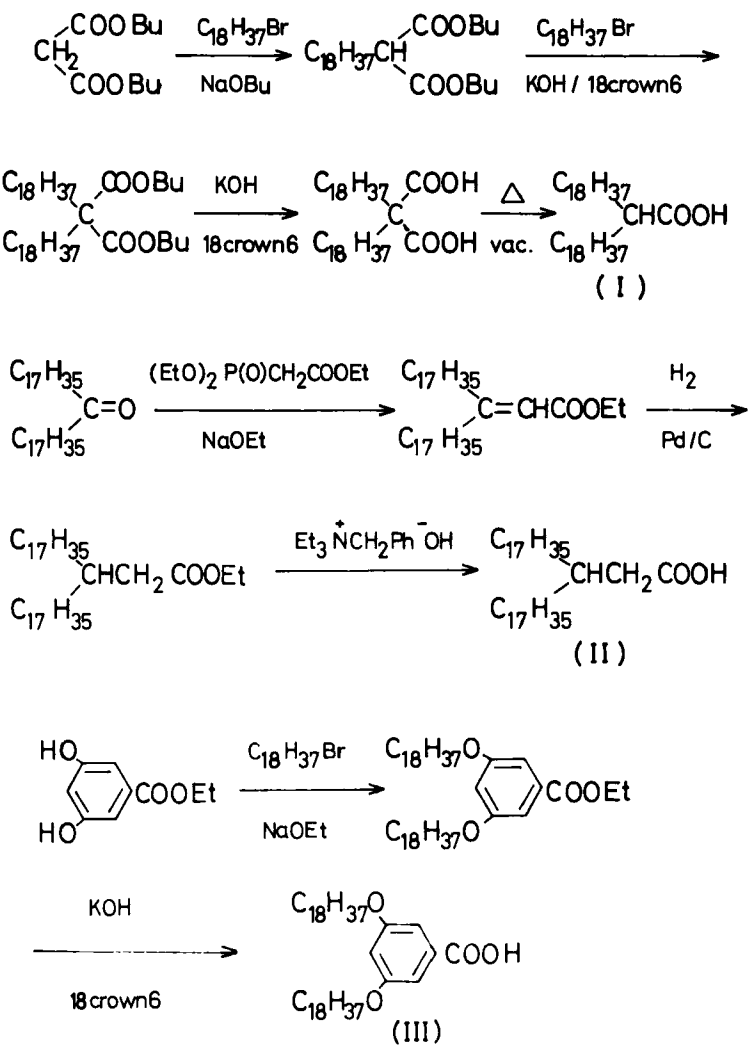

FIGURE 1 Synthetic schemes for branched fatty acids.

could not find any reports on the synthesis of I. In this synthesis, we obtained a mixture of compounds possessing one alkyl chain and two alkyl chains. Fortunately, they could be separated by using their solubility difference in alcohol.

3-Heptadecyleicosanoic acid (II) was synthesized through Wittig reaction[7] and hydrogenation. Stearon (18-pentatriacontanone) was allowed to react with ethyl diethylphosphonoacetate in the presence of sodium ethoxide, resulting in the formation of the desired compound (ethyl 3-heptadecyl-2-eicosenate) and other by-products. The by-products could be removed by repeated recrystallization in ethanol. It was found later, however, that hydrogenation changed the mixture of the desired compound and the by-products into a single species (ethyl 3-heptadecyl-eicosanate), which could be converted to II by hydrolysis. The main by-product can be considered a conjugated diene (ethyl 3-heptadecyl-2,4-eicosadienoate).

3,5-Dioctadecyloxybenzoic acid (III) was synthesized from 1-bromooctadecane and ethyl 3,5-dihydroxybenzoate. In this synthesis, a mixture of the monosubstituted and disubstituted compounds was produced. The monosubstituted compound was converted into a sodium phenoxide and removed as an insoluble part in toluene.

For these syntheses, the use of a phase transfer catalyst such as a crown ether was found to be very effective,[8] particularly in the hydrolysis of the corresponding esters. The conventional method using sodium hydroxide in ethanol did not cause ester cleavage.

Monomolecular film at an air/water interface

Figure 2 shows surface pressure (F) to occupied area (A) isotherms of monomolecular films of the branched fatty acids at the air/water interfaces. (Cd) in the figure means that water phase contains cadmium chloride (0.5 mmol/l).

The monomolecular films of the branched fatty acids have condensed phase on pure water. The presence of cadmium ions makes the films pack more densely. The occupied area values of II and III in the condensed phases are consistent with the values predicted from their molecular models. I, however, has a rather low value which may be due to monomolecular film instability.

Figure 3 shows the time dependence of monomolecular film area.

The monomolecular films were compressed until a surface pressure meter indicated 25 dyn/cm, and then the film areas were controlled to hold the surface pressure value of 25 dyn/cm. If a monomolecular film is unstable, its film area changes with time.[9] Although II, III and arachidic acid gave stable monomolecular films on aqueous cadmium chloride solutions, I did not. The film area of I decreases with time. These phenomena were reproducible.

According to the CPK molecular models, the carboxyl groups of II and III are located in the same plane as the hydrophobic chains and eclipsed by the chains. The carboxyl group of I, however, lies out of the plane of the alkyl chains. This steric effect may cause the film instability. Figure 4 shows the steric structures of I and II. The presence or absence of a methylene group appears to determine the film stability.

In contrast to arachidic acid monomolecular films, II and III show slight viscosity. The surface pressure changes were measured some distance from the teflon barriers and they delayed a little relative to the barrier movement.

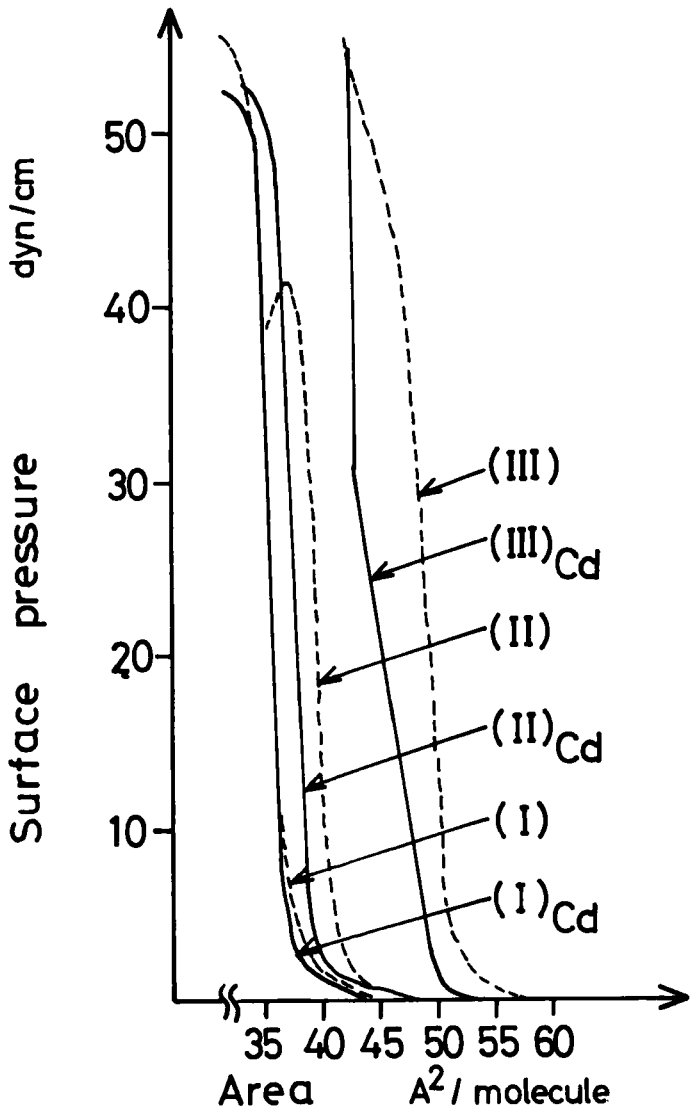

FIGURE 2 Surface pressure (F)—area (A) isotherms at 18°C for branched fatty acid monomolecular films on water surfaces.

Multilayer film grown on a silicon substrate

The stable monomolecular film of II or III formed on an aqueous solution of cadmium chloride could be transferred onto a silicon substrate, the surface of which had been treated with hexamethyldisilazane to make it hydrophobic. The multilayer film deposition was carried out with transfer ratio of almost 1.

The monomolecular film thickness of II was 24 Å and that of III was 28 Å (measured by low angle X-ray diffraction). The CPK molecular models predict

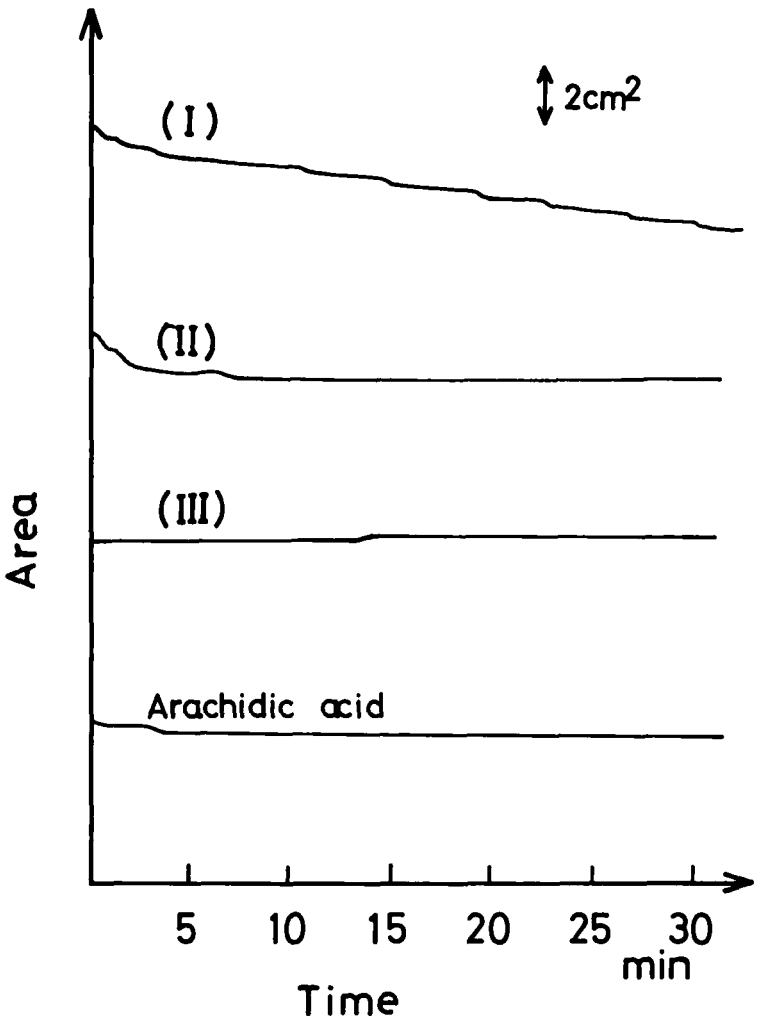

FIGURE 3 Area (A)—time curves for branched fatty acid monomolecular films on aqueous cadmium chloride solutions. The surface pressures were held constant at 25 dyn/cm.

that, if the molecules stand up straight, film thicknesses of II and III should be 27 Å and 32 Å respectively. These results suggest that both the alkyl chains in the films incline at angles of about 30 degrees.

EXPERIMENTAL

A. Synthesis

Apparatus. The structures of the products were established by their IR spectra taken on a Jasco IRA-2 spectrometer and by ^{1}H-NMR spectra taken on a Jeol

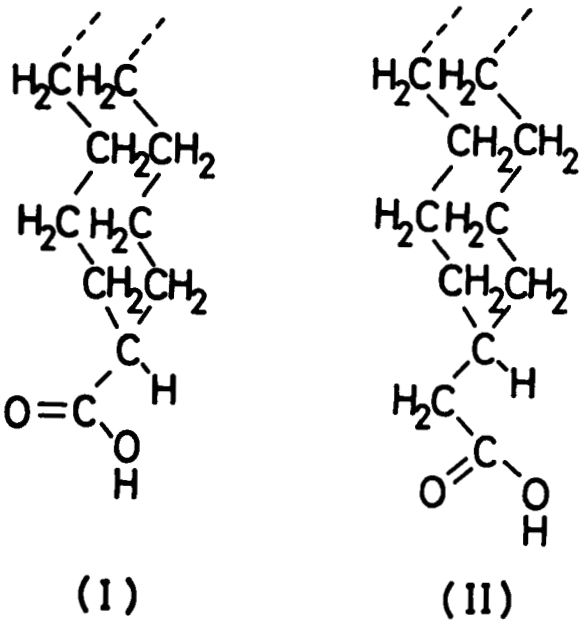

FIGURE 4 Proposed structures of I and II molecules packed closely on a water surface.

FX90Q NMR spectrometer. Elemental analysis of the products was carried out in Shonan Analysis Center Co. Ltd. The melting points of the products were measured on a Du Pont 990 thermal analyzer.

Synthesis of 2-octadecyleicosanoic acid (I). Di-*n*-butyl octadecylmalonate: 1.6 g (0.069 mol) of sodium was dissolved in 100 ml of *n*-butanol, then were added 13.5 g (0.062 mol) of di-*n*-butyl malonate (Tokyo Chemical Co. Ltd.) and 21 g (0.063 mol) of 1-bromooctadecane (Tokyo Chemical). The reaction mixture was refluxed for 5 hr. The *n*-butanol was removed under a vacuum and the resulting solid was dissolved in toluene. The toluene solution was washed with water and dried over sodium sulfate. The toluene was removed under a vacuum and the resulting oil was washed with methanol to give 15 g oil of di-*n*-butyl octadecylmalonate (yield 52%). IR (KBr): 2910, 2850 cm^{-1} (strong (s), —CH_2—); 1735 (s, C=O); 1465 (s, —CH_2—); 1150 (s, —COOBu); 720 (medium(m), —CH_2—). ^{1}H-NMR ($CDCl_3$, δ in ppm): 4.14 (triplet(t), —O—CH_2—, 3.8H); 3.32 (t, —CH—$(COOBu)_2$, 0.93H); 2.0 – 1.0 (—CH_2—, 42H); 0.88 (t, —CH_3, 8.5H).

Di-*n*-butyl dioctadecylmalonate: 1.6 g (0.029 mol) of potassium hydroxide and 7.4 g (0.029 mol) of 18-crown-6 ether (Tokyo Chemical) were dissolved in methanol. The methanol was evaporated. To the remaining solid were added 12 g (0.026 mol) of di-*n*-butyl octadecylmalonate, 8.5 g (0.026 mol) of 1-bromooctadecane and 150 ml of toluene. The reaction mixture was refluxed for 12 hr. The toluene was removed under a vacuum, the remaining material was recrystallized in ethanol to give 12.8 g of di-*n*-butyl dioctadecylmalonate (yield 68%). mp. 38°C. IR(KBr): 2910, 2850 (s, —CH_2—); 1725 (s, C=O); 1470 (s, —CH_2—); 1200 (m, broad,

—COOBu); 720 (m, —CH_2—). ^{1}H-NMR ($CDCl_3$): 4.12 (t, —OCH_2—, 3.6H), 1.8–0.6 (the other H, 88H).

Dioctadecylmalonic acid: 2.3 g (0.042 mol) of potassium hydroxide and 0.18 g (6.8×10^{-4} mol) of 18-crown-6 ether were dissolved in methanol. The methanol was evaporated. To the remaining solid, were added 5 g (6.9×10^{-3} mol) of di-*n*-butyl dioctadecylmalonate and 75 ml of toluene. The reaction mixture was refluxed for 5 hr. A precipitate was formed and filtered. The precipitate was dissolved in ethanol and diluted hydrochloric acid was added to make the solution acidic. An insoluble material was formed and filtered. The material was dissolved in ethanol and diethylamine was added to make a salt as crystal (mp. 125°C). The salt was dissolved in ethanol, and poured into a large amount of diluted hydrochloric acid to produce a precipitate. The precipitate was recrystallized in hexane to give 3.2 g of dioctadecylmalonic acid (yield 76%). mp. 95°C. IR(KBr): 2910, 2850 (s, —CH_2—); 1700 (s, C=O); 1470 (s, —CH_2—); 1260 (m, broad, —COOH); 720 (m, —CH_2—). ^{1}H-NMR ($CDCl_3$): 1.95 (—$(CH_2)_2$C—$(COO—)_2$, 4.1H); 1.7–1.0 (—CH_2—, 64H); 0.88 (t, —CH_3, 5.9H).

2-Octadecyleicosanoic acid (I): Dioctadecylmalonic acid was heated at 150–170°C under a vacuum for 6 hr. The resulting solid was recrystallized in ethanol to give 2-oxtadecyleicosanoic acid. mp. 83°C. IR (KBr): 2910, 2850 cm^{-1} (s, —CH_2—); 1700 (2, C=O); 1470 (s, —CH_2—); 1280 (m, broad, —COOH). ^{1}H—NMR ($CDCl_3$): 2.28 (multiplet(m), >CH—COO, 1.1H); 2.0–1.0 (—CH_2—, 68H); 0.88 (t, —CH_3, 6.5H). Elemental analysis, Calcd. for $C_{38}H_{76}O_2$: C 80.78%; H 13.56%. Found: C 80.87; H 13.87.

Synthesis of 3-heptadecyleicosanoic acid (II). Ethyl 3-heptadecyl-2-eicosenate: 8.4 g (0.36 mol) of sodium was dissolved in 1000 ml of ethanol, then were added 82 g (0.36 mol) of ethyl diethylphosphonoacetate (Tokyo Chemical) and 93 g (0.18 mol) of 18-pentatriacontanone (Tokyo Chemical). The reaction mixture was refluxed under a nitrogen atmosphere for 17 hr, and the ethanol was removed by distillation. The resulting solid was washed with water and methanol. Recrystallizations in ethanol were carried out 10 times to give 26 g of ethyl 3-heptadecyl-2-eicosenate (yield 25%), mp. 43°C. IR(KBr): 2910, 2850 (s, —CH_2—); 1720 (s, C=O); 1640 (s, C=C); 1470 (s, —CH_2—); 1200, 1150 (s, —COOEt); 865 (m, >C=CH—); 730 (s, —CH_2—). ^{1}H—NMR ($CDCl_3$); 5.60 (singlet(s), =CH—, 0.9H), 4.13 (quartet(q), J = 7.1Hz, —OCH_2—, 1.8H), 2.58 (broad(b), cis —CH_2—C=C—C=O, 1.8H), 2.12 (b, trans—CH_2—C=C—C=O, 1.8H), 2.0–1.0 (—CH_2—, ethoxy—CH_3, 63H), 0.88 (t, —CH_3, 6.4H).

Ethyl 3-heptadecyleicosanate: 8.0 g (0.014 mol) of ethyl 3-heptadecyl-2-eicosenate, 1.5 g of 5% Pd/carbon and 60 ml of ethanol were placed in a stainless steel reactor. Hydrogen gas was introduced into the reactor up to a pressure of 80 kg/cm^2. The reaction mixture was stirred and heated at 80°C for 3 hr, and then filtered. Recrystallization in ethanol gave 6.9 g of 3-heptadecyleicosanate (yield 86%). mp. 36°C.IR(KBr): 2910, 2850 (s, —CH_2—); 1740 (s, C=O); 1470 (s, —CH_2—); 1180 (m, —COOEt); 720 (s, —CH_2—). ^{1}H—NMR ($CDCl_3$); 4.12 (q, J = 7.2Hz, —OCH_2—, 2.0H), 2.21 (d, J = 6.6Hz, —CH_2—CO—, 2.0H), 1.87 (b, >CH—, 1.0H), 2.0–1.0 (—CH_2—, ethoxy —CH_3, 67H), 0.88 (t, —CH_3, 6.5H).

3-Heptadecyleicosanoic acid (II): 1.5 g (2.6×10^{-3} mol) of ethyl 3-heptadecyleicosanate, 5 ml of 10% triethyl benzylammonium hydroxide aqueous solution (Tokyo Chemical) and 100 ml of dioxane were heated at 80°C for 15 hr. Diluted hydrochloric acid was added to the mixture to make it acidic. The solvent was removed under a vacuum and the resulting solid was washed with water and methanol. The solid was recrystallized in petroleum benzine and then in ethanol to give 0.47 g of 3-heptadecyleicosanoic acid (yield 33%). mp. 65°C. IR(KBr): 2910, 2850 (s, —CH_2—); 1705 (s, C=O); 1470 (s, —CH_2—); 1280 (m, —COOH); 720 (s, —CH_2—). ^{1}H—NMR ($CDCl_3$): 2.27 (d, J = 6.6Hz, —CH_2—COO—, 1.9H); 2.0–1.0 (—CH_2—, >CH—, 65H); 0.88 (t, —CH_3, 6.0H). Elemental analysis, Calcd. for $C_{37}H_{74}O_2$: C 80.66; H 13.54. Found: C 80.78; H 13.62.

Synthesis of 3,5-dioctadecyloxybenzoic acid (III). Ethyl 3,5-dioctadecyloxybenzoate: 1.4 g (0.060 mol) of sodium was dissolved in 150 ml of ethanol, then were added 4.5 g (0.025 mol) of ethyl 3,5-dihydroxybenzoate (prepared from 3,5-dihydroxybenzoic acid (Tokyo Chemical) and ethanol) and 20 g (0.060 mol) of 1-bromooctadecane. The reaction mixture was refluxed under a nitrogen atmosphere for 24 hr. Additional sodium was added and refluxed for 1 hr. The ethanol was removed by distillation. The remaining solid was extracted by toluene. The toluene was evaporated under a vacuum and the resulting solid was recrystallized in ethanol to give 10.5 g of ethyl 3,5-dioctadecyloxybenzoate (yield 62%). mp. 61°C. IR(KBr): 2910, 2850 (s, —CH_2—); 1720 (s, C=O); 1600 (s, benzene ring); 1470 (s, —CH_2—); 1230, 1170 (s, —COOEt). ^{1}H—NMR ($CDCl_3$); 7.16 (Ph—H next to COOEt, 1.9H), 6.63 (Ph—H, 1.0H), 4.35 (q, J = 7.1Hz, —$COOCH_2$—, 2.0H), 3.96 (t, J = 6.4Hz, —OCH_2—, 4.0H), 2.0–1.0 (—CH_2—, ethoxy—CH_3, 67H), 0.88 (t, —CH_3, 6.3H).

3,5-Dioctadecyloxybenzoic acid (III): To a potassium hydroxide (2.0 g)/18-crown-6 ether (0.5 g) mixture were added 2.0 g (2.9×10^{-3} mol) of ethyl 3,5-dioctadecyloxybenzoate and 100 ml of toluene. The reaction mixture was refluxed for 8 hr. The toluene was removed under a vacuum, and the resulting solid was dissolved in ethanol. Diluted hydrochloric acid was added to the ethanol solution. A precipitate was formed and filtered. Recrystallization of the precipitate in ethanol gave 1.7 g of 3,5-dioctadecyloxybenzoic acid (yield 88%). mp. 80°C. IR(KBr): 2910, 2850 (s, —CH_2—); 1695 (s, C=O); 1600 (s, benzene ring); 1470 (s, —CH_2—); 1300 (m, —COOH); 1175 (s, C—O—C); 720 (m, —CH_2—). ^{1}H—NMR ($CDCl_3$): 7.24 (PhH, 2.0H); 6.68 (PhH, 1.0H); 3.98 (t, J = 6.1Hz, —CH_2—O, 4.0H); 2.0–1.0 (—CH_2—, 64H); 0.88 (t, J = 5.2Hz, —CH_3, 6.2H). Elemental analysis, Calcd. for $C_{43}H_{78}O_4$: C 78.36; H 11.93. Found: C 78.41; H 11.98.

B. Langmuir-Blodgett Film Formation

Apparatus. A Joyce Loebel LB trough was modified to include a temperature regulator and two moving teflon bars instead of the teflon belt. The other parts of the equipment, for example, a Wilhelmy surface balance with filter paper, were not modified. Low angle X-ray diffraction spectra were obtained on a Rigaku X-ray diffractometer.

Deposition procedure. Measurement of surface pressure to occupied area isotherms and formation of LB films were carried out by the ordinary method. Typical conditions were as follows:

Subphase: pure water freshly deionized by ion-exchange resins or aqueous solution of cadmium chloride (0.5 mmol/l).

Temperature: subphase at 18°C, atmosphere at 20–22°C.

Concentration and volume of the branched fatty acids toluene solution poured onto the subphase: 0.5 mg/ml, 70 μl.

Initial area: 350 cm^2.

Compression speed: 20 cm^2/min.

Substrate: Single crystal silicon substrates which had mirror surfaces on both sides were treated with diluted hydrofluoric acid and with a mixture of concentrated sulfuric acid and hydrogen peroxide water (3/1 v/v), and washed with water. After baking the substrates, a silane coupling agent (hexamethyl disilazane) was allowed to react with the substrates, to make their surfaces hydrophobic.

Deposition surface pressure: 25 dyn/cm.

Deposition speed: 0.5 cm/min.

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