Langmuir–Blodgett film formation of succinic acid half-esters containing double long alkoxy chains

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Two types of half-esters of succinic acid have been prepared. One contains a 1,2-dialkylated glyceryl group, while the other has a normal alkyl group as the hydrophobic group. The mono-molecular films of the half-esters developed at the air–water interface were evaluated by π–A curves. Multilayer Langmuir–Blodgett (L–B) films deposited on the substrate are discussed in terms of pinhole defects. Influences of the surface pressure on accumulation, the number of layers, and the chain length of the lipophilic group are analysed. The L–B film made from the double-chained homologues possessed fewer pinhole defects compared with that composed of the single-chained one.

Considerable interest has focused on Langmuir–Blodgett (L–B) films, which show widespread technological potential as a novel class of materials.[1–3] For the development of various functions, there are many requirements to improve or modify them. L–B films comprised of higher fatty acids, such as stearic and arachidic acid and their metal soaps have been fabricated and investigated for use as organic insulators.[4] Observations using electron microscopy and electronic measurements revealed that there are several types of defects in the films.[5–7] A large number of factors could be considered to improve the film state. It is possible that the state and behaviour of the arrangement of the matrix amphiphilic compound at the air–liquid interface are the most dominant factors in this kind of work as well as the preparation of the appropriate raw materials for the film.

It is well known that amphiphilic compounds containing two long chain lipophilic groups have the ability to self-organize. In addition, they provide a well-organized film structure, and their membranes are very extensible and flexible. Furthermore, they arrange and pack in good order at the air–water interface. Their dominant features are compatible with the aim of this work, that is, preparation of 'defect-free films'.

In this study, we synthesized half-esters of succinic acid possessing a (2,3-bis-long-chain-alkoxy)glyceryl group as the double-chained lipophilic group. For comparison, the corresponding single chain analogue was also prepared. We would like to clarify in this work the effect of introducing the double-chained structure and the relationships between the molecular structure and the pinhole defect density in the L–B film on a silicon substrate.[8,9]

Experimental procedures

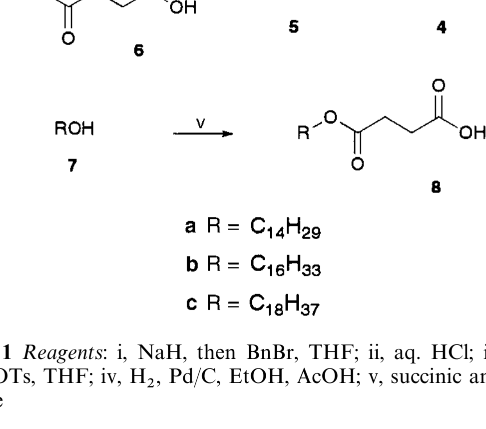
General measurement

Throughout the preparation of the raw materials, Merck precoated TLC plates (Silica gel 60F254, 0.25 mm, Art 5715) were used for the TLC analysis. For preparative column chromatography, Wakogel C-200 was employed. Melting points were recorded on an MP-J3 melting point apparatus (Yanagimoto Co) and are uncorrected. IR spectra were taken with a JASCO spectrometer FTIR-5300 (Japan Spectroscopic Co). The identification of the structures was confirmed from NMR spectra. ^{1}H and ^{13}C NMR spectra were recorded with JEOL FX 90A (90 MHz for ^{1}H NMR and 22.5 MHz for ^{13}C NMR) and JNM-GSX 270 (270 MHz for ^{1}H, 67.5 MHz for ^{13}C) instruments. Chemical shifts are reported in ppm downfield (δ) from internal standard [Me_4Si in $CDCl_3$, $(CD_3)_2SO$ and sodium 4,4-dimethyl-4-silapentanesulfonate (DSS) in D_2O]. J values are in Hz.

Preparation of fatty acids

Scheme 1 shows an outline of the preparation of the amphiphilic double-chained and single-chained succinic acid half-esters. Benzyl ether **2** was prepared according to the literature procedures.[10,11] The 1,2-di-*O*-isopropylidene group was then removed by the usual method using aqueous dilute hydrochloric acid. Compound **3** was then converted into the corresponding 1,2-di-*O*-alkylated triether **4**.

1,2-Di-*O*-alkyl-3-*O*-benzylglycerol 4. Preparation of the bis(tetradecyl) homologue **4a** is described here as an example. The diol **3** (1.91 g, 10.5 mmol) was reacted with sodium hydride (1.0 g, 25 mmol, 60% oil emulsion) in 100 ml of dry tetrahydrofuran (THF) solution with stirring and gentle refluxing. Tetradecyl *p*-toluenesulfonate[12] (9.29 g, 25.2 mmol) was added to the alkoxide solution, and the mixture was heated for 3 h with refluxing, then additional heating was continued for 5 h to remove most of the THF at 140–150 °C. The residue was



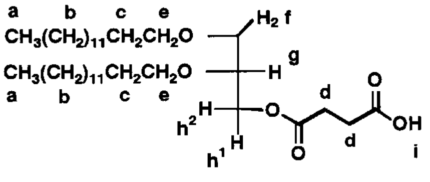
Scheme 1 *Reagents*: i, NaH, then BnBr, THF; ii, aq. HCl; iii, NaH, then ROTs, THF; iv, H_2, Pd/C, EtOH, AcOH; v, succinic anhydride, pyridine

diluted with diethyl ether. The ethereal solution of the crude products was washed with brine and water to pH 7 of the washed water, then dried over anhydrous sodium sulfate. The semi-solid product **4a** was purified by preparative column chromatography. Elution using hexane–ethyl acetate (15 : 1 v/v) afforded **4a** as a waxy product. (4.0 g, yield 67%). The R_f value was 0.86 for each homologue, **4a–c**, (hexane: AcOEt = 3 : 1 v/v).

The ^{1}H NMR spectra are summarized as follows; δ_H (90 MHz, $CDCl_3$) 0.88 (t, 6H, CH_3), 1.28 [br s, 44H, $CH_3(CH_2)_{11}$], 1.60 (m, 4H, $OCH_2CH_2CH_2$), 3.33–3.60 (m, 9H, OCH_2CH_2, $OCHCH_2$), 4.57 (s, 2H, CH_2Ph), 7.30 (m, 5H, Ph).

1,2-Di-*O*-tetradecylglycerol 5a. The 1,2-di-*O*-alkylglycerol **5** was obtained by the reductive debenzylation of the corresponding **4** in the presence of a 10% Pd/C catalyst and hydrogen at atmospheric pressure. The solution, which consisted of 100 ml of ethanol and 20 ml of acetic acid containing 3.74 g (6.5 mmol) of **4a**, was allowed to hydrogenate at 50 °C overnight with agitation. After filtration of the catalyst, the solvent was removed by evaporation under reduced pressure. Silica gel (Wakogel C-200) column chromatography of the product using hexane–ethyl acetate (30 : 1 v/v) gave pure **5a**. (3.8 g, yield 80%). The R_f values were 0.45–0.48 for each of the homologues, **5a–c** (hexane–AcOEt, 15 : 1 v/v). ν/cm^{-1} (KBr) 3470, 2920, 2851, 1467, 1113, 1080. δ_H (90 MHz, $CDCl_3$) 0.89 (t, 6H, CH_3), 1.28 [br s, 44H, $CH_3(CH_2)_{11}$], 1.58 (m, 4H, $OCH_2CH_2CH_2$), 2.22 (br s, 1H, OH), 3.37–3.68 (m, 9H, OCH_2CH_2, $OCHCH_2$). Mps: **5a**, 44–45 °C; **5b**, 54–56 °C; **5c**: 63–64 °C (lit.,[9] 64 °C).

Double-chained mono-ester of succinic acid 6a. To a solution of 1.07 g (2.2 mmol) of **5a** in 20 ml of pyridine in a round-bottomed flask provided with a magnetic stirrer, a dropping funnel, a nitrogen gas tube, and a reflux condenser fitted with a calcium chloride tube, was slowly added pyridine solution (15 ml) containing 1.1 g (11 mmol) of succinic anhydride. The mixture was allowed to stand for 24 h at 40 °C with agitation. After the reaction, the content was diluted with diethyl ether. The ethereal phase was washed with brine and water and then dried with anhydrous sodium sulfate. Removal of the solvent under reduced pressure afforded the crude product. The crude waxy product was chromatographed on a silica gel (Wakogel C-200) column with hexane–ethyl acetate (7 : 1 v/v) to give the pure compound **6a** as a white powder after removal of the eluent (0.67 g, yield 52%, $R_f = 0.08$, hexane–ethyl acetate, 7 : 1 v/v). ν/cm^{-1}, (KBr), 2918, 2851, 1734, 1710, 1469, 1105; δ_H (270 MHz, $CDCl_3$) 0.88 (6H, t, *J* 7.5, **a**), 1.24 (44H, br s, **b**), 1.57 (4H, distorted quin, **c**), 2.68 (4H, distorted t, **d**), 3.42 (2H, t, 7.0, one of **e**), 3.45 (2H, t, *J* 7.0, one of **e**), 3.57 (2H, m, **f**), 3.64 (1H, quin, *J* 6.5, **g**), 4.12 (1H, dd, $\mathbf{h}^1$, J_{gem} 13.0, $\mathbf{Jg{-}h}^1$ 6.5), 4.28 (1H, dd, $\mathbf{h}^2$, J_{gem} 13.0, $J\mathbf{g{-}h}^2 = 4.5$), 4.80 (1H, br s, **i**). Mps: **6a**, 38–40 °C, **6b**, 43–44 °C, **6c**, 48–49 °C.



6a

Single chained mono-ester of succinic acid 8. Mono higher alkyl hydrogen succinates **8** were prepared in a manner similar to the synthesis of **6** just described. The normal higher alcohol **7** was used instead of 1,2-di-*O*-alkylglycerol **5** as the raw material.

The crude waxy product was chromatographed on a silica gel (Wakogel C-200) column with a mixture of hexane–ethyl acetate (3 : 1 v/v) to give the pure compound **8b** (yield 42%, mp 59–60 °C, $R_f = 0.12$); δ_H (90 MHz, $CDCl_3$) 0.91 (3H, t, CH_3), 1.34 [br s, 26H, $CH_3(CH_2)_{13}$], 1.62 (m, 2H, $OCH_2CH_2CH_2$), 2.58 [s, 4H, $C{=}(O)CH_2$], 3.30 (br s 1H, O*H*), 4.08 (t, 2H, OCH_2CH_2); mp of **8c**: 64–65 °C.

The ^{1}H NMR spectrum of each homologue intermediate possessing additional alkyloxy groups was also in fair agreement with their δ values and integration with the theoretical values for **4** and the subsequently prepared dialkoxy glycerol **5** and half-esters of succinic acid **6**.

Preparation of monolayer and measurement of *π–A* curves

The monolayer films of the half-ester of succinic acid were prepared on a Langmuir trough. Deionized distilled water from a Millipore system was used to prepare the subphase for the trough. The specific resistivity of the water used was larger than 17 MΩ cm and its surface tension, as measured by the Wilhelmy plate method, was 71 mN m^{-1}. A chloroform solution of the amphiphilic carboxylic acid was spread on a pure water surface at a subphase temperature (T_{sp}) of 10 °C. Concentrations of the chloroform solution of the double-chained succinic acid monoester (**6a–c**) and mono-chained higher-alkyl hydrogen monosaccinate (**8a–c**) were 2 and 4 mM, respectively.

After 20 min of solvent evaporation, the *π–A* isotherm curves were recorded with a film balance system equipped with an Wilhelmy plate (NL-LB240S-MWA, Nippon Laser Electronics Co, Ltd) using the moving wall method at a barrier speed of 11 mm min^{-1}. The results for the dihexadecanoyl homologue is shown here as an example in Fig. 1. Molecular occupied areas and collapse pressures of the amphiphiles are summarized in Table 1.

Accumulating deposition procedure

Two different kinds of substrates, a silicon wafer (30 × 10 mm) and a glass slide (30 × 10 mm), were used depending upon the purpose of the measurement.

A single crystal silicon wafer, which has a mirror surface on one side, was used for the observation of the deposition state of the accumulated L–B film by its IR spectrum. It was washed using trichloroethylene, acetone and then ethanol under sonication, and further treated with 10% hydrofluoric acid for 5 min followed by hot concentrated nitric acid for 10 min, and then washed and rinsed with water.

On the other hand, in order to evaluate the pinhole defects in the L–B films, the copper decoration method was applied and used to visualize the pinholes. For this purpose the glass slide substrate was successively vapour-deposited with chromium and gold.

During the L–B depositions, the surface pressure was kept at 55 mN m^{-1}. A transfer speed of 3–5 mm min^{-1} was applied for the film deposition. These accumulating conditions were applied for both of the above substrates.

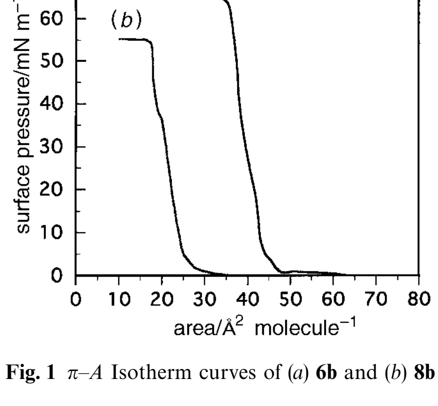


Fig. 1 *π–A* Isotherm curves of (*a*) **6b** and (*b*) **8b**

Table 1 Molecular occupied areas and collapse pressures of amphiphiles

amphiphiles	**6** and **8**	molecular occupied area/Å^2	collapse pressure/mN m^{-1}	molecular occupied area/Å^2	collapse pressure/mN m^{-1}
		pure water		KCl aq. soln.	
double-chained amphiphiles	**6a**	40	61	40	60
	6b	43	65	43	61
	6c	44	68	43	61
				$CdCl_2$ aq. soln.	
single-chained amphiphiles	**8b**	23	54	23	66
	8c	24	60	24	70

Detection of the pinholes on the L–B film

Recently, it was confirmed that conventional fatty acid L–B films on a solid substrate are not perfect but many defects such as pinholes exist in the film. The evaluation of the pinholes was carried out using the copper decoration method through electroplating with the following conditions.[6,13] If the pinholes eventually penetrate the L–B lipid membrane, 'the heads of copper nails' appeared as stains on the surface of the film after the decoration: electrolytic solution: 1% $CuSO_4$ aq. soln. (0.063 M), counter electrode: copper plate, applied voltage: 100 mV, distance between electrodes: 3.0 cm, decoration periods: 5 min.

After the decoration, the small copper stains that appeared during electroplating were counted in a unit area using an optical microscope. This was sufficient to permit the exact evaluation of the defects. The influence of the surface pressure during the deposition and the number of layers in the accumulation upon the defects of the L–B films are discussed. The results are summarized in Fig. 2.

Results and Discussion

Synthesis of the half-esters of the dibasic acids

In order to prepare the raw materials of the L–B film, double- and single-chained fatty acids were synthesized according to the reactions shown in Scheme 1. Synthetic studies along with application of many methods already introduced were accompanied with no pronounced difficulties, although some yields were unsatisfactory. The etherification of the hydroxy groups of **3** was carried out according to Williamson's method using alkyl tosylate. Although some other *O*-alkylating agents, such as the higher alkyl chlorides and bromides were used, the corresponding alkyl toluene-*p*-sulfonates gave the best results. The characterization of each compound was carried out using ^1H NMR and IR spectroscopy. The integral data in the ^1H NMR identified the structure of the end products.

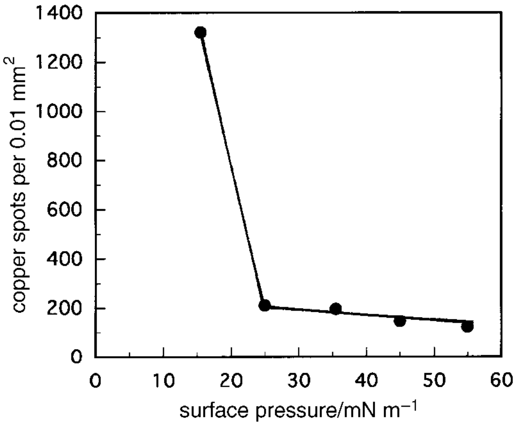


Fig. 2 Correlation between the density of copper spots and surface pressure for a single layer of **6b**

π–A curves of fatty acid films

Fig. 1 shows the *π–A* isotherm curves of the monomolecular films of **6b** and **8b**, which possess a hexadecyloxy hydrophobic chain, at the air–water interface. Both **8** and **6** provided good surface pressures for L–B monolayer formation under these conditions. As summarized in Table 1, the limiting molecular area of **8** was about half that of **6**. They were estimated as 40–44 Å^2 for the double-chained amphiphile series and 23–25 Å^2 for the single chained one, respectively. The collapse pressure of **6** was >60 mN m^{-1} and higher than that of **8**. But the addition of a divalent cation such as cadmium in a sub-phase enhanced the collapse pressure of the L–B film that consisted of a single-chained amphiphile. It has been reported that the stability and the deposition properties of the monolayer on the water surface could be improved by the formation of a poly-ion complex between the hydrophilic groups in the ionic amphiphile and poly-ion in the subphase.[14,15] Equally good results have also been achieved in our experiment. On the other hand, the influence of the chain length on the limiting molecular area was slight regardless of the number of hydrophobic groups in the molecule.

Evaluation of pinhole defects in L–B films

Fig. 2 shows the correlation between the surface pressure (π) and the number of copper spots that appeared on the single layer film prepared under various surface pressures during the copper decoration. The film prepared under the lowest surface pressure at 15 mN m^{-1} showed an extremely large number of copper spots, which means it had many pinhole defects. On the other hand, the film prepared at a surface pressure between 25 and 55 mN m^{-1} clearly had few defects compared with the previously mentioned film. As Fig. 2 shows, the number of copper spots was inversely proportional to the surface pressure, but the influence of pressure was slight at 25 mN m^{-1} or above.

For the influence of the number of accumulating layers consisting of double-chained amphiphiles (**6a–c**), it was confirmed that increasing numbers of layers depressed the formation of the pinholes. As Fig. 3(*a*) shows, the single-layer film had more than 120 spots of copper stain per 0.01 mm^2, more than twenty times greater than the number of spots that appeared in the multi-cumulated films. The effect of the accumulation on the improvement of pinhole defects in the film is clear. While the difference between the single and triple layers was marked, clear differences were not shown in the number of copper stains among multi-layers accumulated over three layers. Also there was no obvious influence of the chain length of the two alkoxy groups over the whole accumulation range.

For the films that consisted of single-chained amphiphiles, **8**, on the other hand, the influence of the chain length of the hydrophobic group was more obvious, as shown in Fig. 4. The

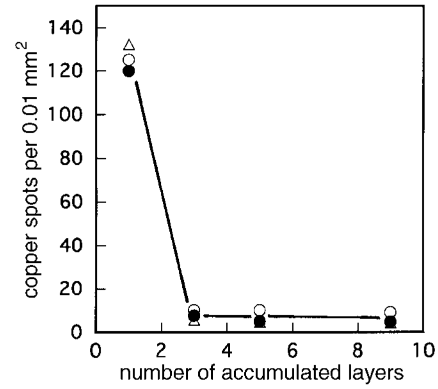


Fig. 3 Influence of number of accumulated layers on the copper spots for (△) **6a**, (○) **6b** and (●) **6c**

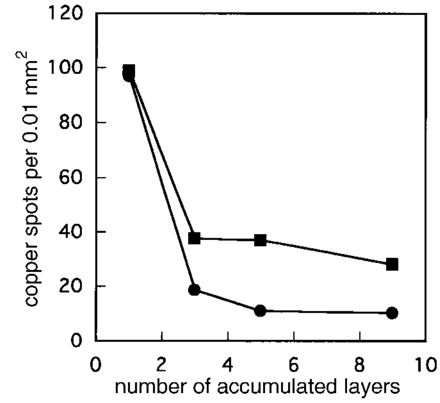


Fig. 4 Influence of number of accumulated layers on the copper spots in 0.4 mM $CdCl_2$ solution for (■) **8b** and (●) **8c**

film made of longer alkyl lipophilic groups, **8c**, had fewer pinholes than those made from **8b**. The number of pinhole defects of **8c** decreased as the number of the accumulated layers increased in a manner similar to **6c** as shown in Fig. 3. The pinhole defect density of the **6c** film was equal to about half that of **8c** when nine L–B films had been accumulated.

The effect of the introduction of a double-chained lipophilic group into an amphiphilic fatty acid was investigated in terms of improvement of pinhole defects in the L–B film. They were discussed based on studies of the π–A isotherm curves and microscopic observations after the copper decoration method by Cu electroplating. Even on the pure water surface containing no univalent and divalent metal cations, double-chained fatty acids were able to form a monolayer which could be accumulated on the substrate as Y-type film by the usual L–B method.

The number of pinhole defects in the film which consisted of the double-chained fatty acids was decreased to one twentieth by forming a multilayer. The effect of the accumulation on elimination of the defects was more pronounced for the double-chained homologues in contrast to the single-chained homologues. On the other hand, the effect of the lipophilic group chain length was small.

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Paper 7/00716G; *Received* 31*st January*, 1997