

low-load regime, nearest-neighboring redox centers would be in adjacent cages, but in the high-load regime, they would be in the same cage. The independence of D_E on load in the high-load regime suggests that there is no advantage to the placement of nearest neighbors in a common cage. The rate limitation defining D_E seems to be imposed by the transfer of electrons from cage to cage, which requires exercising the cross-links. The high de-

pendence of D_E on concentration in the low-load regime would then be understood in terms of the probability that adjacent cages are occupied with redox centers. The quantitative implications of these ideas are now under study.

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Polymerized Monolayers of Single-, Double-, and Triple-Chain Silane Amphiphiles and Permeation Control through the Monolayer-Immobilized Porous Glass Plate in an Aqueous Solution^{1,2}

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Abstract: Single-chain ($C_{18}Si$), double-chain ($2C_{18}Si$), and triple-chain ($3C_{18}Si$) amphiphiles having triethoxysilane head groups were prepared. A monolayer of dialkylsilane amphiphiles ($2C_{18}Si$) could be polymerized to form a Si-O-Si linkage at the air-water interface on the acidic subphase of pH 2. The polymerized monolayer was easily transferred on a porous glass plate (average pore size 5 nm) by the Langmuir-Blodgett technique and could be covalently bonded with Si groups on the glass surface. Permeation of NaCl and water-soluble fluorescent probes (NQ_1) through the porous glass plate was controlled by a phase transition of the immobilized lipid monolayer. When the single-chain $C_{18}Si$ and the triple-chain $3C_{18}Si$ monolayers were immobilized on a porous glass plate, these monolayers hardly acted as a gate membrane for permeation. This is because, in the case of the single-chain $C_{18}Si$ monolayer, the polymerization on the subphase decreased the molecular packing of the monolayer and the polymerized monolayer could not be well transferred on the porous glass plate. Silane groups of the triple-chain amphiphile ($3C_{18}Si$) could not be polymerized in the monolayer because of the bulkiness of three alkyl chains, and the monomeric monolayer could not be transferred with a good transfer ratio on the substrate.

Permeability controllable, lipid-immobilized membranes have been developed as models to study the transport properties of biological membranes.³⁻⁷ We have reported that signal-receptive, permeability-controllable, multibilayer-corked nylon capsule membranes⁸ and multibilayer-immobilized polyion complex films,⁹ where the multibilayers act as a gate membrane responding to external stimuli. These multibilayer-immobilized systems are easily prepared and physically stable for permeation membranes, which show clear physicochemical properties of a lipid bilayers. However, they are too thick (1-100 μm) compared with a single bilayer structure of biological membranes (5-7 nm) and are thought to have some defects in fine structures at interbilayers.

The Langmuir-Blodgett (LB) technique^{10,11} transferring lipid monolayers from a water surface is well-known to prepare well-oriented ultrathin films in a molecular level on a substrate. Recently, LB multilayer films supported on a porous substrate have been utilized for filtration purposes, e.g., for ion permeation, pervaporation, and gas separation.¹²⁻¹⁹ However, for the utilization of LB films as permeability-controllable membranes in an aqueous phase, we should consider whether the LB films are swollen between interlayers and are stable for flaking in an aqueous solution at harsh conditions (at a high temperature or a high ionic strength) or not.

In this paper, we prepare silane-functionized monolayer-forming amphiphiles having single, double, and triple alkyl chains and polymerize their Langmuir monolayers with a Si-O-Si linkage on a water subphase, which are immobilized covalently on a porous glass plate by LB techniques (see Figure 1). The lipid monolayer immobilized on a porous glass plate acts as a gate membrane for permeations of ions and water-soluble fluorescent probes re-

sponding to the phase transition from solid to liquid crystalline state of the lipid monolayer. This is the first study to control the permeability with the thinnest (2 nm) lipid monolayer film. Sagiv

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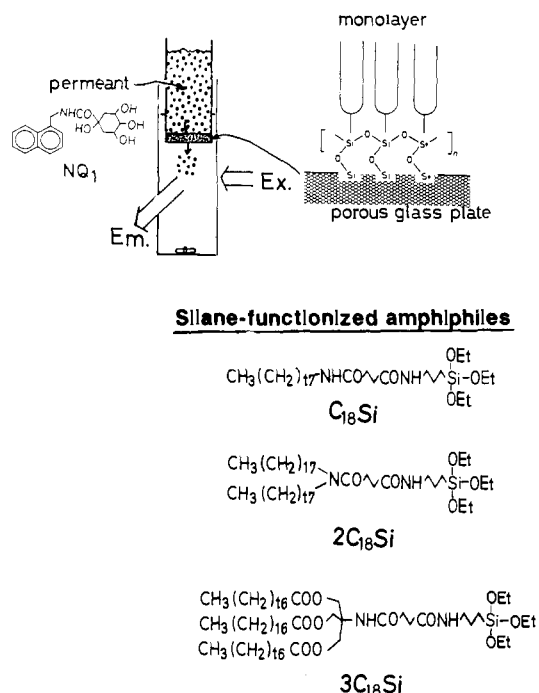


Figure 1. Structures of silane-functionalized amphiphiles (C₁₈Si, 2C₁₈Si, and 3C₁₈Si) and apparatus set up for permeation experiments.

and co-workers have shown that well-organized mono- and multilayers can be prepared on a flat glass plate by spontaneous adsorption of some kinds of silane-functionalized compounds.²⁰⁻²³

Experimental Section

Materials. Preparation of a freely water-soluble nonionic permeation probe, 1-(1,3,4,5-tetrahydroxycyclohexanecarboxamide)naphthalene (NQ₁), was reported elsewhere.²⁴ The structure and the purity of obtained silane amphiphiles were confirmed by thin-layer chromatography with a flame ionization detector, NMR and IR spectroscopy, and elemental analysis (C, H, and N within ±0.2%).

[γ-(N-Octadecylsuccinylamino)propyl]triethoxysilane (C₁₈Si). *N*-Octadecylsuccinic acid (mp 104 → 125 °C, liquid-crystalline behavior) was prepared from octadecylamine and succinic anhydride in dry tetrahydrofuran under reflux conditions for 24 h. *N*-Octadecylsuccinamoyl chloride prepared from the obtained acid and SOCl₂ was allowed to react with (γ-aminopropyl)triethoxysilane in benzene at room temperature for 12 h: yield 2.57 g (33%, recrystallized from ethanol); mp 34 °C; *R_f* 0.75 (ether); ¹H NMR (CDCl₃) δ 0.5 (t, 2 H, CH₂Si), 0.9 (t, 3 H, CH₃), 1.3-1.9 (m, 43 H, CH₂CO and CH₃CH₂OSi), 3.5-4.2 (m, 10 H, CH₂N and CH₂O).

[γ-(N,N-Dioctadecylsuccinylamino)propyl]triethoxysilane (2C₁₈Si). *N,N*-Dioctadecylsuccinamic acid was prepared from *N,N*-dioctadecylamine and succinic anhydride: yield 14.5 g (94%); mp 67 °C. *N,N*-Dioctadecylsuccinamoyl chloride was allowed to react with (γ-aminopropyl)triethoxysilane in benzene at room temperature for 12 h: yield 6.2 g (47%, recrystallized three times from ethanol); mp near room temperature; *R_f* 0.72 (95:5 ether/H₂O); ¹H NMR (CDCl₃) δ 0.5 (t, 2 H, CH₂Si), 0.9 (t, 6 H, CH₃), 1.3-1.9 (m, 79 H, CH₂, CH₂CO, and CH₃CH₂OSi), 3.7-4.2 (m, 12 H, CH₂N and CH₂O).

Tris(octadecanoyloxymethoxy)[(γ-(triethoxysilyl)propyl)succinamyl]amino]methane (3C₁₈Si). [Tris(octadecanoylmethyl)amino]methane (mp 66 °C for *p*-toluenesulfonate salts) was prepared from stearic acid and [tris(hydroxymethyl)amino]methane according to the literature.²⁵ The triester was allowed to react with an excess amount of succinyl dichloride in benzene at room temperature in the presence of triethylamine. Tris[(octadecanoyloxymethyl)chlorosuccinamylamino]-

methane was purified by reprecipitation with benzene-hexane three times. The obtained acid chloride was reacted with γ-(triethoxysilyl)propylamine in benzene at room temperature for 12 h: yield 0.67 g (24%, recrystallized from ethanol three times); mp 55-57 °C; *R_f* 0.75 (98:2 ether/H₂O); NMR (CDCl₃) δ 0.5 (t, 2 H, CH₂Si), 0.9 (t, 9 H, CH₃), 1.3-1.5 (m, 56 H, CH₂ and CH₃CH₂OSi), 2.2-2.5 (t, 10 H, CH₂CO), 3.5-4.0 (m, 8 H, CH₂OSi and CH₂N), 4.4 (s, 6 H, CH₃O).

Monolayer Measurements. Highly purified water by Milli-Q (Millipore Co. Ltd.) was used as a subphase (18 MΩ cm). A benzene solution (0.8 mg mL⁻¹) of C₁₈Si, 2C₁₈Si, or 3C₁₈Si was spread on a subphase (pH 2 with HCl or pH 5.8 with Milli Q water) in a Teflon-coated trough (475 × 150 mm²) with a microprocessor-controlled Teflon barrier (San-Esu Keisoku Co., Fukuoka, Japan).²⁶ Thirty minutes after spreading, the monolayer in gaseous state was continuously compressed at the speed of 180 mm² s⁻¹ and surface pressure (π)-area (*A*) isotherms were memorized automatically in a microcomputer at a temperature range of 20-50 °C.

Transfer of Monolayers. Transferring a silane-functionalized monolayer onto a porous glass plate (10 × 10 × 0.9 mm, average pore diameter 5 nm or 20 nm, average pore volume 0.44-0.50 mL g⁻¹) was carried out as follows. The glass plate was washed with acetone in an ultrasonic bath and then activated in 1 N HCl aqueous solution for 2 h at room temperature in advance. The activated glass plate had been immersed in the subphase before spreading the monolayer and was withdrawn at a speed of 10 mm min⁻¹ at the respective surface pressure of the monolayer. The silyl groups of the transferred monolayer were covalently bonded with a Si-O-Si linkage on the porous glass plate by drying at room temperature for 10 h and then heating at 70 °C for 40 min.

The structures of multiple LB films of silane monolayers transferred onto a CaF₂ plate was analyzed by FT-IR spectra (instrument: Model 4200, Shimadzu Co., Tokyo). The phase-transition behavior of LB films was studied by differential scanning calorimetry (DSC) in aqueous solutions heated from 0 to 90 °C at 2 °C min⁻¹ (instrument: SSC-575, Seiko Electric Co., Tokyo).

Permeation Measurements. The monolayer-immobilized glass plate was attached at the bottom of a polyethylene tube (8-mm i.d.) and soaked in a 1-cm quartz cell as shown in Figure 1. NaCl (0.2 M) or water-soluble fluorescent probe (NQ₁, 1 × 10⁻³ M) was dissolved in the upper aqueous solution, and permeations through the monolayer-immobilized glass plate were followed by increases in electrical conductance for NaCl and increases in fluorescent intensity at 340 nm (excited at 280 nm) for NQ₁ probe in the lower aqueous phase. The quartz cell and polyethylene tube were temperature controlled within ±0.2 °C. Permeation experiments were carried out at various temperatures (10-60 °C) above and below the phase-transition temperature (*T_c*) of the immobilized monolayer.

Relative permeation rates, *P*/(cm² s⁻¹), were obtained from the following equation according to previous papers:⁸

$$P = Jd / (C_0 S) \quad (1)$$

where *d* and *S* are thickness (a 0.9-mm-thick porous glass plate was used for convenience sake) and area (57 mm²) of the glass for permeation, respectively. *J* and *C₀* are a flux of permeation and an initial concentration of NaCl (0.2 M) or NQ₁ probes (1 mM) in the upper cell, respectively. The *P* values in the table and figures are the average of at least three data points and contain an experimental error of ±5%.

Results and Discussion

Surface Pressure (π)-Area (*A*) Isotherms of Monolayers. π-*A* curves of monolayers of single-chain C₁₈Si, double-chain 2C₁₈Si, and triple-chain 3C₁₈Si amphiphiles on Milli-Q water (pH 5.8) and on the acidic water subphase (pH 2 with HCl) are shown in Figure 2. In the cases of C₁₈Si and 2C₁₈Si monolayers, π-*A* curves largely changed depending on the pH of the subphase. On the neutral subphase at pH 5.8, both monolayers showed two steep rises in curves corresponding to the expanded liquid and condensed solid phases, respectively. The built-up multilayers (*n* = 30) when transferred onto a CaF₂ plate showed sharp absorptions in the FT-IR spectra, corresponding to a Si-O-C stretching,^{27,28} at 1080 and 1103 cm⁻¹, which suggests that C₁₈Si and 2C₁₈Si amphiphiles exist in the monomeric triethoxysilyl form in the monolayer at the neutral pH. The monomeric monolayers could not be raised

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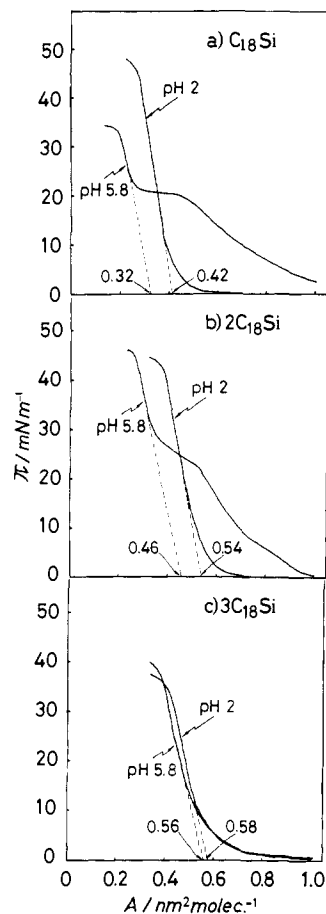


Figure 2. Surface pressure (π)-area (A) isotherms of silane amphiphiles ($C_{18}Si$, $2C_{18}Si$, and $3C_{18}Si$) on the Milli-Q water (pH 5.8) and the acidic subphase (pH 2 with HCl) at 20 °C.

with a good transfer ratio at the lower surface pressure of 20 mN m^{-1} (at the expanded liquid phase).

In contrast, the $C_{18}Si$ and $2C_{18}Si$ monolayers showed only a condensed solid phase on the pH 2 subphase in π - A isotherms. The built-up multilayers ($n = 30$) on a CaF_2 plate showed clearly absorptions corresponding to a Si-O-Si stretching at 1026 and 1095 cm^{-1} instead of Si-O-C absorptions.^{27,29} The $C_{18}Si$ and $2C_{18}Si$ monolayers could be easily transferred even at the low surface pressure (10–40 mN m^{-1}). These results indicate that $C_{18}Si$ and $2C_{18}Si$ monolayers can be smoothly polymerized to form Si-O-Si linkages on the acidic subphase³⁰ and transferred smoothly in the polymeric form.

Molecular packing of $C_{18}Si$ and $2C_{18}Si$ monolayers on the subphase can be estimated from π - A isotherms. In the case of single-chain $C_{18}Si$ monolayer, the limiting area per molecule extrapolated at zero pressure (A_0) on the pH 5.8 subphase was relatively large (0.32 nm^2) compared with other single-chain carboxylic acids (0.20–0.25 nm^2)³¹ due to the steric effect of the large triethoxysilyl head group and two amide groups in a hydrophobic alkyl chain. After polymerization on the acidic subphase, A_0 value for $C_{18}Si$ monolayer increased to 0.42 nm^2 and the collapse pressure also increased compared with those for the monomeric form. This means that molecular packings in monolayers expanded with the formation of Si-O-Si linkages, but the stability of the monolayer increased by the polymerization. In the case of double-chain $2C_{18}Si$ monolayers, the increase of the A_0 value by polymerization on the acidic subphase (0.46 \rightarrow 0.54 nm^2) was not so large, and the A_0 value at pH 2 was similar to

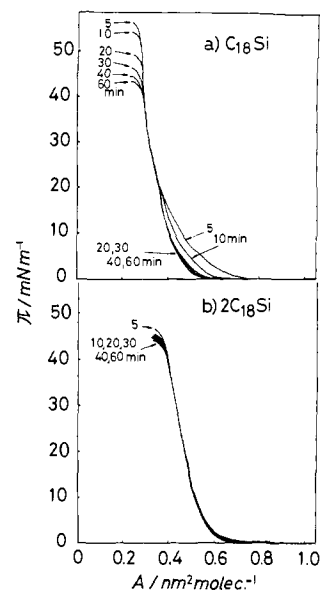


Figure 3. Time dependences of π - A isotherms for (a) $C_{18}Si$ and (b) $2C_{18}Si$ monolayers that were spread on the acidic (pH 2) subphase and compressed after waiting the respective time at 20 °C.

those for other dialkyl amphiphiles such as phospholipids (0.40–0.50 nm^2).³²

When triple-chain $3C_{18}Si$ amphiphiles were spread on the subphase, the π - A isotherms were hardly changed at pH 5.8 and 2. The built-up film ($n = 30$) from the pH 2 subphase did not show absorptions corresponding to a Si-O-Si stretching (1026 and 1095 cm^{-1}). These results indicate that $3C_{18}Si$ amphiphiles cannot polymerize in the acidic conditions, probably because the bulky trialkyl chains do not allow to form Si-O-Si linkages at the hydrophilic head group in the monolayer state.

Polymerization Behavior of Monolayers. Figure 3 shows time dependences of π - A isotherms when $C_{18}Si$ and $2C_{18}Si$ amphiphiles were spread on the pH 2 subphase and compressed after waiting the respective time. In the case of single-chain $C_{18}Si$ monolayer, the area per molecule (A_0) and the collapse area increased but the collapse pressure decreased gradually with increasing the time on the acidic subphase (with increasing the extent of polymerization). The increase of A_0 indicates again that the molecular packing of single alkyl chains begins to disorder with increasing the formation of Si-O-Si linkages. The decrease of the collapse pressure and increase of the collapse area mean that the $C_{18}Si$ monolayer is getting brittle or fragile with proceeding cross-linked polymerization of single-chain silane groups. In contrast, π - A isotherms for $2C_{18}Si$ monolayers hardly depended on the polymerization time on the acidic subphase. This indicates that dialkylsilane groups form a linear Si-O-Si linkage and the relatively soft monolayer is polymerized, which does not disturb the molecular packing of long dialkyl chains of the monolayer.

When the monolayer is estimated to be second-order solution in the expanded form at the low surface pressure on the subphase, the following equation is obtained thermodynamically:

$$\pi A = nRT + nA_0\pi \quad (2)$$

The molecular weight (M_w) of polymeric monolayers such as proteins and poly(vinyl stearate) has been reported to be estimated from the extrapolated value of eq 2 at zero surface pressure:^{33,34}

$$M_w = RT / (\pi A)_{\pi \rightarrow 0} \quad (3)$$

The good linear relations ($r = 0.999$) between πA and π values of eq 2 were obtained below $\pi = 0.2$ mN m^{-1} for π - A isotherms of Figure 3. From the intercept of πA in eq 2 and 3, molecular

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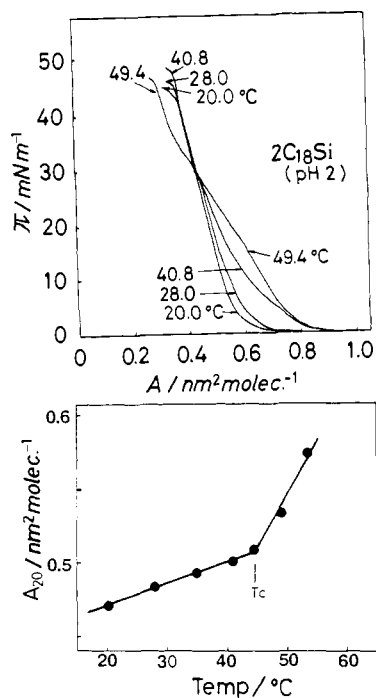


Figure 4. Temperature dependences of (a) π - A isotherms and (b) the area per molecule at 20 mN m⁻¹ (A_{20}) for 2C₁₈Si polymerized monolayers on the pH 2 subphase.

weight (degree of polymerization) at each time can be obtained for C₁₈Si and 2C₁₈Si monolayers. The degree of polymerization of both C₁₈Si and 2C₁₈Si monolayers increased with time and reached ca. 300 (M_w (6–15) $\times 10^4$) after waiting 60 min on the acidic subphase.

Phase-Transition Temperatures of Monolayers. π - A isotherms of 2C₁₈Si monolayers were obtained at various temperatures (10–55 °C), and the area per molecule at 20 mN m⁻¹ (A_{20}) is plotted against temperature in Figure 4. The A_{20} value increased drastically near 44 °C, which agrees with the results that built-up multilayer films of polymeric 2C₁₈Si showed a sharp endothermic peak at 44 °C ($\Delta H = 5.5$ kcal mol⁻¹) in an aqueous solution by DSC measurements. Dispersion of polymeric 2C₁₈Si amphiphiles in acidic solutions also showed the relatively broad phase transition near 42–44 °C ($\Delta H = 6.4$ kcal mol⁻¹) by DSC measurements. These results indicate that polymeric 2C₁₈Si monolayers have the phase transition temperature (T_c) from solid to liquid crystalline state at 44 °C. The similar phase transition was observed for the monomeric 2C₁₈Si monolayers near 44 °C from temperature dependence of π - A isotherms and DSC measurements, although the enthalpy change ($\Delta H = 2.6$ kcal mol⁻¹) was small relative to that for polymeric monolayers.

The 3C₁₈Si LB films transferred from both the pH 2 and pH 5.8 subphases showed the relatively broad endothermic peak at 50–55 °C ($\Delta H = 8.2$ – 8.6 kcal mol⁻¹) due to the phase transition to a liquid-crystal state by DSC measurements. Monomeric LB films of single-chain C₁₈Si showed an endothermic peak at 35 °C ($\Delta H = 3.4$ kcal mol⁻¹), which agrees with the melting point (34–35 °C) of monomeric C₁₈Si compounds. In the case of polymeric C₁₈Si LB films, the broad and small peak was observed in the range 31–45 °C ($\Delta H = 1.0$ kcal mol⁻¹). This indicates again that the molecular packing is decreased in the polymeric form compared with the monomeric single-chain C₁₈Si monolayers.

Transfer Ratio of Monolayers. When a flat glass and a porous glass plate (10 \times 10 \times 0.9 mm) were raised from the subphase, transfer ratios of monolayers of C₁₈Si, 2C₁₈Si, and 3C₁₈Si amphiphiles at both pH 5.8 and pH 2 are summarized in Table I. Transfer experiments were carried out after waiting 60 min, when C₁₈Si and 2C₁₈Si monolayers can be polymerized to $D_p = 300$. All glass plates were cleaned just before use according to the procedure described in the Experimental Section. On a flat glass plate, all monolayers were transferred completely with a transfer

ratio higher than 0.92 independent of the subphase pH. In contrast, transfer behaviors to porous glass plates largely depended on the pH of the subphase (polymeric or monomeric state), the pore size of the glass, and the amphiphile structures.

In the case of 2C₁₈Si monolayers, the polymeric monolayers on the pH 2 subphase could be transferred completely on the 5-nm porous glass. On the other hand, the monomeric form of 2C₁₈Si monolayer showed a low transfer ratio (0.85) for the 5-nm porous glass plate. Thus, the 2C₁₈Si monolayer could be transferred onto a rough surface of the porous glass plate by polymerization at the head groups of amphiphiles. However, the polymeric 2C₁₈Si monolayers were transferred with the low ratio onto the large pore size (20 nm) glass. The area per molecule of a polymer chain of 2C₁₈Si monolayers ($D_p = 300$) can be roughly calculated to be 135 nm² from the unit molecular area (0.45 nm²). The area per polymer chain is large enough to cover or traverse over the average pore area (19.5 nm²) of the 5-nm porous glass but not over the pore (314 nm²) of the 20-nm porous glass plate.

In the case of single-chain C₁₈Si monolayers, even the polymeric monolayers were not raised completely on a porous glass plate (transfer ratio 0.84), and the surface pressure decreased gradually during a transfer process. Since the molecular packing was reduced by polymerization, the monolayer was not stable enough to be transferred onto the rough surface of the porous glass. In the case of trialkyl 3C₁₈Si amphiphiles, the monolayers were not polymerized even in the acidic conditions, and monomeric amphiphiles could not be transferred with a good transfer ratio (0.73–0.78) onto the porous glass plate. Thus, only the polymeric dialkyl 2C₁₈Si monolayers can be transferred completely onto the 5-nm porous glass but not onto the large pore size (20 nm) glass plate.

Permeation Measurements. The monolayers that had been transferred from the subphase were covalently bonded with Si–O–Si linkages on a porous glass plate (size 10 \times 10 \times 9 mm, average pore diameter 5 or 20 nm) by heating. Permeation of the water-soluble probes NQ₁ through the monolayer-immobilized glass plate was followed fluorophotometrically by using the apparatus shown in Figure 1 at various temperatures below and above the phase transition (T_c) of the lipid monolayer. Arrhenius plots are shown in Figure 5, where the 5-nm porous glass plate was employed. The original, porous glass plate was semipermeable to NQ₁ probes and gave the usual straight Arrhenius plot.

In contrast, when the glass plate with the polymeric 2C₁₈Si monolayers transferred from the pH 2 subphase and covalently bonded was employed, the permeability was decreased ca. 10 times relative to that of the original glass, and the Arrhenius plot gave a discontinuity (5 times enhancement) near 44 °C, consistent with the T_c of the monolayer obtained from the temperature dependence of π - A isotherms and DSC measurements (Figure 5b). Thus, the immobilized, 2 nm-thick 2C₁₈Si monolayer can control the permeability by the phase transition from solid to liquid crystalline state. The glass plate immobilized with the monomeric 2C₁₈Si monolayer transferred from the neutral subphase was relatively permeable at low temperatures below T_c and gave a slightly curved Arrhenius plot near T_c , probably because of the low transfer ratio of monolayers and the disordered structures of monomeric monolayers in the solid state. DSC measurements have showed that the enthalpy change ($\Delta H = 2.6$ kcal mol⁻¹) of the monomeric 2C₁₈Si LB films is half that of the polymeric ones ($\Delta H = 5.5$ kcal mol⁻¹).

In the case of single-chain C₁₈Si monolayer-immobilized glass plate, the polymerized monolayer was relatively permeable compared with the monomeric one (see Figure 5a). This shows that (i) the area per molecule was increased from 0.32 to 0.42 nm² by polymerization (see Figure 2a), (ii) ΔH values at T_c were decreased from 3.4 to 1.0 kcal mol⁻¹ by polymerization, and (iii) the transfer ratio onto the 5-nm porous glass was not improved by polymerization (see Table I). In the case of the triple-chain 3C₁₈Si monolayers, both monolayers transferred from pH 2 and pH 5.8 subphases showed a similar permeability, which changed slightly near the $T_c = 55$ °C of trialkyl monolayers (Figure 5c). This reflects that 3C₁₈Si monolayers cannot be polymerized even

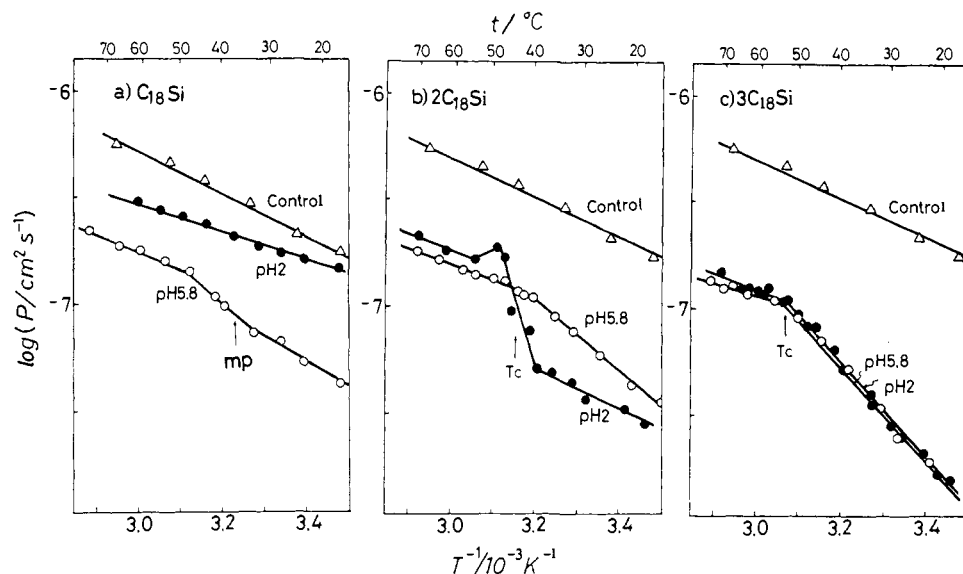


Figure 5. Arrhenius plots of permeation of NQ₁ probes through (a) C₁₈Si, (b) 2C₁₈Si, and (c) 3C₁₈Si monolayers-immobilized glass plates (5 nm pore size). Monolayers were transferred from the pH 2 and pH 5.8 subphases and immobilized on the glass by heating. Permeability through an original porous glass is shown as a control. Arrows indicate the phase-transition temperature (T_c) of each monolayer determined by the temperature dependence of π -A curves or DSC measurements.

Table I. Transfer Ratio of Silane-Functionized Monolayers on Glass Plates at 20 °C^a

monolayer	pH of subphase	surface pressure/ (mN m ⁻¹)	transfer ratio	
			flat glass	porous glass ^b
C ₁₈ Si	2	25.0 ± 0.5	0.94	0.84
	5.8	25.0 ± 0.5	0.94	0.83
2C ₁₈ Si	2	20.0 ± 0.5	1.07	1.19 (0.87) ^c
	5.8	40.0 ± 0.5	1.19	0.85
3C ₁₈ Si	2	25.0 ± 0.5	0.92	0.78
	5.8	25.0 ± 0.5	0.96	0.73

^a Transfer speed 10 mm min⁻¹. ^b Average pore diameter 5 nm, average pore volume 0.44 mL g⁻¹. ^c Porous glass plate having large pores; average pore diameter 20 nm; average pore volume 0.50 mL g⁻¹.

on the acidic condition and cannot be transferred with a good transfer ratio onto the porous glass plate.

Figure 6a shows the permeation of the relatively small probe, NaCl, through the 2C₁₈Si monolayer-immobilized glass plate. Even the polymeric monolayer was relatively permeable for a small NaCl permeant and showed only the small inflection at T_c compared with the permeation of a large NQ₁ fluorescent probe (see Figure 5b). This means that the polymeric 2C₁₈Si monolayer still has small defects, and small ions can pass or diffuse through these disorders but the large NQ₁ probes can not. In Figure 6b, Arrhenius plots of NQ₁ probe permeations when the 2C₁₈Si monolayers were transferred on a large pore size glass (average pore diameter 20 nm) are shown. The decrease of permeability and the rate enhancement near T_c were very small compared with those for the 5-nm glass plate (see Figure 5b). This reflects that the polymeric 2C₁₈Si monolayer ($D_p = 300$, area per polymer chain 135 nm²) cannot cover the large pore area (314 nm²) of the 20-nm pore glass plate and can be transferred with a low transfer ratio of 0.87 onto a large pore-size glass (see Table I).

Summary

A covalently bonded, silane-functionized monolayer on a porous glass plate can control the permeability by using the phase transition of the monolayer, depending on (i) the amphiphile structures, (ii) the polymerization of monolayers, (iii) the molecular size of permeants, and (iv) the pore sizes of the glass plate. The good results were obtained when the relatively large dye molecules permeate through the polymeric dialkyl chain 2C₁₈Si monolayer that was immobilized onto the 5-nm porous glass plate. This is the thinnest monolayer membrane to date that acts as a temperature-sensitive permeation valve. The covalently bonded

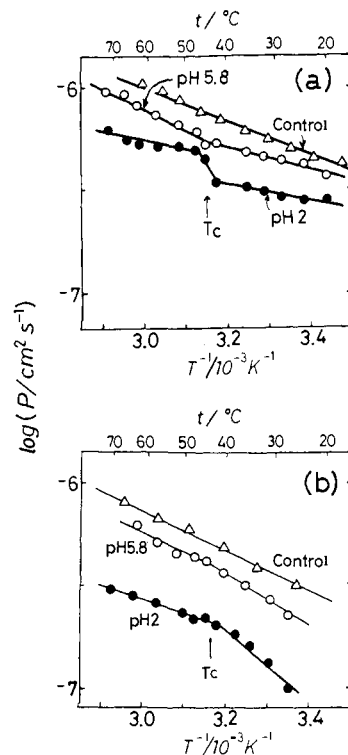


Figure 6. Arrhenius plots of (a) NaCl permeation through the polymeric (pH 2) and monomeric (pH 5.8) 2C₁₈Si monolayers immobilized on the glass plate whose average pore size is 5 nm and (b) NQ₁ permeation through the polymeric (pH 2) and monomeric (pH 5.8) 2C₁₈Si monolayers immobilized on the glass plate whose average pore size is 20 nm.

C₁₈Si, 2C₁₈Si, and 3C₁₈Si monolayers were physically stable even in a hot aqueous solution and showed a good reproducibility of permeation experiments after washing with CHCl₃ or other organic solvents several times.

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