

## Syntheses and Reactions of Metal Organics. XVIII. Syntheses of (1H,1H,2H,2H-Polyfluoroalkyl)trimethoxysilanes and Surface Modification of Glass Plate

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Four silane coupling agents, (1H,1H,2H,2H-polyfluoroalkyl)trimethoxysilanes ((1H,1H,2H,2H-henicosafuorododecyl)trimethoxysilane,  $C_{10}F_{21}C_2H_4Si(OCH_3)_3$ , (1H,1H,2H,2H-heptadecafluorododecyl)trimethoxysilane,  $C_8F_{17}C_2H_4Si(OCH_3)_3$ , (1H,1H,2H,2H-tridecafluorooctyl)trimethoxysilane,  $C_6F_{13}C_2H_4Si(OCH_3)_3$ , and (1H,1H,2H,2H-nonafluorohexyl)trimethoxysilane,  $C_4F_9C_2H_4Si(OCH_3)_3$ ), were prepared by the hydrosilylation of trichlorosilane with the corresponding 1H,1H,2H-polyfluoro-1-alkene in the presence of hydrogen hexachloroplatinate-(IV), followed by reaction with sodium methoxide. The surface modification of glass plate was attempted using these products. From measurements of the contact angles  $\theta$  ( $^\circ$ ) of water and oleic acid against a modified glass plate surface, the coupling agents were found to have high modification ability. The modification produced a glass surface with high oxidation resistance.

In general, silane coupling agents to promote surface modification and/or adhesion are the most familiar example of the  $R_nSiX_{4-n}$  ( $n=1, 2,$  and  $3$ ) class of organosilane materials having two types of substituents where R is a nonhydrolyzable organic group that may be relatively inert in one case such as a hydrocarbon radical, or may be reactive to particular organic systems in the other case. The X functionality is a hydrolyzable group; often an alkoxy group.<sup>1)</sup> In a previous paper, we reported the syntheses of fluoroalkyl and fluoroaryl titanates<sup>2)</sup> as well as the syntheses of fluoroalkyl silicates.<sup>3)</sup> Although these alkoxides were expected to be stable against moisture, since many compounds having a fluorinated carbon structure possess water repellency, all of the products were very sensitive to water and decomposed easily. We also reported the syntheses and characterizations of titanium and silicon compounds having both polyfluoroalkanoxyloxy group(s) and alkoxy group(s).<sup>4,5)</sup>

In our last paper, the syntheses of four silane coupling agents, (1H,1H,2H,2H-polyfluoroalkyl)dimethoxy(methyl)silanes, and the surface modification of glass plate using these coupling agents were reported.<sup>6)</sup> The hydrosilylation of dichloro(methyl)silane with 1H,1H,2H-polyfluoro-1-alkene was highly regioselective. In regard to water and oil repellency on the modified glass surface, (1H,1H,2H,2H-henicosafuorododecyl)dimethoxy(methyl)silane, which had the longest fluorocarbon chain of the four coupling agents, displayed the highest repellent ability. The glass surface modified with this coupling agent also displayed the highest oxidation resistance. These results were obtained by measuring the contact angles of water and oleic acid after treatment of the modified glass in hot concentrated nitric acid.

In this paper, the syntheses and characterization of four silane coupling agents, which have no methyl group

bonded to the silicon atom, are reported. The applications for the surface modification of glass plate using these coupling agents and the oxidation resistance of the modified glass surface against nitric acid were investigated by measuring the contact angles of water and oleic acid.

### Experimental

Special precautions were adopted in order to avoid hydrolysis of the starting materials and products; all experiments were carried out under an atmosphere of purified nitrogen to preclude oxygen and moisture.

**Materials.** Trichlorosilane (bp 31—32  $^\circ C$ ) was purchased from Tokyo Kasei Kogyo Co., Ltd. and used without further purification. 1H,1H,2H-Henicosafuoro-1-dodecene ( $C_{10}F_{21}CH=CH_2$ , bp 59—61  $^\circ C/345$  Pa), 1H,1H,2H-heptadecafluoro-1-decene ( $C_8F_{17}CH=CH_2$ , bp 148—149  $^\circ C$ ), 1H,1H,2H-tridecafluoro-1-octene ( $C_6F_{13}CH=CH_2$ , bp 100  $^\circ C$ ), and 1H,1H,2H-nonafluoro-1-hexene ( $C_4F_9CH=CH_2$ , bp 59  $^\circ C$ ) were purchased from Japan Halon Co., Ltd. and purified by distillation. Hydrogen hexachloroplatinate-(IV) (Kojima Chemicals Co., Ltd.) and sodium methoxide (Kanto Chemical Co., Inc.) were used without further purification. The solvents used were purified by the usual methods. Glass plate (micro slide glass, thickness 1.3 mm, 76 mm  $\times$  26 mm) was obtained from Matsunami Glass Inc., Ltd.

**Measurements.** FT-IR spectra were measured in a liquid film or by a KBr method with a JEOL JIR 5300 spectrophotometer. Each spectrum was recorded at a resolution of 4  $cm^{-1}$  with a total of 30 scans. Pulsed Fourier Transform 100-MHz  $^1H$  and 25-MHz  $^{13}C$  NMR were run in  $CDCl_3$  with TMS as an internal standard using a JEOL JNR-PX-100 spectrometer at room temperature:  $^1H$  NMR spectra (pulse repetition time, 5s; number of accumulations, 20) and  $^{13}C$  NMR spectra (pulse repetition time, 2.0 s; number of accumulations, 40000). FT mode 90-MHz  $^{19}F$  NMR was recorded at 27  $^\circ C$  on a JEOL JNM-FX-90Q in  $CDCl_3$

with fluorobenzene ( $\delta = -113.6^{\circ}$ ) from  $\text{CFCl}_3$  in  $\text{CDCl}_3$ ) as an external standard: pulse repetition time, 0.5 s; number of accumulations, 20. The assignments of the  $^1\text{H}$  NMR and  $^{19}\text{F}$  NMR spectra were referred to the data book.<sup>7)</sup> The contact angles  $\theta$  ( $^{\circ}$ ) were measured at 23  $^{\circ}\text{C}$  with an Elma-Kougaku Co. Gonio-type apparatus.

**Syntheses of (1H, 1H, 2H, 2H-Polyfluoroalkyl)-trimethoxysilanes.** **Synthesis of (1H, 1H, 2H, 2H-Henicosafuorododecyl)trimethoxysilane,  $\text{C}_{10}\text{F}_{21}\text{C}_2\text{H}_4\text{Si}(\text{OCH}_3)_3$ :** Trichlorosilane (25.0 g, 185 mmol), 1H, 1H, 2H-henicosafuoro-1-dodecene (67.2 g, 123 mmol), and a methanolic 0.1 M (1 M = 1 mol dm $^{-3}$ ) hydrogen hexachloroplatinate(IV) solution (0.20 cm $^3$ ) were put in a 200-ml glass ampoule tube with rigid exclusion of moisture. After sealing the tube under reduced pressure, the mixture was allowed to react at 100  $^{\circ}\text{C}$  for 70 h in an oil bath, then the tube was broken. The product, trichloro(1H, 1H, 2H, 2H-henicosafuorododecyl)silane was obtained by fractional distillation under reduced pressure (white solid, yield 82.6 g, 98.6%): Bp 85–86  $^{\circ}\text{C}/80$  Pa. To a stirred solution of trichloro(1H, 1H, 2H, 2H-henicosafuorododecyl)silane, 35.0 g (51.4 mmol) in 30 cm $^3$  1,1,2-trichloro-1,2,2-trifluoroethane (F-113), a methanolic 3.6 M sodium methoxide solution (65.0 cm $^3$ , 233 mmol) was added at 0  $^{\circ}\text{C}$  in a two-necked 200-ml flask connected with a three-way stop cock. After the mixture was stirred for 1 h at room temperature, the sodium chloride produced was removed by filtration. (1H, 1H, 2H, 2H-Henicosafuorododecyl)trimethoxysilane was obtained as a colorless liquid by fractional distillation under reduced pressure (yield 26.0 g, 75.8%): Bp 93–94  $^{\circ}\text{C}/53$  Pa; IR 2949, 2918, 2848, 1444, 1342, 1200, 1153, 1093, 1030, 901, 837, 812, 737, 708, 706, 661, 555, 528, and 447 cm $^{-1}$ ;  $^1\text{H}$  NMR  $\delta = 0.76$ –0.94 (2H, m, Si-CH $_2$ ), 1.82–2.42 (2H, m, CF $_2$ -CH $_2$ ), and 3.58 (9H, s, OCH $_3$ );  $^{13}\text{C}$  NMR  $\delta = -0.65$  (s, Si-CH $_2$ ), 25.1 (t,  $J = 23.4$  Hz, CF $_2$ -CH $_2$ ), 50.3 (s, OCH $_3$ ), and 95.7–136.1 (m, other carbons);  $^{19}\text{F}$  NMR  $\delta = -14.4$  (2F, m, b), -11.4 (2F, m, c), -10.7 (2F, m, d and e), -9.8 (10F, m, e-i), -5.0 (2F, m, j), and 30.4 (3F, m, a) for  $\text{CF}_3^a\text{CF}_2^b\text{CF}_2^c\text{CF}_2^d\text{CF}_2^e\text{CF}_2^f\text{CF}_2^g\text{CF}_2^h\text{CF}_2^i\text{CF}_2^j\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ .

**Syntheses of (1H, 1H, 2H, 2H-Heptadecafluorodecyl)trimethoxysilane,  $\text{C}_8\text{F}_{17}\text{C}_2\text{H}_4\text{Si}(\text{OCH}_3)_3$ , (1H, 1H, 2H, 2H-Tridecafluorooctyl)trimethoxysilane,  $\text{C}_6\text{F}_{13}\text{C}_2\text{H}_4\text{Si}(\text{OCH}_3)_3$ , and (1H, 1H, 2H, 2H-Nonafuorohexyl)trimethoxysilane,  $\text{C}_4\text{F}_9\text{C}_2\text{H}_4\text{Si}(\text{OCH}_3)_3$ :**

The synthetic methods and purification techniques were almost the same as those for the preparation of (1H, 1H, 2H, 2H-henicosafuorododecyl)trimethoxysilane.

(1H, 1H, 2H, 2H-Heptadecafluorodecyl)trimethoxysilane was obtained by fractional distillation under reduced pressure (colorless liquid, yield 59.4% vs. trichloro(1H, 1H, 2H, 2H-heptadecafluorodecyl)silane (colorless liquid, yield 86.5%, bp 95  $^{\circ}\text{C}/400$  Pa)): Bp 75–79  $^{\circ}\text{C}/93$  Pa; IR 2951, 2848, 1471, 1444, 1362, 1354, 1352, 1350, 1319, 1242, 1203, 1151, 1095, 1028, 972, 957, 899, 800, 812, 735, 708, 658, 563, 530, 445, and 401 cm $^{-1}$ ;  $^1\text{H}$  NMR  $\delta = 0.76$ –0.94 (2H, m, Si-CH $_2$ ), 1.82–2.42 (2H, m, CF $_2$ -CH $_2$ ), and 3.58 (9H, s, OCH $_3$ );  $^{13}\text{C}$  NMR  $\delta = -0.59$  (s, Si-CH $_2$ ), 25.8 (t,  $J = 23.4$  Hz, CF $_2$ -CH $_2$ ), 50.3 (s, OCH $_3$ ), and 97.3–136.1 (m, other carbons);  $^{19}\text{F}$  NMR  $\delta = -14.5$  (2F, m, b), -11.4 (2F, m, c), -10.8 (2F, m, d), -9.9 (6F, m, e-g), -5.0 (2F, m, h), and 30.4 (3F, m, a) for

$\text{CF}_3^a\text{CF}_2^b\text{CF}_2^c\text{CF}_2^d\text{CF}_2^e\text{CF}_2^f\text{CF}_2^g\text{CF}_2^h\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ .

(1H, 1H, 2H, 2H-Tridecafluorooctyl)trimethoxysilane (colorless liquid, yield 70.9% vs. trichloro(1H, 1H, 2H, 2H-tridecafluorooctyl)silane (colorless liquid, yield 98.0%, bp 43  $^{\circ}\text{C}/20$  Pa)): Bp 69–71  $^{\circ}\text{C}/280$  Pa; IR 2951, 2846, 1360, 1352, 1317, 1240, 1193, 1146, 1093, 1024, 899, 837, 812, 810, 733, and 444 cm $^{-1}$ ;  $^1\text{H}$  NMR  $\delta = 0.75$ –0.93 (2H, m, Si-CH $_2$ ), 1.87–2.42 (2H, m, CF $_2$ -CH $_2$ ), and 3.58 (9H, s, OCH $_3$ );  $^{13}\text{C}$  NMR  $\delta = -0.59$  (s, Si-CH $_2$ ), 25.2 (t,  $J = 23.4$  Hz, CF $_2$ -CH $_2$ ), 50.3 (s, OCH $_3$ ), and 97.5–136.2 (m, other carbons);  $^{19}\text{F}$  NMR  $\delta = -14.5$  (2F, m, b), -11.5 (4F, m, c and d), -10.1 (2F, m, e), -5.0 (2F, m, f), and 30.2 (3F, m, a) for  $\text{CF}_3^a\text{CF}_2^b\text{CF}_2^c\text{CF}_2^d\text{CF}_2^e\text{CF}_2^f\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ .

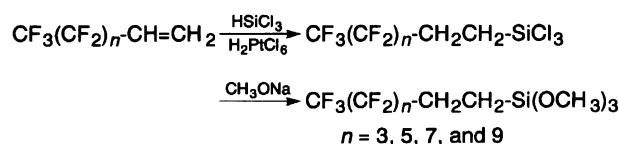
(1H, 1H, 2H, 2H-Nonafuorohexyl)trimethoxysilane (colorless liquid, yield 49.9% vs. trichloro(1H, 1H, 2H, 2H-nonafluorohexyl)silane (colorless liquid, yield 82.0%, bp 195  $^{\circ}\text{C}$ ): Bp 43  $^{\circ}\text{C}/800$  Pa; IR 2951, 2847, 1354, 1321, 1221, 1167, 1134, 1094, 901, 879, 845, 810, 760, and 445 cm $^{-1}$ ;  $^1\text{H}$  NMR  $\delta = 0.75$ –0.94 (2H, m, Si-CH $_2$ ), 1.82–2.43 (2H, m, CF $_2$ -CH $_2$ ), and 3.58 (9H, s, OCH $_3$ );  $^{13}\text{C}$  NMR  $\delta = -0.6$  (s, Si-CH $_2$ ), 25.0 (t,  $J = 24.2$  Hz, CF $_2$ -CH $_2$ ), 50.4 (s, OCH $_3$ ), and 96.3–136.3 (m, other carbons);  $^{19}\text{F}$  NMR  $\delta = -14.2$  (2F, m, b), -12.5 (2F, m, c), -5.0 (2F, m, d), and 30.3 (3F, m, a) for  $\text{CF}_3^a\text{CF}_2^b\text{CF}_2^c\text{CF}_2^d\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ .

**Surface Modification of Glass Plate.** A few plates of glass were allowed to react with the silane coupling agents in 100 cm $^3$  F-113 at various concentrations for 2 h at 47  $^{\circ}\text{C}$  (boiling point) under an atmosphere of purified nitrogen. The surface-modified glass was rinsed with fresh F-113 and dried. After the glass was treated thermally in an oven at 150  $^{\circ}\text{C}$  for 2 h, the contact angles of water and oleic acid were measured against these glass samples. The contact angles  $\theta$  ( $^{\circ}$ ) were measured using  $1.0 \times 10^{-6}$  dm $^3$  of water or oleic acid drops. The contact angles were evaluated by extrapolating to time zero from a plot of the advancing contact angle vs. time.<sup>8)</sup>

**Measurement of Oxidation Resistance of Modified Glass Surface.** The surface-modified glass plates which were treated with four types of coupling agents in a 30 mM F-113 solution were heated in 100 cm $^3$  concentrated nitric acid for 30, 60, 90, and 120 min at 100  $^{\circ}\text{C}$ . After oxidation, each sample was rinsed with water and dried at room temperature for 1 d. Then, the contact angles for water and oleic acid were measured as described above.

## Results and Discussion

**Syntheses.** The synthetic processes are shown in Scheme 1. The syntheses of trichloro(1H, 1H, 2H, 2H-polyfluoroalkyl)silanes in high yields were achieved successfully using the reaction in sealed glass ampoules. In general, Si-CH $_2$ -CH $_2$ -X-type compounds were mainly formed by the platinum-catalyzed addition reaction of the compounds containing Si-H bonding with the compounds having a general formula CH $_2$ =CH-X, where



Scheme 1.

the X group is not conjugated with C=C.<sup>9</sup>) From the <sup>1</sup>H NMR spectra of the (1H,1H,2H,2H-polyfluoroalkyl)-trimethoxysilanes, only three kinds of proton signals, such as Si-CH<sub>2</sub>, Si-CH<sub>2</sub>-CH<sub>2</sub>, and Si-OCH<sub>3</sub> were observed in every compound, and another proton signal, such as Si-CH or Si-CH-CH<sub>3</sub>, was not observed. The same phenomena were observed in <sup>13</sup>C NMR spectra measurements. These results indicated that the hydrosilylation reaction of trichlorosilane with 1H,1H,2H-polyfluoro-1-alkene was highly regioselective.

**Surface Modification of Glass.** Figures 1 and 2 show the results of the contact angles of water and oleic acid, respectively. These data clearly showed that the contact angles on the surface of modified glass were dependent on the fluorocarbon chain length. From the modification of the glass surface by using the silane coupling agents, it was found that the hydrophilic glass surface could be covered effectively by the longer fluorocarbon chains. Consequently, the effect on the contact angles of the hydrocarbon moiety, Si-CH<sub>2</sub>-CH<sub>2</sub>-, was reduced according to an increment of *n* of -(CF<sub>2</sub>)<sub>*n*</sub>CF<sub>3</sub>. In conclusion, these data indicated that the fluorocarbon, which displayed water and oil repellency, was increased on the top-surface (see Fig. 3) of the modified glass with the length of the fluorocarbon chain. The largest contact angles of water on the modified glass surface were 118°. This contact angle was larger than that of poly(tetrafluoroethylene) (110°).<sup>10</sup> In regard to water and oil repellency on the modified glass surface, (1H,1H,2H,2H-henicosafuorododecyl)trimethoxysilane displayed the highest repellent ability. The contact angles of water on the glass surface modified with (1H,1H,2H,2H-henicosafuorododecyl)dimethoxy-

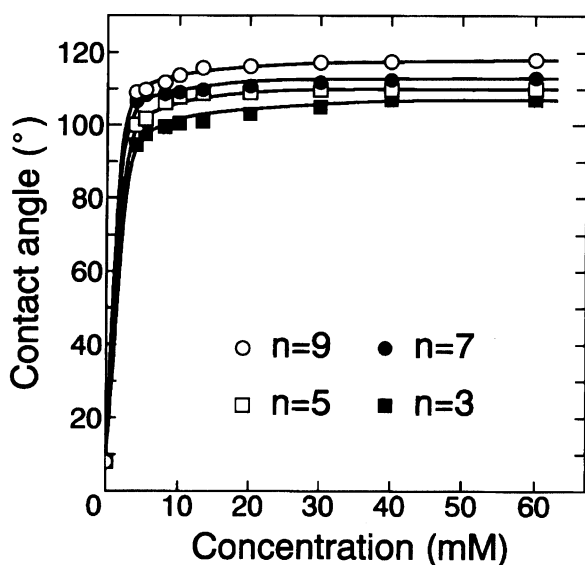


Fig. 1. Relation between contact angles  $\theta$  ( $^{\circ}$ ) of water against the surface-modified glass plate and the concentration of silane coupling agents. The symbol *n* is the number of CF<sub>2</sub> groups in CF<sub>3</sub>(CF<sub>2</sub>)<sub>*n*</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>3</sub>)<sub>3</sub>.

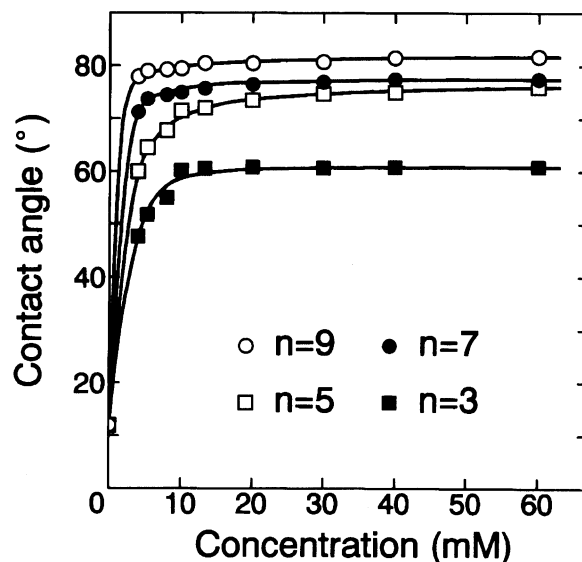


Fig. 2. Relation between contact angles  $\theta$  ( $^{\circ}$ ) of oleic acid against the surface-modified glass plate and the concentration of silane coupling agents. The symbol *n* is the number of CF<sub>2</sub> groups in CF<sub>3</sub>(CF<sub>2</sub>)<sub>*n*</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>3</sub>)<sub>3</sub>.

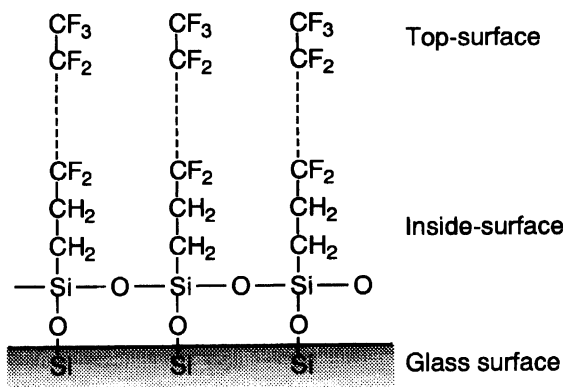


Fig. 3. Possible illustration of the glass surface modified with (1H,1H,2H,2H-polyfluoroalkyl)trimethoxysilanes.

(methyl)silane, which contains the same fluorocarbon chain length, were 110°.<sup>9</sup>) The difference in contact angle may be caused by the structural difference of the silane coupling agents. The glass surface modified with (1H,1H,2H,2H-henicosafuorododecyl)trimethoxysilane has no Si-CH<sub>3</sub>, which can not increase the contact angles in comparison with the fluorocarbon chain, and the fluorocarbon chains tend to pack together to construct the siloxane networks. In other words, the top-surface modified with (1H,1H,2H,2H-henicosafuorododecyl)-trimethoxysilane was more enriched with fluorocarbon chain than that modified with (1H,1H,2H,2H-henicosafuorododecyl)dimethoxy(methyl)silane.

**Surface Free Energy of the Modified Surface.** From Eqs. 1 and 2, the solid surface free energy can be estimated by use of the contact angles  $\theta$  ( $^{\circ}$ ) obtained

from two different liquids against a solid.<sup>11-15)</sup>

$$\gamma_S = \gamma_S^d + \gamma_S^p \quad (1)$$

$$\gamma_L(1 + \cos \theta) = 2\sqrt{\gamma_S^d \gamma_L^d} + 2\sqrt{\gamma_S^p \gamma_L^p} \quad (2)$$

Where  $\gamma_S$  and  $\gamma_L$  are the solid surface free energy and the liquid surface tension, respectively, and superscripts d and p refer to the dispersion force and polar components, respectively. The values of the  $\gamma_L$ ,  $\gamma_L^d$ , and  $\gamma_L^p$  of water are 72.8, 21.8, and 51.0 ( $\text{mJ m}^{-2}$ ),<sup>13)</sup> and those of oleic acid are 30.4, 19.3, and 11.1 (catalog data of Japan Oil & Fats Co., Ltd.), respectively. The contact angles  $\theta$  ( $^\circ$ ) of water and oleic acid on the modified surfaces (modified with 60 mM solution and  $n=3, 5, 7,$  and 9) are shown in Table 1. These data were used for the estimation of the surface free energy of the modified glass, and the results are shown in Table 2. From these data, significant differences of the surface free energy between  $n=5, 7,$  and 9 were not confirmed.

**Oxidation Resistance against Modified Glass Surface.** After oxidation of the surface-modified glass by hot concentrated nitric acid, the contact angles of water and oleic acid were measured. Figures 4 and 5 show the results of the contact angles for water and oleic acid, respectively. The contact angles of the glass surface modified with (1H,1H,2H,2H-polyfluoroalkyl)trimethoxysilane were reduced slightly by the oxidation. These reduction rates were smaller than those of (1H,1H,2H,2H-polyfluoroalkyl)dimethoxy(methyl)silanes treatment.<sup>6)</sup> The same phenomena were observed in the case of oleic acid. These results indicated that the reduction of the contact angles on the oxidized glass surface was also dependent on the fluorocarbon chain

Table 1. The Contact Angles  $\theta$  ( $^\circ$ ) of Water and Oleic Acid on the Modified Surfaces Treated with 60 mM Silane Coupling Solution

Liquids	$n^a)$			
	3	5	7	9
Water	107.0	110.0	113.0	118.0
Oleic acid	60.9	76.0	77.5	81.8

a) The symbol  $n$  is the number of  $\text{CF}_2$  groups in (1H,1H,2H,2H-polyfluoroalkyl)trimethoxysilane [ $\text{CF}_3(\text{CF}_2)_n\text{-CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ ].

Table 2. The Surface Free Energy of the Modified Glass Surface Treated with 60 mM Silane Coupling Solution

Energy ( $\text{mJ m}^{-2}$ )	$n^a)$			
	3	5	7	9
$\gamma_S^d$	22.8	12.1	13.5	14.2
$\gamma_S^p$	0.2	1.2	0.5	0.1
$\gamma_S$	23.0	13.3	14.0	14.3

a) The symbol  $n$  is the number of  $\text{CF}_2$  groups in (1H,1H,2H,2H-polyfluoroalkyl)trimethoxysilane [ $\text{CF}_3(\text{CF}_2)_n\text{-CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ ].

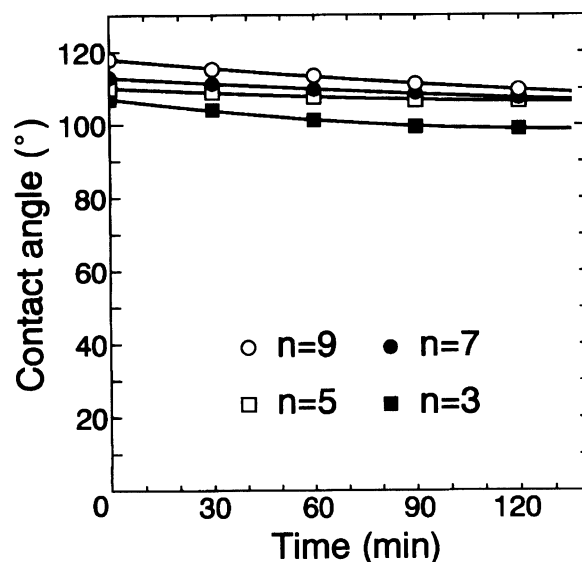


Fig. 4. Relation between contact angles  $\theta$  ( $^\circ$ ) of water against the oxidized glass surface and the oxidation time in nitric acid. The symbol  $n$  is the number of  $\text{CF}_2$  groups in  $\text{CF}_3(\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ .

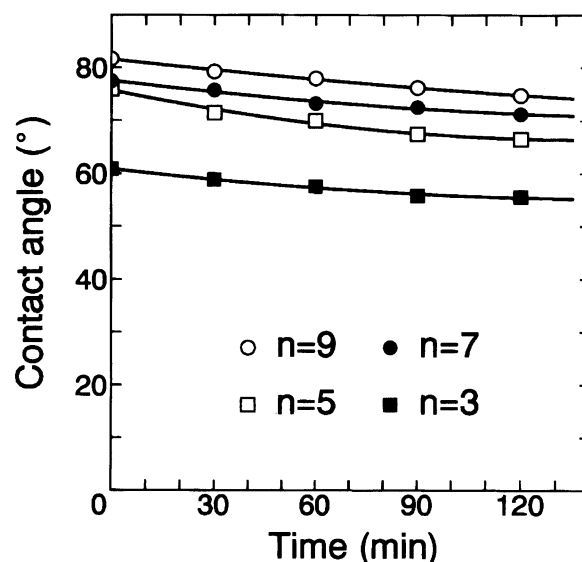


Fig. 5. Relation between contact angles  $\theta$  ( $^\circ$ ) of oleic acid against the oxidized glass surface and the oxidation time in nitric acid. The symbol  $n$  is the number of  $\text{CF}_2$  groups in  $\text{CF}_3(\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ .

length. The effect on the contact angle reduction by the oxidation was reduced by removing the  $\text{Si-CH}_3$  structure from the silane coupling agents having a fluorocarbon chain.

The estimation method for the surface free energy mentioned above was applied for the oxidized surface. These data (Table 3) show that the most minimum change of the surface free energy on the glass surface modified with (1H,1H,2H,2H-henicosafuorododecyl)-trimethoxysilane ( $n=9$ ) was observed by nitric acid oxidation.

Table 3. The Surface Free Energy of the Oxidized Modified-Surfaces vs. Oxidation Time

Oxidation time(min)	Energy (mJ m <sup>-2</sup> )	n <sup>a)</sup>			
		3	5	7	9
30	$\gamma_s^d$	21.3	15.0	13.4	14.0
	$\gamma_s^p$	0.7	0.8	0.7	0.2
	$\gamma_s$	22.0	15.8	14.1	14.2
60	$\gamma_s^d$	19.1	15.1	14.2	13.5
	$\gamma_s^p$	1.5	1.0	0.8	0.4
	$\gamma_s$	20.6	16.1	15.0	13.9
90	$\gamma_s^d$	18.6	16.2	13.9	13.0
	$\gamma_s^p$	2.1	1.0	1.0	0.8
	$\gamma_s$	20.7	17.2	14.9	13.8
120	$\gamma_s^d$	18.2	17.0	13.6	12.9
	$\gamma_s^p$	2.3	0.9	1.3	1.1
	$\gamma_s$	20.5	17.9	14.9	14.0

a) The symbol  $n$  is the number of CF<sub>2</sub> groups in (1H, 1H,2H,2H-polyfluoroalkyl)trimethoxysilane [CF<sub>3</sub>(CF<sub>2</sub>) <sub>$n$</sub> -CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>3</sub>)<sub>3</sub>].

In our glass modification method, the silane coupling agents were allowed to react with hydroxyl groups on the glass surface, the unreactive coupling agents were removed by washing with F-113, and then the surfaces were treated thermally to make the siloxane network. It is well known that scientific information between a surface and ca. 50 Å depth under the surface can be obtained from ESCA measurements. From the ESCA measurement against the modified glass surface, a Na peak could be observed.<sup>6)</sup> It may be indicated that the depth of the siloxane network should be less than 50 Å, if the surfaces were completely covered with the siloxane network. We then made a thick siloxane film using (1H,1H,2H,2H-henicosafuorododecyl)trimethoxysilane by spreading it on a glass surface (without washing with F-113) and treating it thermally in an oven at 150 °C for 2 h, and measured the contact angle of water on the film. The contact angle was 115°. In the case of this siloxane film, the top-surfaces may not be composed of fluorocarbons (CF<sub>2</sub> and CF<sub>3</sub>) only, but may contain Si-O-Si, Si-C, and so on. The value of the contact angle (115°) was slightly lower than the modified glass surface (118°). From these results of the observation of Na by ESCA measurements and the contact angle of water on the siloxane film, it is proposed that the siloxane network of the modified glass surface may be a monolayer and the top-surface should be CF<sub>3</sub>, because the contact angle is larger than that of poly(tetrafluoroethylene). Moreover, these results indicate that the covering rate of the siloxane network on the modified surface is very high.

From the ESCA results in the last paper,<sup>6)</sup> the authors discussed two possible mechanisms of contact angle reduction by oxidation. The first possibility was

that the reduction was caused by the oxidation of a hydrocarbon moiety existing in the inside-surface (see Fig. 3) of the modified glass. The second was that some of the Si-O-Si bonds formed by the condensation reaction of the silane coupling agents with the glass surface were hydrolyzed by the reaction with water in hot concentrated nitric acid; thus -Si-O-Si-Glass → -Si-OH + HO-Si-Glass.

After treatment of the modified glass in concentrated hydrochloric acid, which has no oxidation ability, in the same way as the treatment in nitric acid, the contact angles of water were not reduced at all. From this result, the idea that the oxidation of the hydrocarbon moiety in these silane coupling agents led to the contact angle reduction is supported. The high oxidation resistance of the modified surface by treating with silane coupling agents having longer fluorocarbon chains must be come from the oxidation-protection ability against the inside-surface by fluorocarbon chains possessing high C-F bond energy (115.7 kcal mol<sup>-1</sup> (1 kcal=4.184 kJ)<sup>10)</sup>).

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