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Syntheses and Reactions of Metal Organics. XVII. Synthesis of Silane Coupling Agent Having Fluorocarbon Chain and Surface Modification of Glass Plate

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Four silane coupling agents, 1H, 1H, 2H, 2H-polyfluoroalkyl(dimethoxy)(methyl)silanes (1H, 1H, 2H, 2H-henicosafluorododecyl(dimethoxy)(methyl)silane, $C_{10}F_{21}C_2H_4Si(CH_3)(OCH_3)_2$, 1H,1H,2H,2H-heptadecafluorodecyl(dimethoxy)(methyl)silane, $C_8F_{17}C_2H_4Si(CH_3)(OCH_3)_2$, 1H,1H,2H,2H-tridecafluorooctyl(dimethoxy)(methyl)silane, $C_6F_{13}C_2H_4Si(CH_3)(OCH_3)_2$, and 1H, 1H, 2H, 2H-nonafluorohexyl(dimethoxy)(methyl)silane, $C_4F_9C_2H_4Si(CH_3)(OCH_3)_2$), were prepared by the hydrosilylation of dichloro(methyl)silane with the corresponding 1H,1H,2H-polyfluoro-1-alkene in the presence of hydrogen hexachloroplatinate(IV), followed by the 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 oxidation resistance of the modified glass surface was also investigated.

Metal alkoxides have been the subject of extensive research owing to their potential as precursor materials for several applications, such as new ceramics, adhesives, and coupling agents, which are due to molecular bridges between the interfaces of an inorganic filler and an organic polymer. A number of worldwide commercial applications for coupling agents made from monoalkoxyl-type titanates like titanium isopropoxide tris(2-heptylundecanoyloxide) are now very substantial as indicated by more than hundred patents.[1—4]

Recently, dramatic developments have been made in the utilization of organofluoro compounds as new high-performance materials. In our previous paper, the syntheses of fluoroalkyl and fluoroaryl titanates[5] as well as fluoroalkyl silicates were reported.[6] Although these alkoxides were expected to be stable against moisture from the general water repellency of the fluorinated carbon structure, all the products were very sensitive to water to be readily decomposed. We also reported on the syntheses and characterization of titanium butoxide tris(polyfluoroalkanoate)s[7] and dimethoxysilanediyl bis(polyfluoroalkanoate)s.[8] The Ti–OR bond was hydrolyzable in the titanium compounds,[7] but the Ti–OCORf (Rf=polyfluoroalkyl group) bond was relatively stable in water. However, in the silicon compounds[8] the moieties of the SiOCORf and the SiOR were hydrolyzed with exactly the same ease and these compounds were decomposed easily by atmospheric moisture. Then, these silicon compounds could not be applied for surface modification.

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 alkoxyl group.

In this paper, the syntheses and characterization of four silane coupling agents, which have a nonhydrolyzable Si–C linkage with a polyfluoroalkyl group, 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 the use of nitric acid were investigated by measuring the contact angles of water and oleic acid. As a contamination in our daily life has been thought to be produced from oil and fats in many cases, oleic acid was used for an example of oil and fats.

Experimental

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

Materials. Dichloro(methyl)silane (bp 41°C), 1H,1H,2H-henicosafluoro-1-dodecene ($C_{10}F_{21}CH{=}CH_2$, bp 59—61°C/345 Pa), 1H, 1H, 2H-heptadecafluoro-1-decene ($C_8F_{17}CH{=}CH_2$, bp 148—149°C), 1H,1H,2H-tridecafluoro-1-octene($C_6F_{13}CH{=}CH_2$, bp 100°C), and 1H,1H,2H-nonafluoro-1-hexene ($C_4F_9CH{=}CH_2$, bp 59°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, 76×26 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, 2.0s; number of accumulations, 40000). The FT mode 90-MHz ^{19}F NMR was recorded at 27°C on a JEOL JNM-FX-90Q in $CDCl_3$ with fluorobenzene ($\delta=-113.6$ ppm[9]) from $CFCl_3$ in $CDCl_3$) as an external standard; pulse repetition time, 0.5s; number of accumulations, 20. The assignments of the ^1H NMR and ^{19}F NMR spectra were referred to the data book.[9] Gas chromatography was performed with a Hitachi 663-30 (G-100 40 m column, film thickness 2.0×10^{-6} m, I.D. 1.2 mm, FID) and the intensities were, measured with a Hitachi D-2500 chromato integrator. The contact angles θ(°) were measured at 23°C with a Elma-Kougaku Co. Gonio-type apparatus. ESCA data were taken with a Shimadzu ESCA-750.

Syntheses of Dichloro(1H,1H,2H,2H-polyfluoroalkyl)(methyl)silanes. Synthesis of Dichloro (1H, 1H, 2H, 2H- Henicosafluorododecyl)(methyl)silane, $C_{10}F_{21}C_2H_4Si(CH_3)Cl_2$: Dichloro(methyl)silane (15.8 g, 137 mmol), 1H,1H,2H-henicosafluoro-1-dodecene (49.9 g, 91.3 mmol), and 0.1 M (1 M=1 mol dm^{-3}) methanol solution of hydrogen hexachloroplatinate(IV) (0.15 cm^3) were put in a 200-ml glass ampoule tube with rigid exclusion of moisture. After sealing of the tube in reduced pressure, the mixture was allowed to react at 100°C for 50 h in an oil bath, then the tube was broken. The product, dichloro(1H,1H,2H,2H-henicosafluorododecyl)(methyl)silane was obtained by fractional distillation under reduced pressure (white solid, yield 54.1 g, 89.5%): Bp 113—115°C/320 Pa, mp 53°C; IR 2971, 2910, 1375, 1342, 1207, 1149, 1111, 1076, 1070, 1022, 899, 881, 831, 787, 752, 733, 712, 690, 663, 642, 557, 526, 465, and 418 cm^{-1}; ^1H NMR $\delta=0.86$ (3H, s, CH_3), 1.25—1.42 (2H, m, $Si-CH_2$), and 1.95—2.56 (2H, m, CF_2-CH_2); ^{13}C NMR $\delta=4.79$ (s, CH_3), 11.9 (s, $Si-CH_2$), 25.1 (t, $J=23.4$ Hz, $CF_2-\underline{C}H_2$), and 98.5—124.5 (m, another carbons); ^{19}F NMR $\delta=-13.0$ (2F, m, b), −9.8 (4F, m, c and d,), −8.5 (10F, m, e-i), −2.4 (2F, m, j), and 32.1 (3F, t, $J=9.2$ Hz, a) for $CF_3^aCF_2^bCF_2^cCF_2^dCF_2^eCF_2^fCF_2^gCF_2^hCF_2^iCF_2^jCH_2CH_2Si(CH_3)Cl_2$. Although the synthesis of dichloro(1H,1H,2H,2H-henicosafluorododecyl)(methyl)silane was carried out at 41°C (bp of dichloro(methyl)silane) in atmospheric pressure for 50 h in a two-necked 200-ml flask, the yield was only 12.6%.

Syntheses of Dichloro(1H,1H,2H,2H-Heptadecafluorodecyl)(methyl)silane, $C_8F_{17}C_2H_4Si(CH_3)Cl_2$, Dichloro(1H, 1H, 2H, 2H- Tridecafluorooctyl)(methyl)silane, $C_6F_{13}C_2H_4Si(CH_3)Cl_2$, and Dichloro(1H, 1H,2H,2H-Nonafluorohexyl)(methyl)silane, $C_4F_9C_2H_4Si(CH_3)Cl_2$: The procedures and purification techniques were almost the same as those for the preparation of dichloro(1H,1H,2H,2H-henicosafluorododecyl)(methyl)silane.

Dichloro(1H,1H,2H,2H-heptadecafluorodecyl)(methyl)silane was a colorless liquid (yield 92.9%): Bp 82—83°C/225 Pa; IR 2953, 2912, 1508, 1443, 1421, 1419, 1365, 1319, 1242, 1205, 1151, 1115, 1072, 1024, 972, 957, 930, 897, 872, 833, 827, 791, 746, 723, 704, 658, 621, 557, 540, and 474 cm^{-1}; ^1H NMR $\delta=0.84$ (3H, s, CH_3), 1.25—1.43 (2H, m, $Si-CH_2$), and 1.96—2.56(2H, m, CF_2-CH_2); ^{13}C NMR $\delta=4.85$ (s, CH_3), 12.0 (s, $Si-CH_2$), 25.1 (t, $J=23.4$ Hz, $CF_2-\underline{C}H_2$), and 98.7—124.5 (m, another carbons); ^{19}F NMR $\delta=-12.9$ (2F, m, b), −9.7 (4F, m, c and d), −8.5 (6F, m, e—g), −2.4 (2F, m, h), and 32.3 (3F, t, $J=9.2$ Hz, a) for $CF_3^aCF_2^bCF_2^cCF_2^dCF_2^eCF_2^fCF_2^gCF_2^hCH_2CH_2Si(CH_3)Cl_2$.

Dichloro(1H,1H,2H,2H-tridecafluorooctyl)(methyl)silane was a colorless liquid (yield 81.5%): Bp 69—70°C/440 Pa; IR 2980, 2954, 2912, 1443, 1420, 1365, 1363, 1317, 1209, 1146, 1120, 1070, 1020, 951, 897, 829, 812, 791, 748, 735, 733, 708, 706, 648, 604, 540, and 474 cm^{-1}; ^1H NMR $\delta=0.84$ (3H, s, CH_3), 1.24—1.46 (2H, m, $Si-CH_2$), and 1.96—2.57 (2H, m, CF_2-CH_2); ^{13}C NMR $\delta=5.0$ (s, CH_3), 12.1(s, $Si-CH_2$), 25.3 (t, $J=23.5$ Hz, $CF_2-\underline{C}H_2$), and 97.4—134.9 (m, another carbons); ^{19}F NMR $\delta=-14.0$ (2F, m, b), −10.7 (4F, m, c and d), −9.5 (2F, m, e), −3.6 (2F, m, f), and 30.9 (3F, m, a) for $CF_3^aCF_2^bCF_2^cCF_2^dCF_2^eCF_2^fCH_2CH_2Si(CH_3)Cl_2$.

Dichloro(1H, 1H, 2H, 2H- nonafluorohexyl)(methyl)silane was a colorless liquid (yield 92.2%): Bp 48—49°C/30 Pa; IR 2980, 2954, 2912, 1538, 1443, 1419, 1356, 1321, 1267, 1223, 1169, 1134, 1072, 1043, 1011, 930, 928, 897, 879, 847, 829, 791, 737, 735, 690, 646, 594, 540, and 474 cm^{-1}; ^1H NMR $\delta=0.84$ (3H, s, CH_3), 1.24—1.46 (2H, m, $Si-CH_2$), and 1.98—2.56 (2H, m, CF_2-CH_2); ^{13}C NMR $\delta=5.0$ (s, CH_3), 11.9 (t, $J=3.7$ Hz, $Si-CH_2$), 25.1 (t, $J=23.8$ Hz, $CF_2-\underline{C}H_2$), and 97.7—136.3 (m, another carbons); ^{19}F NMR $\delta=-13.8$ (2F, m, b), −11.9 (2F, m, c), −3.6 (2F, m, d), and 30.9 (3F, m, a) for $CF_3^aCF_2^bCF_2^cCF_2^dCH_2CH_2Si(CH_3)Cl_2$.

Syntheses of 1H,1H,2H,2H-Polyfluoroalkyl(dimethoxy)(methyl)silanes. Synthesis of 1H,1H,2H,2H-Henicosafluorododecyl(dimethoxy)(methyl)silane, $C_{10}F_{21}C_2H_4Si(CH_3)(OCH_3)_2$: To a stirred solution of dichloro(1H,1H,2H,2H-henicosafluorododecyl)(methyl)silane, 20.0 g (30.3 mmol) in 30 cm^3 1,1,2-trichloro-1,2,2-trifluoroethane (F-113), a methanolic 2 M sodium methoxide solution 31.0 cm^3 (62 mmol) was added at 0°C into a two-necked 200-ml flask connected with a three-way stop cock. After the mixture was stirred for 1 h at room temperature, sodium chloride produced was removed by filtration. 1H,1H,2H,2H-Henicosafluorododecyl(dimethoxy)(methyl)silane was obtained as a colorless liquid by fractional distillation under reduced pressure (yield 9.52 g, 48.3%): Bp 108—109°C/400 Pa; IR 2947, 2843, 1508, 1471, 1444, 1423, 1362, 1340, 1317, 1246, 1151, 1093, 1028, 987, 901, 843, 812, 779, 735, 733, 710, 661, 555, and 528 cm^{-1}; ^1H NMR $\delta=0.16$ (3H, s, CH_3), 0.71—1.01 (2H, m, $Si-CH_2$), 1.77—2.40 (2H, m, CF_2-CH_2), and 3.52 (6H, s, OCH_3); ^{13}C NMR $\delta=-6.3$ (s, CH_3), 3.1 (s, $Si-CH_2$), 25.0 (t, $J=23.2$ Hz, $CF_2-\underline{C}H_2$), 50.1 (s, OCH_3), and 97.1—136.0 (m, another carbons); ^{19}F NMR $\delta=-14.4$ (2F, m, b), −11.3 (2F, m, c), −10.7 (2F, m, d), −9.7 (10F, m, e—i), −4.7 (2F, m, j), and 30.4 (3F, m, a) for $CF_3^aCF_2^bCF_2^cCF_2^dCF_2^eCF_2^fCF_2^gCF_2^hCF_2^iCF_2^jCH_2CH_2Si(CH_3)(OCH_3)_2$.

Syntheses of 1H,1H,2H,2H-Heptadecafluorodecyl(dimethoxy)(methyl)silane, $C_8F_{17}C_2H_4Si(CH_3)(OCH_3)_2$, 1H, 1H, 2H, 2H- Tridecafluorooctyl(dimethoxy)(methyl)silane, $C_6F_{13}C_2H_4Si(CH_3)(OCH_3)_2$, and 1H, 1H, 2H, 2H- Nonafluorohexyl(dimethoxy)(methyl)silane, $C_4F_9C_2H_4Si(CH_3)(OCH_3)_2$: The synthetic methods and purification techniques were almost the same as those for the preparation of 1H,1H,2H,2H-henicosafluorododecyl(dimethoxy)(methyl)silane.

1H,1H,2H,2H-Heptadecafluorodecyl(dimethoxy)(methyl)silane was obtained by fractional distillation under reduced pressure (colorless liquid, yield 70.7%): Bp 98°C/930 Pa; IR 2947, 2843, 1508, 1446, 1362, 1354, 1319, 1211, 1151, 1092, 1028, 972, 928, 901, 843, 812, 779, 739, 731, 704, 656, 590, 588, 559, 555, and 530 $\mathrm{cm^{-1}}$; ^{1}H NMR $\delta=0.16$ (3H, s, $\mathrm{CH_3}$), 0.71—1.01 (2H, m, $\mathrm{Si{-}CH_2}$), 1.77—2.40 (2H, m, $\mathrm{CF_2{-}CH_2}$), and 3.51 (6H, s, $\mathrm{OCH_3}$); ^{13}C NMR $\delta=-6.3$ (s, $\mathrm{CH_3}$), 3.2 (s, $\mathrm{Si{-}CH_2}$), 25.1 (t, $J=23.8$ Hz, $\mathrm{CF_2{-}\underline{C}H_2}$), 50.1 (s, $\mathrm{OCH_3}$), and 97.2—136.0 (m, another carbons); ^{19}F NMR $\delta=-14.4$ (2F, m, b), -11.3 (2F, m, c), -10.8 (2F, m, d), -9.8 (6F, m, e—g), -4.7 (2F, m, h), and 30.5 (3F, m, a) for $\mathrm{CF_3^aCF_2^bCF_2^cCF_2^dCF_2^eCF_2^fCF_2^gCF_2^hCH_2CH_2Si(CH_3)(OCH_3)_2}$.

1H, 1H, 2H, 2H- Tridecafluorooctyl(dimethoxy)(methyl)silane (colorless liquid, yield 53.8%): Bp 90°C/930 Pa; IR 2947, 2943, 1508, 1444, 1423, 1365, 1362, 1352, 1317, 1240, 1193, 1146, 1092, 1024, 949, 899, 843, 812, 779, 735, 731, 708, 654, 627, 625, 565, and 530 $\mathrm{cm^{-1}}$; ^{1}H NMR $\delta=0.16$ (3H, s, $\mathrm{CH_3}$), 0.71—1.01 (2H, m, $\mathrm{Si{-}CH_2}$), 1.77—2.40 (2H, m, $\mathrm{CF_2{-}CH_2}$), and 3.52 (6H, s, $\mathrm{OCH_3}$); ^{13}C NMR $\delta=-6.3$ (s, $\mathrm{CH_3}$), 3.2 (t, $J=3.1$ Hz, $\mathrm{Si{-}CH_2}$), 25.0 (t, $J=23.8$ Hz, $\mathrm{CF_2{-}\underline{C}H_2}$), 50.1(s, $\mathrm{OCH_3}$), and 97.2—136.2 (m, another carbons); ^{19}F NMR $\delta=-14.3$ (2F, m, b), -11.2 (4F, m, c and d), -9.8 (2F, m, e), -4.7 (2F, m, f), and 30.4 (3F, m, a) for $\mathrm{CF_3^aCF_2^bCF_2^cCF_2^dCF_2^eCF_2^fCH_2CH_2Si(CH_3)(OCH_3)_2}$.

1H,1H,2H,2H-Nonafluorohexyl(dimethoxy)(methyl)silane (colorless liquid, yield 60.9%): Bp 90°C/930 Pa; IR 2947, 2845, 2916, 1508, 1444, 1423, 1354, 1321, 1265, 1263, 1134, 1090, 1042, 1011, 928, 901, 879, 843, 810, 739, 735, 706, 688, 663, 621, 592, 528, 463, and 459 $\mathrm{cm^{-1}}$; ^{1}H NMR $\delta=0.16$ (3H, s, $\mathrm{CH_3}$), 0.75—0.95 (2H, m, $\mathrm{Si{-}CH_2}$), 1.80—2.42 (2H, m, $\mathrm{CF_2{-}CH_2}$), and 3.52 (6H, s, $\mathrm{OCH_3}$); ^{13}C NMR $\delta=-6.3$ (s, $\mathrm{CH_3}$), 3.1 (t, $J=2.4$ Hz, $\mathrm{Si{-}CH_2}$), 25.0 (t, $J=23.8$ Hz, $\mathrm{CF_2{-}\underline{C}H_2}$), 50.1 (s, $\mathrm{OCH_3}$), and 97.7—135.0 (m, another carbons); ^{19}F NMR $\delta=-14.2$ (2F, m, b), -12.3 (4F, m, c), -4.7 (2F, m, d), and 30.3 (3F, m, a) for $\mathrm{CF_3^aCF_2^bCF_2^cCF_2^dCH_2CH_2Si(CH_3)(OCH_3)_2}$.

Surface Modification of Glass Plate. A few plates of glass were allowed to react with the aforesaid silane coupling agents in 100 $\mathrm{cm^3}$ F-113 at various concentration for 2 h at 47°C (boiling point). The solvent, F-113, is a good solvent against these coupling agents. The surface modified glass was rinsed with flesh F-113 and dried. After the glass was treated thermally in an oven at 150°C for 2 h, the contact angles of water and oleic acid were measured against these glass samples. The contact angles θ(°) were measured using 1.0×10^{-6} $\mathrm{dm^3}$ 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.[10]

Measurement of Oxidation Resistance against Modified Glass Surface. The surface modified glass plates which were treated with four types of coupling agents at the concentration of 30 mM F-113 solution were heated in 100 $\mathrm{cm^3}$ concentrated nitric acid for 30, 60, 90, and 120 min at 100°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 same as described above.

Results and Discussion

Syntheses. The syntheses of dichloro(1H,1H,2H, 2H-polyfluoroalkyl)(methyl)silanes in high yield were achieved successfully by using the reaction in sealed glass ampoule. In general, $\mathrm{Si{-}CH_2{-}CH_2{-}X}$ type compounds were mainly formed by platinum-catalyzed addition reaction of the compounds containing Si–H bonding with the compounds having general formula of $\mathrm{CH_2{=}CH{-}X}$, where X group is not conjugated with C=C.[11] From the ^{1}H NMR spectra of dichloro(1H,1H, 2H,2H-polyfluoroalkyl)(methyl)silanes, only three kinds of proton signals, such as $\mathrm{Si{-}C\underline{H}_2}$, $\mathrm{Si{-}CH_2{-}C\underline{H}_2}$, and $\mathrm{Si{-}C\underline{H}_3}$, were observed in every compound, and another proton signal, such as $\mathrm{Si{-}C\underline{H}}$ or $\mathrm{Si{-}CH{-}C\underline{H}_3}$, was not observed at least. The same phenomena were observed from ^{13}C NMR spectra measurements. These results indicated that the hydrosilylation reaction of dichloro(methyl)silane with 1H,1H,2H-polyfluoro-1-alkene was high regioselective.

Modification of Glass Surface. Figures 1 and 2 show the results of 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 glass surface by using the silane coupling agents, hydrophilic glass surface could be covered effectively by the longer fluorocarbon chains. Consequently, the effect on the contact angles of the hydrocarbon moieties, such as $\mathrm{Si{-}CH_3}$ and $\mathrm{Si{-}CH_2{-}CH_2{-}}$, were reduced according to an increment of n of $-(\mathrm{CF_2})_n\mathrm{CF_3}$. In conclusion, these data indicated that the top-sur-

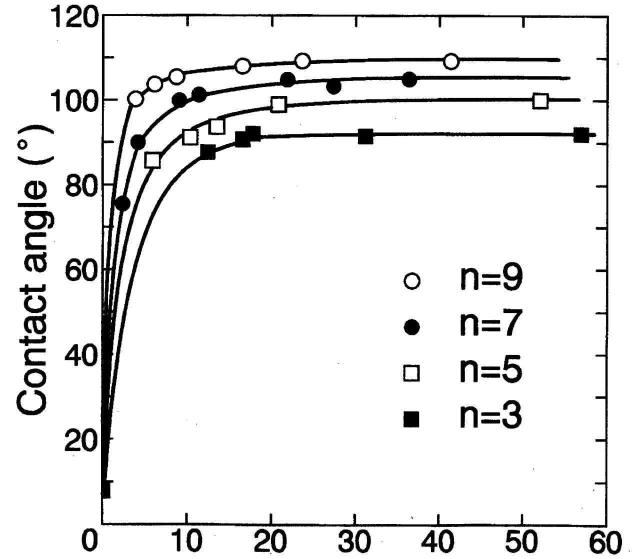

Fig. 1. Relation between contact angles θ(°) of water against the surface modified glass plate and the concentration of silane coupling agents. The symbol n are for $\mathrm{CF_3(CF_2)_nCH_2CH_2Si(CH_3)(OCH_3)_2}$.

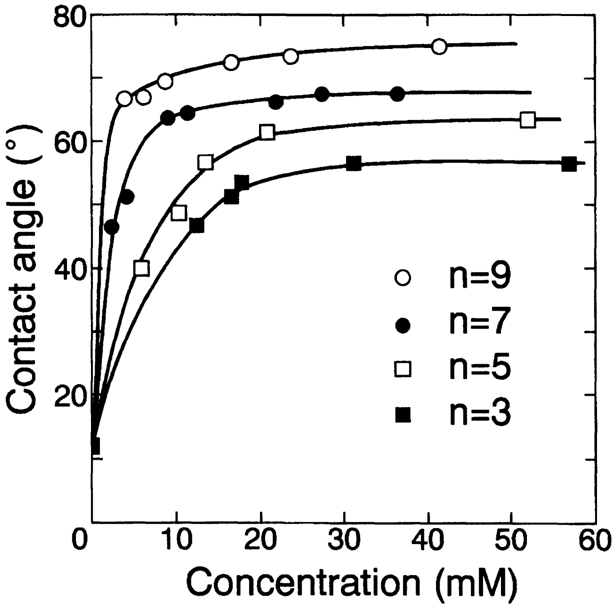

Fig. 2. Relation between contact angles θ(°) of oleic acid against the surface modified glass plate and the concentration of silane coupling agents. The symbol n are for $CF_3(CF_2)_nCH_2CH_2Si(CH_3)(OCH_3)_2$.

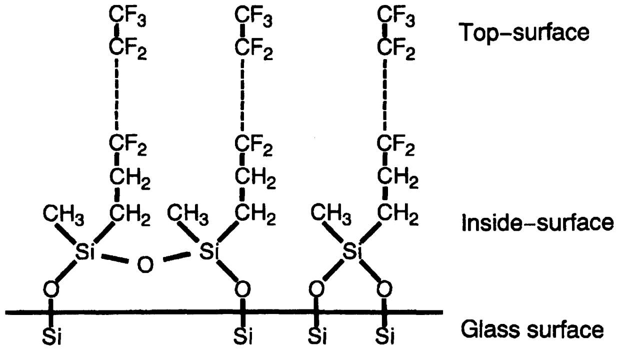

Fig. 3. Possible illustration of the glass surface modified with 1H,1H,2H,2H-polyfluoroalkyl(dimethoxy)(methyl)silanes.

face (see Fig. 3) of the modified glass was enriched with fluorocarbon, which displayed water and oil repellency, as the fluorocarbon chain length increasing. The largest contact angle of water on the modified glass surface exhibited 110°. This contact angle is as large as that of polytetrafluoroethylene.[12] In regard to water and oil repellency on the modified glass surface, 1H,1H,2H,2H-henicosafluorododecyl(dimethoxy)(methyl)silane displayed the highest ability.

Oxidation Resistance against Modified Glass Surface. After the 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-henicosafluorododecyl(dimethoxy)(methyl)silane were gradually reduced by the oxidation. On the other hand, the contact angles modified with 1H,1H,2H,2H-nonafluorohexyl(dimethoxy)(methyl)silane were reduced rapidly. 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 were also dependent on the fluorocarbon chain length.

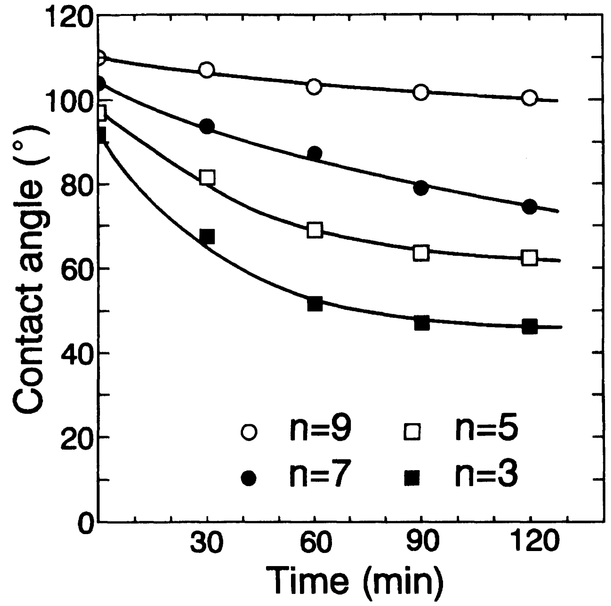

Fig. 4. Relation between contact angles θ(°) of water against the oxidized glass surface and the oxidation time in nitric acid. The symbol n are for $CF_3(CF_2)_nCH_2CH_2Si(CH_3)(OCH_3)_2$.

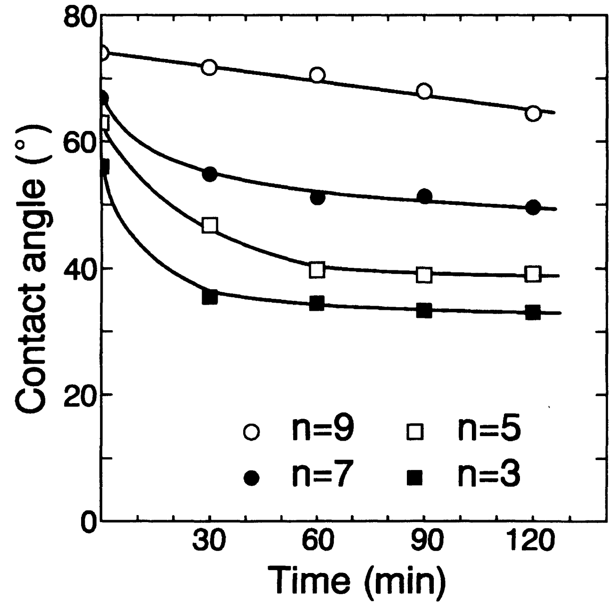

Fig. 5. Relation between contact angles θ(°) of oleic acid against the oxidized glass surface and the oxidation time in nitric acid. The symbol n are for $CF_3(CF_2)_nCH_2CH_2Si(CH_3)(OCH_3)_2$.

From the ESCA measurements of the glass surface modified with 1H,1H,2H,2H-henicosafluorododecyl-

(dimethoxy)(methyl)silane and its oxidized (120 min oxidation) one, the following facts were observed. The atomic ratios of O/Si : C/Si : F/Si : F/C=1.97 : 1.25 : 0.87 : 0.70 were obtained from the modified surface (non-oxidized). On the other hand, the values of O/Si : C/Si : F/Si : F/C=1.99 : 0.75 : 0.56 : 0.74 were observed from the oxidized surface. The atomic ratios of C/Si and F/Si are reduced by the oxidation, but the ratios of F/C are not very different. These data showed that the atomic content of fluorine and carbon on the glass surface was reduced by the oxidation. From these results, two possibilities of the mechanism of the contact angle reduction can be discussed. The first of this possibility is that the oxidation occurs in the neighborhood of hydrocarbon moiety, which exists in the inside-surface of the modified glass (see Fig. 3) and is easy to be oxidized in comparison with the fluorocarbon chain. Because, the C–C chain of fluorocarbon is shielded by compactly arranged fluorine atoms, and additionally, C–F bond energy (115.7 kcal mol^{-1} (1 kcal=4.184 kJ)[12]) is larger than that of C–H (99.5 kcal mol^{-1}). The second is that some of the Si–O–Si bondings formed by condensation reaction of silane coupling agents with glass surface are hydrolyzed by the reaction with water in hot concentrated nitric acid; such as –Si–O–Si–Glass → –Si–OH+ HO–Si–Glass.

The high oxidation resistance of the modified surface by treating with silane coupling agents having longer fluorocarbon chain must be arisen from the protection abilities against inside-surface and/or the Si–O–Si bonding by fluorocarbon chains possessing high C–F bond energy.

Additional studies on the mechanism of the oxidation resistance by ESCA analysis are now in progress.

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