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Synthesis of and Glass Surface Modification with Fluorinated Silane Coupling Agents with a Benzene Ring as a Spacer

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Abstract: Fluorinated silane coupling agents with a benzene ring as a spacer, C_nF_{2n+1}-C_6H_4-SiX_3 (n=4, 6 and 8; X=Cl, OCH_3 and NCO), were synthesized and their properties were examined to improve the surface modifying properties of the conventional fluorinated silane coupling agents. The silane coupling agents with a chloro- and methoxy-type hydrolytic groups were synthesized by the reactions of tetrachlorosilane and tetramethoxysilane with the intermediate, Rf-C_6H_4-MgBr, obtained through the Grignard reaction of the product of the reaction between *p*-dibromobenzene and perfluoroalkyl iodide in the presence of copper powder. The isocyanato-type silane coupling agents were obtained by allowing the chloro-type coupling agents synthesized to react with silver cyanate. All of the silane coupling agents thus synthesized were colorless transparent liquids. Evaluations were made on the glass surface modified with each of the coupling agents in terms of water contact angle, thermal stability, oxidation resistance, and acid resistance. The coupling agents had the properties similar to those of the conventional fluorinated silane coupling agents with the exception of thermal stability, showing that the newly synthesized agents were thermally stable up to about 300℃.

Key words: synthesis, silane coupling agent, fluoroalkyl, thermal stability, surface modification of glass

1 Introduction

Almost all materials in the atmosphere have hydroxyl groups, such as a metal-OH and a glass-OH, or adsorbed water molecules on the surfaces. Silane coupling agents react with these hydroxyl groups to bind to the material surface forming siloxane bonds, thus modifying the surface. Introduction of organic molecule with a certain function into silane coupling agent molecule will then enable to give the function to the material surface. For example, if the introduced molecule has a fluoroalkyl group, the material surface acquires water and oil repellency (1-9) and if it has a quaternary ammonium group the surface becomes antibacterial (10). Surface modification using silane coupling agents is thus possible to provide the material surface with various functions.

Fluorinated compounds are very special in that they are water and oil repellent, highly lubricative, incombustible, and chemically inert. Fluorinated materials with these characteristics have recently been marketed and used as highly functional materials.

We have so far synthesized fluorinated silane coupling agents represented by the formula Rf-CH_2-CH_2-SiX_3 [Rf = fluoroalkyl group, X = Cl, OCH_3 and NCO] and shown that the glass surfaces modified with these coupling agents exhibit a high water and oil repellency, acid resistance, and oxidation resistance (1-8,11-13). In

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addition, we modified the dental material surface with $F(CF_2)_{10}CH_2CH_2Si(OCH_3)_3$ and found a water contact angle on the modified surface higher than that on the intact surface (9). This finding has led us to a study on the modification of denture surface with this coupling agent in the hope that the modified surface becomes contamination resistant. Actually, when a surface-modified denture was placed in a heavy smoker's cavity for 4 months, it was highly contamination resistant. While resin composites for dental use are prone to coloration by various colorants contained in foods and tobacco smoke, they were found to acquire the resistance to coloration by tea extract, tobacco extract, and oil orange (sudan I olive) when their surface was modified with the coupling agent (14-16).

However, these fluorinated silane coupling agents with an ethylene chain as spacer attached to the material surface lose their fluoroalkyl groups at high temperatures through gradual breakdown of the ethylene moiety by oxidation (3,6,7) and the effect of surface modification is reduced. The glass surface modified with the conventional fluorinated silane coupling agents is as thermally stable as PTFE (normal highest heat resisting point: 260℃) and its highest heat resisting point was around 280℃ (12).

The present paper describes the synthesis of fluorinated silane coupling agents with a benzene ring, instead of an ethylene chain in the conventional fluorinated silane coupling agents, as a spacer (**Scheme 1**) and the surface modifying properties of the agents synthesized.

2 Experimantal

2·1 Materials

The following chemicals were used as purchased: *p*-bromobenzene, copper bronze powder, butyllithium/hexane solution (1.6 mol/l), and potassium hydroxide (Kanto Chemicals), tetrachlorosilane and tetramethoxysilane (Wako Pure Chemicals Kogyo), silver cyanate (Kojima Chemicals), magnesium sulfate (Nakalai Tesque), and perfluorooctyl iodide, perfluorohexyl iodide, and perfluorobutyl iodide (Daikin Fine Chemicals).

Dimethyl sulfoxide (Nakalai Tesque, **DMSO**) was distilled under a reduced pressure of 150Pa after being dehydrated with calcium chloride and then calcium hydride and the fraction at 45-47℃ was used. Diethyl ether and benzene (Kanto Chemicals) were used after dehydration with calcium chloride, calcium hydride, and metallic sodium and distillation. (Perfluoro-*t*-butyl)methyl ether (Sumitomo 3M, **HFE-7100**) was distilled under atmospheric pressure over calcium hydride after being dehydrated with calcium chloride and the fraction at 61℃ was used.

2·2 Measurements

^{1}H-NMR and ^{19}F-NMR spectra, FT-IR spectrum, and mass spectrum were measured with a Bruker DPX 400 (^{1}H: 400MHz, ^{19}F: 376MHz), a Nicolet 360 FT-IR spectrometer, and a JMS-SX102A (JEOL), respectively. Water contact angle was measured using a Kyowa CA-X goniometer.

2·3 Synthesis of Silane Coupling Agents

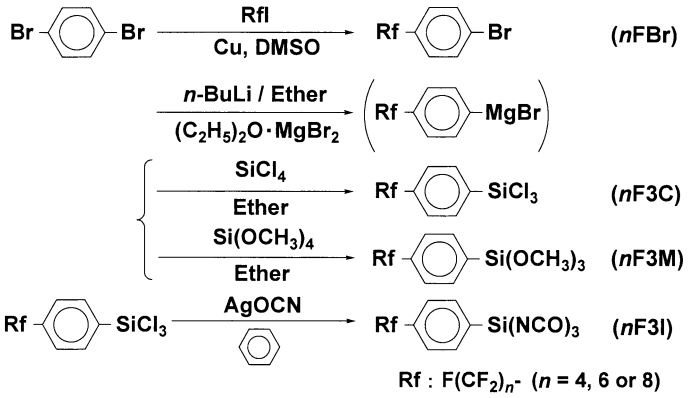
Fluorinated silane coupling agents with a benzene ring were synthesized according to **Scheme 1**.

2·3·1 Synthesis of $F(CF_2)_8$-C_6H_4-Br (**8FBr**)

In a 300-mL round bottom flask equipped with a reflux condenser and a dropping funnel were placed 47.1 g (200 mmol) of *p*-dibromobenzene, 35.4 g (557 mmol) of copper bronze powder, and 60 mL of DMSO as solvent. Perfluorooctyl iodide, $C_8F_{17}I$ (60.5 g, 111 mmol), was slowly added dropwise into the above mixture and the resultant mixture was refluxed for 24 h in a nitrogen atmosphere. Excess copper powder was separated by filtration from the refluxed mixture and water (100 mL) was added to the filtrate. After the deposited precipitates ($Cu(OH)_2$) were filtered, the product in the filtrate was extracted into diethyl ether, the layer of which was washed with water and dried with magnesium sulfate. After diethyl ether was removed by vacuum distillation, the residue was distilled under a reduced pressure to give 27.9 g of a white solid (8FBr) (yield: 44%). Bp: 65-70℃/10 Pa. ^{1}H-NMR ($CDCl_3$, TMS standard): δ7.46 (d (doublet), J = 8.57 Hz, 2H (benzene ring proton at *m*-position from CF_2, abbreviated hereafter to *m*-H); 7.66 (d, J = 8.57 Hz, 2H (benzene ring proton at *o*-position from CF_2, abbreviated hereafter to *o*-H). IR (cm^{-1}):1243 (s), 1193 (vs), 1143 (vs) (νC-F); 592 (m)(νC-Br). MS (m/z (rel. int.)): 574 (18, M^+); 555 (8, $[M\text{-}F]^+$; 205 (100, $[CF_2C_6H_4Br]^+$); 126 (24, $[CF_2C_6H_4]^+$); 69 (8, $[CF_3]^+$).

2·3·2 Synthesis of $F(CF_2)_6$-C_6H_4-Br (**6FBr**) and $F(CF_2)_4$-C_6H_4-Br (**4FBr**)

The synthesis was performed in a way similar to that



Scheme 1

for 8FBr.

6FBr: A colorless transparent liquid 6FBr (31.4 g) was obtained with use of 61.2 g (260 mmol) of *p*-dibromobenzene, 41.8 g (658 mmol) of copper bronze powder, and 66.8 g (150 mmol) of perfluorohexyl iodide (yield: 47%). Bp: 60-68℃/12 Pa. ^{1}H-NMR ($CDCl_3$): δ7.46 (d, J = 8.44 Hz, 2H, *m*-H); 7.66 (d, J = 8.44 Hz, 2H, *o*-H). IR (cm^{-1}): 1236 (vs), 1195 (vs), 1145 (vs) (νC-F); 588 (m) (νC-Br). MS (m/z (rel. int.)): 474 (15, M^+); 205 (100, $[CF_2C_6H_4Br]^+$); 126 (34, $[CF_2C_6H_4]^+$); 69 (10, $[CF_3]^+$).

4FBr: A colorless transparent liquid 4FBr (28.4 g) was obtained with use of 60.0 g (252 mmol) of *p*-dibromobenzene, 42.6 g (670 mmol) of copper bronze powder, and 44.3 g (128 mmol) of perfluorobutyl iodide (yield: 43%). Bp: 60-65℃/50 Pa. ^{1}H-NMR ($CDCl_3$):δ7.46 (d, J = 8.36 Hz, 2H, *m*-H); 7.66 (d, J = 8.36 Hz, 2H, *o*-H). IR (cm^{-1}): 1232 (vs), 1134 (vs) (νC-F); 590 (m) (νC-Br). MS (m/z (rel. int.)): 374 (29, M^+); 205 (100, $[CF_2C_6H_4]^+$); 126 (42, $[CF_2C_6H_4]^+$); 69 (14, $[CF_3]^+$).

2・3・3 Synthesis of $F(CF_2)_8$-C_6H_4-$SiCl_3$ (**8F3C**)

In a 300-mL round bottom flask equipped with a reflux condenser, a dropping funnel, and a thermometer measurable down to -80℃ were placed 12.9 g (22.5 mmol) of 8FBr and 40 mL of diethyl ether in a nitrogen atmosphere. A solution of butyllithium in hexane (27.5 mL, 44.0 mmol) was added dropwise in 20 min to the above mixture cooled at -30℃ (coolant: methanol/ice) while stirring and the stirring was continued for 15 min. To this reaction system was added dropwise in 10 min 11.3 g (43.6 mmol) of magnesium bromide etherate dissolved in 10 mL of diethyl ether. Afterward, 11.1 g (65.4 mmol) of tetrachlorosilane was added quickly to the reaction mixture cooled down to -75℃ (coolant: dry ice/acetone). Ten minutes later, the mixture was warmed to room temperature and stirred for 24 h and the ether was removed by vacuum distillation. To the residue was added 30 mL of HFE-7100 to precipitate magnesium hydroxide. After the hydroxide precipitated was separated by filtration in a nitrogen atmosphere, the filtrate was distilled at a reduced pressure to give 3.30 g of a colorless transparent liquid, 8F3C (yield: 24%). Bp: 67-69℃/13 Pa. ^{1}H-NMR ($CDCl_3$): δ7.73 (d, J = 7.64 Hz, 2H, *m*-H); 7.95 (d, J = 7.64 Hz, 2H, *o*-H). IR (cm^{-1}): 3073 (w), 3044 (w), 2963 (w) (νC-H); 1304 (vs), 1281 (vs), 1167 (vs), 1107 (vs) (νC-F); 645 (m) (νSi-Cl). MS (m/z (rel. int.)): 628 (6, M^+); 259 (100, $[CF_2C_6H_4SiCl_3]^+$); 126 (11, $[CF_2C_6H_4]^+$); 69 (10, $[CF_3]^+$).

2・3・4 Synthesis of $F(CF_2)_6$-C_6H_4-$SiCl_3$ (**6F3C**) and $F(CF_2)_4$-C_6H_4-$SiCl_3$ (**4F3C**)

The synthesis was done in a way similar to that used for 8F3C.

6F3C: A colorless transparent liquid (5.64 g), 6F3C, was obtained with use of 22.9 g (48.2 mmol) of 6FBr, 31.0 mL of a butyllithium solution in hexane (49.6 mmol), 12.5 g (48.4 mmol) of magnesium bromide etherate, and 13.3 g (78.4 mmol) of tetrachlorosilane (yield: 22%). Bp: 59-61℃/20 Pa. ^{1}H-NMR ($CDCl_3$): δ7.74 (d, J = 8.08 Hz, 2H, *m*-H); 7.96 (d, J = 8.08 Hz, 2H, *o*-H). IR (cm^{-1}): 3073 (w), 3041 (w), 2959 (w), 2930 (w) (νC-H); 1242 (s), 1207 (vs), 1148 (vs), 1122 (vs) (νC-F); 688 (m) (νSi-Cl). MS (m/z (rel. int.)): 528 (8, M^+); 259 (100, $[CF_2C_6H_4SiCl_3]^+$); 126 (18, $[CF_2C_6H_4]^+$); 69 (13, $[CF_3]^+$).

4F3C: A colorless transparent liquid (3.30 g), 4F3C, was obtained with use of 9.84 g (26.2 mmol) of 4FBr, 31.0 mL of a butyllithium solution in hexane (49.6 mmol), 12.6 g (48.8 mmol) of magnesium bromide etherate, and 12.6 g (74.1 mmol) of tetrachlorosilane (yield: 29%). Bp: 60-62℃/21 Pa. ^{1}H-NMR ($CDCl_3$): δ7.74 (d, J = 8.36 Hz, 2H, *m*-H); 7.96 (d, J = 8.36 Hz, 2H, *o*-H). ^{19}F-NMR ($CDCl_3$): δ125.38 (m, 2F, d); -122.47 (m, 2F, c); -111.16 (m, 2F, b); -80.91 (m, 3F, a) for CF_3^a-CF_2^b-CF_2^c-CF_2^d-C_6H_4-$SiCl_3$. IR (cm^{-1}): 2964 (w), 2877 (w), 2863 (w) (νC-H); 1236 (s), 1207 (vs), 1135 (vs), 1108 (vs) (νC-F); 690 (m) (νSi-Cl). MS (m/z (rel. int.): 428 (9, M^+); 259 (100, $[CF_2C_6H_4SiCl_3]^+$); 126 (21, $[CF_2C_6H_4]^+$); 69 (8, $[CF_3]^+$). HRMS (EI) (m/z (rel. int.)): obsd. 427.9030 (11.8, M^+ (calcd. 427.9004 for C10 H4^{35}Cl3 F9 Sil).

2·3·5 Synthesis of $F(CF_2)_8$-C_6H_4-$Si(OCH_3)_3$ (**8F3M**)

Into a flask equipped similarly to that used in 2·3·3 were taken 17.0 g (29.6 mmol) of 8FBr and 40 mL of diethyl ether and 39.3 mL of a butyllithium solution in hexane (59.2 mmol) was added dropwise in 20 min at -30℃ to the above mixture while stirring. Fifteen minutes later, 15.3 g (59.2 mmol) of magnesium bromide etherate dissolved in 10 mL of diethyl ether was added dropwise in 10min at -30℃. The reaction mixture was then cooled down to -75℃ and 13.5 g (88.8 mmol) of tetramethoxysilane was quickly added to the mixture, which was warmed up to room temperature in 10min and stirred for 24 h. The ether was removed by vacuum distillation from the reaction mixture and 30 mL of HFE-7100 was added to the residue to precipitate magnesium hydroxide, which was then separated by filtration in a nitrogen atmosphere. A colorless transparent liquid (9.03g), 8F3M, was obtained after the solvent was removed by distillation at a reduced pressure (yield: 38%). Bp: 68-70℃/11 Pa. ^{1}H-NMR ($CDCl_3$): δ7.61 (d, J = 8.11 Hz, 2H, *m*-H); 7.77 (d, J = 8.11 Hz, 2H, *o*-H); 3.56 (s, 9H, OCH_3). ^{19}F-NMR ($CDCl_3$): δ-125.94 (m, 2F, h); -122.52 (m, 2F, g); -121.59 (m, 6F, d, e and f); -121.03 (m, 2F, c); -110.86 (m, 2F, b); -80.70 (m, 3F, a) for Cf_3^a-CF_2^b-CF_2^c-CF_2^d-CF_2^e-CF_2^f-CF_2^g-CF_2^h-C_6H_4-$Si(OCH_3)_3$. IR (cm^{-1}): 2948 (w), 2846 (w) (νC-H); 1241 (vs), 1213 (vs), 1151 (vs), 1089 (vs) (νC-F); 945 (m) (νSi-O). MS (m/z (rel. int.)): 616 (19, M^+); 247 (8, $[CF_2C_6H_4Si(OCH_3)_3]^+$); 121 (100, $[Si(OCH_3)_3]^+$). HRMS(EI) (m/z (rel. int.)): obsd. 616.0359 (78.3, M^+ (calcd. 616.0362 for C17H13O3F17Si1).

2·3·6 Synthesis of $F(CF_2)_6$-C_6H_4-$Si(OCH_3)_3$ (**6F3M**) and $F(CF_2)_4$-C_6H_4-$Si(OCH_3)_3$ (**4F3M**)

The synthesis was made in a way similar to that used for 8F3M.

6F3M: A colorless transparent liquid (2.29 g), 6F3M, was obtained with use of 3.42 g (7.20 mmol) of 6FBr, 7.73 mL of a butyllithium solution in hexane (11.9 mmol), 3.10 g (12.0 mmol) of magnesium bromide etherate, and 2.74 g (18.0 mmol) of tetramethoxysilane (yield: 17%). Bp: 52-54℃/90 Pa. ^{1}H-NMR ($CDCl_3$): δ7.61 (d, J = 7.81 Hz, 2H, *m*-H); 7.79 (d, J = 7.81 Hz, 2H, *o*-H); 3.64 (s, 9H, OCH_3). IR (cm^{-1}): 3081 (w), 3056 (w) (νC-H); 1240 (vs), 1205 (vs), 1148 (vs) (νC-F); 1013 (m) (νSi-O). MS (m/z (rel int.)): 516 (25, M^+); 247 (76, $[CF_2C_6H_4Si(OCH_3)_3]^+$); 121 (100, $[Si(OCH_3)_3]^+$).

4F3M: A colorless transparent liquid (5.90 g), 4F3M, was obtained with use of 15.5 g (41.2 mmol) of 4FBr, 39.0 mL of a butyllithium solution in hexane (58.7 mmol), 14.0 g (54.2 mmol) of magnesium bromide etherate, and 15.4 g (101 mmol) of tetramethoxysilane (yield: 34%). Bp: 68-72℃/330 Pa. ^{1}H-NMR ($CDCl_3$): δ7.53 (d, J = 7.78 Hz, 2H, *m*-H); 7.71 (d, J = 7.78 Hz, 2H, *o*-H); 3.57 (s, 9H, OCH_3). IR (cm^{-1}): 2948 (w), 2846 (w) (νC-H); 1238 (vs), 1205 (vs), 1135 (vs), 1089 (vs) (νC-F); 1004 (m) (νSi-O). MS (m/z (rel. int.)): 416 (29, M^+); 247 (44, $[CF_2C_6H_4Si(OCH_3)_3]^+$); 121 (100, $[Si(OCH_3)_3]^+$). HRMS(EI) (m/z (rel. int.)): obsd. 416.0487 (9.8, M^+ (calcd. 416.0940 for C13H13O3F9 Si1).

2·3·7 Synthesis of $F(CF_2)_8$-C_6H_4-$Si(NCO)_3$ (**8F3I**)

Into a 100-mL round bottom flask equipped with a reflux condenser and dropping funnel was taken 3.65 g of silver cyanate and 40 mL of benzene in a nitrogen atmosphere and the mixture was stirred to give a suspension, to which 4.34 g (6.89 mmol) of 8F3C was slowly added dropwise. The reaction mixture was refluxed for 4 h with heating and the unreacted silver cyanate was separated by filtration. Vacuum distillation of the filtrate gave a colorless transparent liquid (1.66 g), 8F3I (yield: 37%). Bp: 90-97℃/19 Pa. ^{1}H-NMR ($CDCl_3$): δ7.44 (d, J = 8.57 Hz, 2H, *m*-H); 7.66 (d, J = 8.57 Hz, 2H, *o*-H). IR (cm^{-1}): 2959 (w), 2853 (w) (νC-H); 2274 (vs) (νN=C=O); 1249 (vs), 1202 (vs), 1147 (vs), 1112 (vs), 1085 (vs) (νC-F). MS (m/z (rel. int.)): 649 (19, M^+); 280 (100, $[CF_2C_6H_4Si(NCO)_3]^+$); 154 (17, $[Si(NCO)_3]^+$).

2·3·8 Synthesis of $F(CF_2)_6$-C_6H_4-$Si(NCO)_3$ (**6F3I**) and $F(CF_2)_4$-C_6H_4-$Si(NCO)_3$ (**4F3I**)

The synthesis was carried out in a way similar to that used for 8F3I.

6F3I: A colorless transparent liquid (3.09 g), 6F3I, was obtained with use of 5.82 g (11.0 mmol) of 6F3C and 5.89 g (39.3 mmol) of silver cyanate (yield: 51%). Bp: 94-100℃/19 Pa. ^{1}H-NMR ($CDCl_3$): δ7.67 (d, J = 8.12 Hz, 2H, *m*-H); 7.76 (d, J = 8.12 Hz, 2H, *o*-H). ^{19}F-NMR ($CDCl_3$): δ-125.98 (m, 2F, f); -122.63 (m, 2F, e); -121.56 (m, 2F, d); -121.23 (m, 2F, c); -111.28 (m, 2F, b); -80.71 (m, 3F, a) for CF_3^a-CF_2^b-CF_2^c-CF_2^d-CF_2^e-CF_2^f-C_6H_4-$Si(NCO)_3$. IR (cm^{-1}): 3041 (w), 2959 (w), 2923 (w) (νC-H); 2270 (vs) (νN=C=O); 1288 (vs), 1245 (vs), 1198 (vs), 1143 (vs) (νC-F). MS (m/z (rel. int.)): 549 (10, M^+); 280 (100, $[CF_2C_6H_4Si(NCO)_3]^+$); 154 (17, $[Si(NCO)_3]^+$).

4F3I: A colorless transparent liquid (1.52 g) , 4F3I, was obtained with use of 3.30 g (7.68 mmol) of 4F3C and 4.03 g (26.9 mmol) of silver cyanate (yield: 44%). Bp: 75-80℃/29 Pa. ^{1}H-NMR ($CDCl_3$): δ7.72 (d, J = 8.04 Hz, 2H, *m*-H); 7.83 (d, J = 8.04 Hz, 2H, *o*-H). IR (cm^{-1}): 3002 (w), 2959 (w) (νC-H); 2317 (vs) (νN=C=O); 1264 (vs), 1198 (vs), 1139 (vs) (νC-F). MS (m/z (rel. int.)): 449 (13, M^+); 280 (100, $[CF_2C_6H_4Si(NCO)_3]^+$); 154 (11, $[Si(NCO)_3]^+$).

2·4 Modification of Glass Surface

The glass surface was modified with each of the synthesized fluorinated silane coupling agents, 8F3C, 6F3C, 4F3C, 8F3M, 6F3M, 4F3M, 8F3I, 6F3I and 4F3I and the effects of coupling agent concentration and modification time were examined on water contact angle on the modified glass surface to determine the optimum modifying conditions. The glass was used after being immersed in an aqueous 1N KOH solution for 2 h, washed thoroughly with distilled water, and dried in a desiccator.

2·4·1 Determination of optimum coupling agent concentration

Modification of glass surface was conducted by immersing a glass plate into a solution at a given concentration of each of 8F3C, 8F3M, and 8F3I in HFE-7100 for 24 h at the boiling point of the solution in a nitrogen atmosphere. After being immersed into the modifying solvent and then distilled water for a few minutes to convert the hydrolyzable groups to hydroxyl groups, the treated glass plate was heated for 30 min at 150℃ in an oven to make a siloxane network on the surface (3,6,7). The glass plate was cooled down to room temperature in a desiccator and water contact angle on the surface was measured. Contact angle measurements were performed using a sessile drop method in which a 0.9 μL water droplet was placed on the horizontal glass plate (3,6,7,17). In this way, the necessary and sufficient minimum concentration of each coupling agent was determined for the highest contact angle.

2·4·2 Determination of optimum modification time

Modification of glass surface was carried out for a given time using a solution of each of 8F3C, 8F3M, and 8F3I in HEF-7100 at the optimum modification concentration determined in 2·4·1 and the optimum modification time was determined from measurements of water contact angle on the modified surface.

2·5 Evaluation of Thermal Resistance, Oxidation Resistance, and Acid Resistance of Modified Glass Surface

Modified glass surface was prepared using the optimum coupling agent concentration and optimum modification time determined in 2·4·1 and 2·4·2 and its thermal resistance, oxidation resistance, and acid resistance were evaluated.

2·5·1 Evaluation of thermal resistance of modified glass surface

The modified glass plate prepared in **2·5** was heated for 2 h at a given temperature in an oven. After the treated glass plate was cooled down to room temperature in a desiccator, water contact angle was measured on the plate, the value of which was used to evaluate the thermal resistance of the modified surface.

2·5·2 Evaluation of oxidation resistance and acid resistance of modified glass surface

After the modified glass plate prepared in **2·5** was immersed in concentrated nitric acid or hydrochloric acid for a given time at 80℃, it was washed thoroughly with distilled water and dried at room temperature. The oxidation resistance and acid resistance of the treated surface were evaluated in terms of the value of water contact angle on the surface.

3 Results and Discussion

3·1 Synthesis

Synthesis of *n*F3C, *n*F3M, and *n*F3I was performed according to **Scheme 1**. Since the intermediate, Rf-

C_6H_4-MgBr, of *n*F3C and *n*F3M was unstable, the reaction was permitted to proceed without its isolation. Dropwise addition of *n*F3C to AgOCN dispersed in benzene gave *n*F3I. Although all the silane coupling agents obtained were stable in nitrogen atmosphere, their benzene solutions were found to become turbid when they contacted moisture and the agents were easily hydrolyzed.

3·2 Determination of Optimum Coupling Agent Concentration

Figure 1 shows the results of water contact angle measurements on the glass surface modified with each of the silane coupling agents with a C_8F_{17} moiety. The ordinate is for water contact angle on the modified glass surface and the abscissa is for the concentration of coupling agent solution in HFE-7100. The contact angle remained almost constant above 20 mM for the coupling agents with chloro- and isocyanato-type hydrolyzable groups, while it was constant above 30 mM for the agent with methoxy-type hydrolyzable group. Based on this finding, the necessary and sufficient minimum coupling agent concentration for modification was determined to be 30 mM. The values of water contact angle were 111, 113, and 115° on the glass surfaces modified with the coupling agents with methoxy-, isocyanato-, and chloro-type hydrolyzable groups, respectively, when the coupling agent solutions in HFE-7100 used were at this concentration. The rate of hydrolysis was in the increasing order, Si-Cl > Si-NCO >> Si-OCH_3 (18), and the agent showing a higher hydrolysis rate gave a higher water contact angle. On the basis of this result, the coupling agents with the shorter fluorocarbon chains were also used at 30 mM to modify glass surface.

3·3 Determination of Optimum Modification Time

Figure 2 shows the relationship between modification time and contact angle for the coupling agents with a C_8F_{17} moiety used to modify glass surface. The ordinate is for water contact angle on the modified surface and the abscissa is for modification time. The effect of modification time on the contact angle was found rather slight for the agents with chloro- and isocyanato-type hydrolyzable groups because both agents showed a rapid rise in the modification time curve compared with the agent with methoxy-type hydrolyzable group. This finding led to the optimum modification time of 2 h that gives satisfactory water repellency to glass surface for these two coupling agents. On the other hand, the agent with a methoxy-type hydrolyzable group needed 6 h to attain a constant water contact angle. This would be due to a lower reactivity with hydroxyl groups on the glass surface of methoxy-type hydrolyzable group. Then, the modification time was determined to be 6 h for this coupling agent.

3·4 Evaluation of Thermal Resistance of Modified Glass Surface

Glass surface was modified by the coupling agent under the optimum conditions and heat treated at a given temperature. **Figure 3** shows the relationship between water contact angle and heating temperature. The ordinate is for water contact angle on the modified glass surface and the abscissa is for heating temperature.

The contact angle on the modified glass surface was higher than 100° even after 2 h heating up to nearly 300℃ for the chloro- and isocyanato-type coupling agents independently of fluorocarbon chain length. With the methoxy-type coupling agents, the glass surface modified with 4F3M showed a larger decrease in

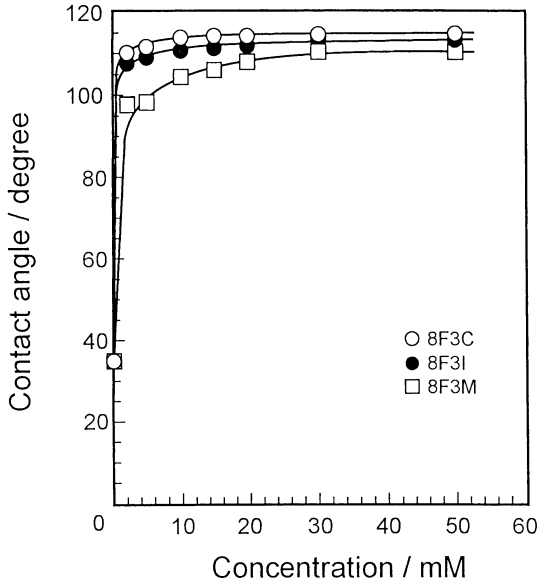


Fig. 1 Relation between Water Contact Angle on the Glass Surface Modified with Each of 8F3C, 8F3I, and 8F3M and Coupling Agent Concentration.

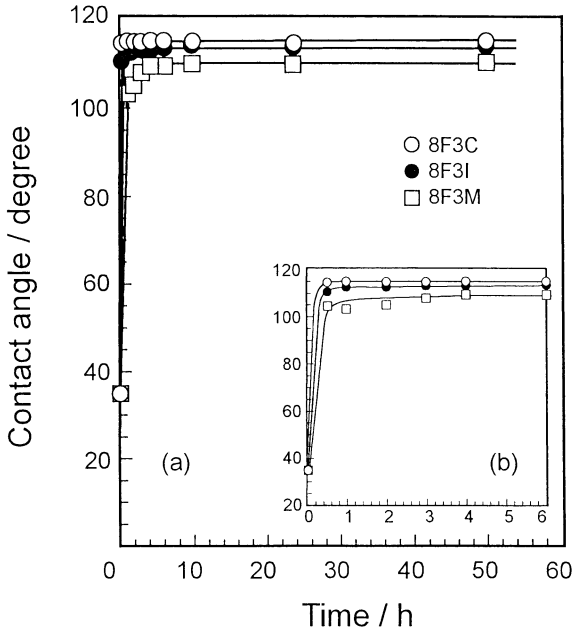


Fig. 2 Relation between Water Contact Angle on the Glass Surface Modified with Each of 8F3C, 8F3I, and 8F3M and Modification Time ((b) in the Figure is the Enlarged 0-6h Portion of (a)).

the contact angle than the other agents, whereas the surfaces modified with 8F3M and 6F3M exhibited a contact angle higher than 100° after being heated to nearly 300℃, which indicated that the glass surface modified with the coupling agents has a high thermal stability. It seems that the difference of the hydrolysis rate of the hydrolyzable group in the silane coupling agents influences in the bonding amount and the energy between the substrate and the silane layer indicating the thermal stability (3).

3·5 Evaluation of Oxidation Resistance and Acid Resistance of Modified Glass Surface

Modified glass surface was treated using the procedures given in 2·5·2. **Figures 4** and **5** show changes in water contact angle with immersion time in conc. HNO_3 and HCl, respectively. The contact angle remained over 100° on the surface modified with the chloro- and isocyanato-type coupling agents after 2 h treatment independently of fluorocarbon chain length. The resistance of 4F3M was lower than that of 6F3M and 8F3M which gave a contact angle higher than 100°, a fact showing that the modified surface is highly resistant to oxidation and acid.

While for the conventional silane coupling agents ($Rf\text{-}CH_2CH_2\text{-}SiX_3$) the moiety of $\text{-}CH_2CH_2\text{-}$ as a spacer

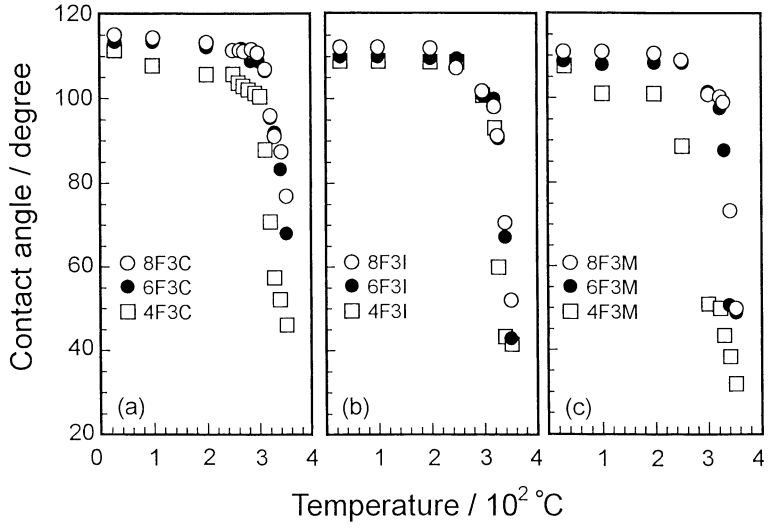


Fig. 3 Relation between Water Contact Angle on the Modified Glass Surface and Heating Temperature: (a) chloro-type; (b) isocyanato-type; (c) methoxy-type.

is easily broken by oxidation (4,7,10,11), the newly synthesized silane coupling agents with a benzene ring as a spacer were found to be highly thermoresistant because of the difficulty with which the spacer moiety is destroyed by oxidation. This might suggest that the introduction of benzene ring, possessing a higher thermostability than the aliphatic chains, promotes the π-π interaction between benzene rings, thereby forming a highly stable silane layer on the modified glass surface (8).

4 Conclusions

Nine fluorinated silane coupling agents with a benzene ring were synthesized and glass surface was modified with each of them. Water contact angle on the

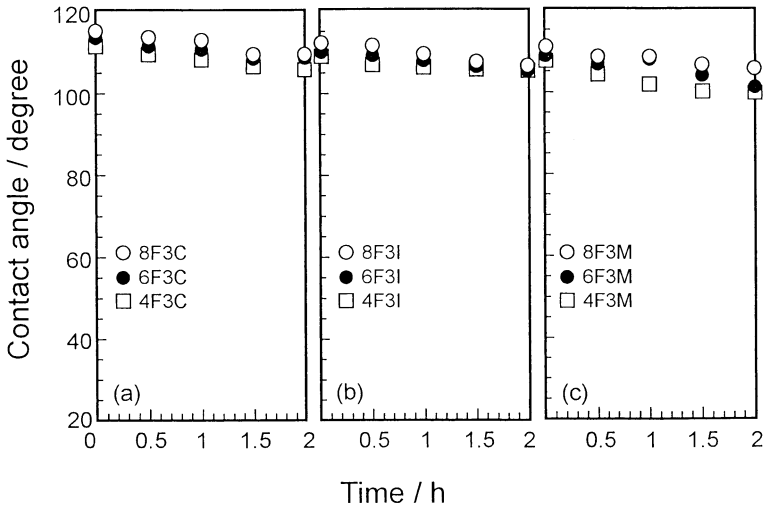


Fig. 4 Relation between Water Contact Angle on the Modified Glass Surface and Treating Time in Hot Concentrated HNO_3: (a) chloro-type; (b) isocyanato-type; (c) methoxy-type.

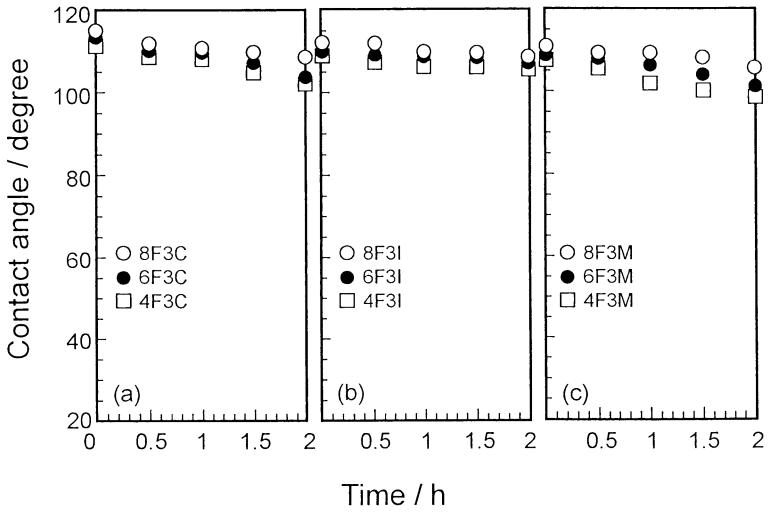


Fig. 5 Relation between Water Contact Angle on the Modified Glass Surface and Treating Time in Hot Concentrated HCl: (a) chloro-type; (b) isocyanato-type; (c) methoxy-type.

modified surface was used to evaluate its water repellency. Evaluations were also made on the thermal resistance, oxidation resistance, and acid resistance of the modified surface.

The experimental results obtained showed that the newly synthesized coupling agents are as water repellent as the conventional silane coupling agents. The synthesized agents with a longer fluorocarbon chain exhibited a higher water contact angle. The surface modified with the coupling agents having a hydrolyzable group that is highly reactive with hydroxyl groups on the substrate surface (chloro-type > isocyanato-type >> methoxy-type) exhibited a high water contact angle, showing an excellent water repellency. In particular, the modified surface had a better thermal stability than the surface modified with the conventional agents and was stable up to 300℃.

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