Synthesis and Applications of a Variety of Fluoroalkyl End-Capped Oligomers/Silica Gel Polymer Hybrids

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ABSTRACT: Fluoroalkyl end-capped trimethoxyvinylsilane oligomers, trimethoxyvinylsilane–N,N-dimethylacrylamide cooligomers, and trimethoxyvinylsilane–acryloylmorpholine cooligomers were polymerized with hydrolysis and condensation between tetraethoxysilane (TEOS) and trimethoxysilyl segments in oligomers to afford homogeneous fluoroalkyl end-capped oligomers/silica gel polymer hybrids under mild conditions. Similarly, fluoroalkyl end-capped N,N-dimethylacrylamide oligomers and acryloylmorpholine oligomers reacted with TEOS under mild conditions to afford the fluorinated oligomers/silica gel polymer hybrids. The formation of these fluorinated oligomers/silica gel polymer hybrids is due to the homogeneous incorporation of fluoroalkyl end-capped oligomers into the silica gel networks through the intermolecular hydrogen bonding interaction between the residual silanol groups in silica gels and amido groups of fluorinated oligomers. We have also succeeded in preparing new fluorinated polymer hybrids by the use of fluoroalkyl end-capped N,N-dimethylacrylamide co-oligomer-containing silsesquioxane segments. Thermal stability of a variety of fluoroalkyl end-capped oligomers/silica gel polymer hybrids thus obtained was found to increase significantly compared to those of the parent fluoroalkyl end-capped oligomers. In addition, in these fluorinated oligomers/silica gel polymer hybrids, their sol solutions are applicable to the surface modification of glass to exhibit not only a strong oleophobicity imparted by fluorine but also a good hydrophilicity on the glass surface. Therefore, these fluorinated oligomers/silica gel polymer hybrids are suggested to have high potential for new functional materials through their unique properties imparted by not only fluorine but also by the hybrid counterparts. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 169–177, 2005

Key words: fluoropolymer; oligomers; composites; TGA; surfaces

INTRODUCTION

Advanced hybrid organic/inorganic composites have recently attracted much attention because these materials in general could show improved properties superior to those of the parent materials.[1,2] Usually, these hybrids are prepared through a sol–gel reaction by incorporating organic polymers with alkoxysilanes such as tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS). There have been hitherto a variety of studies on the organic polymers/silica gel hybrids that are dispersed at the molecular level by utilizing the sol–gel reactions with alkoxysilanes in the presence of organic polymers.[3] Partially longer fluoroalkylated polymers are a useful class of materials because of their unique balance of properties such as low surface free energy, low coefficient of friction, and solvent and chemical resistance, which cannot be achieved by the corresponding nonfluorinated polymers.[4] It is very interesting to prepare fluorinated polymer/inorganic polymer hybrids from the viewpoints of the development of new fluorinated functional materials. However, the preparation and applications of these fluorinated polymer hybrids have been very limited except for some reports on the synthesis of poly(methacrylic acid)/TEOS/2-perfluorooctylethyltriethoxysilane polymer hybrids,[5] poly(vinylidene fluoride)/SiO_2 hybrid composites,[6] fluorinated polyimides,[7] telechelic perfluoropolyethers-containing triblock copolymers,[8] and Nafion[TR] resin[9]/silica composites. In our comprehensive studies of longer fluoroalkylated polymers, we have already reported that fluoroalkyl end-capped oligomers exhibit

a variety of unique properties such as high solubility, surface active properties, antibacterial activity, anti-HIV-1 activity, and the formation of nanometer size-controlled self-assembled molecular aggregates, which cannot be achieved by the corresponding randomly fluoroalkylated polymers and fluoroalkylated block polymers.[10] In these fluoroalkyl end-capped oligomers, fluoroalkyl end-capped trimethoxyvinylsilane oligomers [R_F-[$CH_2CHSi(OMe)_3$]$_n$-R_F; $n = 2, 3$; R_F = fluoroalkyl group] were also demonstrated to be applicable to the surface modification of glass, and the modified glass treated with this fluorinated oligomeric silane-coupling agent exhibits excellent oleophobic and hydrophobic characteristics imparted by fluorine above their surfaces.[11] In addition, fluoroalkyl end-capped acryloylmorpholine - trimethoxyvinylsilane cooligomers, which were prepared by the co-oligomerizations of fluoroalkanoyl peroxides with the corresponding monomers, were demonstrated to have good hydrophilicity with a strong oleophobicity imparted by fluorine above the glass surface.[12] It is strongly suggested that fluoroalkyl end-capped oligomers possessing trimethoxysilyl segments could react easily with alkoxysilanes to afford fluorinated oligomers/silica gel polymer hybrids possessing a variety of unique properties such as surface-active properties and biological activities imparted by fluorine. Therefore, it is in particular interest to prepare novel fluoroalkylated oligomers/silica gel polymer hybrids by the use of fluoroalkyl end-capped oligomers through a sol–gel reaction by incorporating fluorinated oligomers with alkoxysilanes. In this article, we report on the synthesis and applications of novel fluoroalkyl end-capped oligomers/silica gel polymer hybrids by the sol–gel reactions of the corresponding fluoroalkyl end-capped oligomers with TEOS.

EXPERIMENTAL

Measurements

Molecular weights were measured by using a Shodex DS-4 (pomp, Tokyo, Japan) and Shodex RI-71 (Detector) gel permeation chromatography (GPC) calibrated with standard polystyrene using THF as the eluant. Contact angles were measured by the use of the goniometer-type contact angle meter (ERMA G-1-1000, Erma, Inc, Tokyo, Japan). Fourier transform infrared (FTIR) spectra were measured by using a Shimadzu FTIR-8400 FTIR spectrophotometer (Kyoto, Japan). XPS measurements were performed by the use of Shimadzu ESCA 750. Thermal analyses were recorded on a Rigaku Denki TG8101 D differential thermobalance (Tokyo, Japan). Specific surface areas of the fluorinated polymer hybrids were measured by using a Shimadzu Flow Sorb III 2305/2310.

Materials

N,N-dimethylacrylamide (DMAA) and acryloylmorpholine (ACMO) were used as received from Kohjin Co., Ltd. (Tokyo, Japan). N-(1,1-dimethyl-3- oxobutyl)acrylamide (DOBAA) was used as received from Kyowa Hakko Kogyou Co., Ltd. (Tokyo, Japan). Trimethoxyvinylsilane and Si-MMA were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan) and Sigma Aldrich Japan Co. (Tokyo, Japan), respectively. A variety of fluoroalkyl end-capped homo- and co-oligomers were prepared by the reactions of fluoroalkanoyl peroxides with the corresponding monomers according to our previously reported methods.[11–14]
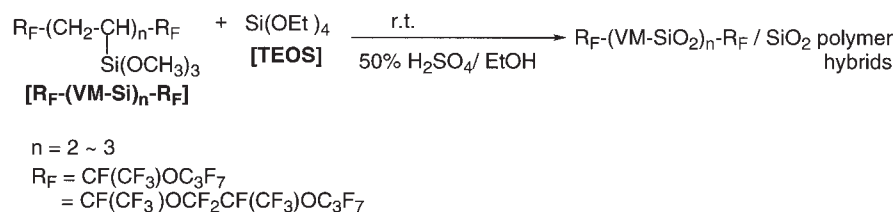
General procedure for the preparation of fluoroalkyl end-capped oligomers/silica gel polymer hybrids

In an ethanol solution (5 ml) of R_F-(DMAA)$_n$-R_F [R_F = $CF(CF_3)OC_3F_7$: $M_n = 2020$ ($M_w/M_n = 1.12$) (0.4 g)] were dissolved TEOS (2.0 g) and aqueous $1N$ HCl (1.0 g). The mixture was stirred with a magnetic stirring bar at room temperature for 2 days. After the removal of the solvent, a transparent homogeneous hybrid was obtained. This glassy silica gel was purified by Soxhlet extraction with chloroform to afford the expected fluorinated polymer hybrid (0.21 g).

Similarly, a variety of fluoroalkyl end-capped oligomers/SiO$_2$ polymer hybrids were prepared by using R_F-(ACMO)$_n$-R_F oligomer, R_F-(DOBAA)$_n$-R_F, R_F- (VM-Si)$_n$-R_F (in these oligomers, 50% H_2SO_4 was used as an acid catalyst for the preparation of the expected fluorinated hybrids), R_F-(VM-Si)$_x$-(DMAA)$_y$-R_F,[12] R_F-(VM-Si)$_x$-(ACMO)$_y$-R_F,[12] and R_F-(Si-MMA)$_x$-(DMAA)$_y$-R_F.[13]

Contact angle measurements

The contact angles for glasses were measured with the use of the goniometer-type contact angle meter (Erma G-1-1000), according to our previously reported method.[15] Briefly, the glass plates (10 × 10 mm^2 pieces) were dipped into the sol ethanol solutions of fluoroalkyl end-capped oligomers/silica gel polymer hybrids at room temperature and left for 5 min. They were lifted from the solution at a constant rate of 0.5 mm/min and subjected to heat treatment for 30 min at 50°C. After the heat treatment, the contact angles of water and dodecane for these glass plates were measured. In addition, these glass plates were dipped into chloroform solutions at room temperature and left for 1 day, and then the contact angles of water and dodecane on the glass plates were measured under similar conditions.

R_F-(CH$_2$-CH)$_n$-R$_F$ + Si(OEt)$_4$ → [r.t., 50% H$_2$SO$_4$/EtOH] → R_F-(VM-SiO$_2$)$_n$-R$_F$ / SiO$_2$ polymer hybrids

Si(OCH$_3$)$_3$ [TEOS]

[R_F-(VM-Si)$_n$-R$_F$]

n = 2 ~ 3
R_F = CF(CF$_3$)OC$_3$F$_7$
    = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$

Run	R_F in R_F-(VM-Si)$_n$-R_F (g)	TEOS (g)	50 % H$_2$SO$_4$	Time (day)	Product:Yield (%)[a]
1	R_F = CF(CF$_3$)OC$_3$F$_7$ (1.0)	1.0 (4.8 mmol)	40	3	70
2	R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$ (1.0)	1.0	20	3	64

a) Isolated yield based on R_F-(VM-Si)$_n$-R_F (1.0 g) and SiO$_2$ [4.8 mmol (0.29 g)]

Scheme 1

RESULTS AND DISCUSSION

In an ethanol solution of fluoroalkyl end-capped trimethoxyvinylsilane oligomer, R_F-[CH$_2$CHSi(OMe)$_3$]$_n$-R_F [R_F-(VM-Si)$_n$-R_F; R_F = CF(CF$_3$)OC$_3$F$_7$], TEOS and aqueous 50% H$_2$SO$_4$ were added. The mixture was stirred with a magnetic stirring bar at room temperature for 3 days. After the removal of the solvent, a transparent homogeneous hybrid was obtained. This glassy silica gel was purified by Soxhlet extraction with chloroform to afford the expected fluoroalkylated polymer hybrid. Similarly, longer fluoroalkylated trimethoxyvinylsilane oligomer was able to react with TEOS to afford the corresponding fluorinated oligomer/silica gel polymer hybrid. These results are shown in Scheme 1. [After hydrolysis and condensation reactions of R_F-(VM-Si)$_n$-R_F oligomers and R_F-(VM-Si)$_x$-(DMAA)$_y$-R_F [or R_F-(VM-Si)$_x$-(ACMO)$_y$-R_F] with TEOS, the structures of the obtained hybrids should be changed. Thus, the structures of these polymer hybrids are abbreviated to R_F-(VM-SiO$_2$)$_n$-R_F/SiO$_2$ and R_F-(VM-SiO$_2$)$_x$-(DMAA)$_y$-R_F [or R_F-(VM-SiO$_2$)$_x$-(ACMO)$_y$-R_F] polymer hybrids, respectively.

As shown in Scheme 1, R_F-(VM-SiO$_2$)$_n$-R_F/SiO$_2$ polymer hybrids were obtained in excellent-to-moderate isolated yields (64–70%) under mild conditions. However, we could not observe the polymerization of R_F-(VM-Si)$_n$-R_F with hydrolysis and condensation of TEOS by the use of aqueous HCl as catalysts under various conditions, although the solutions containing these substrates are clear. This finding would depend upon the strong hydrophobicity of R_F-(VM-Si)$_n$-R_F oligomers. FTIR spectra of each fluorinated hybrid in Scheme 1 showed an ≈1240-cm^{-1} peak with C—F stretching band. The X-ray fluorescence analyses (C: 18.5%; O: 37.2%; F: 22.7%; Si: 21.5%) of the obtained hybrid (Run 1) in Scheme 1 also showed the presence of fluorinated oligomer. From these findings, it was clarified that R_F-(VM-Si)$_n$-R_F oligomers could be tightly bound into the silica matrix through the sol–gel process of R_F-(VM-Si)$_n$-R_F with TEOS.
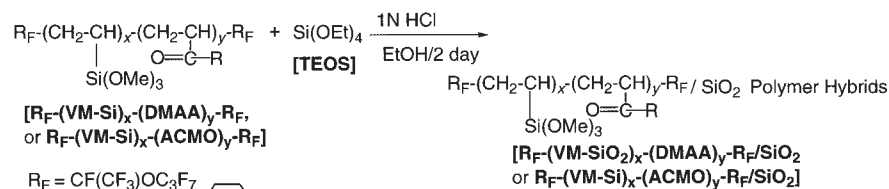
Furthermore, hybridization of fluoroalkyl end-capped trimethoxyvinylsilane–acryloylmorpholine co-oligomers [R_F-(VM-Si)$_x$-(ACMO)$_y$-R_F] and trimethoxyvinylsilane–N,N-dimethylacrylamide co-oligomers [R_F-(VM-Si)$_x$-(DMAA)$_y$-R_F] with TEOS was carried out under acidic conditions as shown in Scheme 2.

R_F-(VM-Si)$_x$-(ACMO)$_y$-R_F and R_F-(VM-Si)$_x$-(DMAA)$_y$-R_F co-oligomers were found to react smoothly with TEOS by the use of 1N HCl as a catalyst to afford fluorinated co-oligomers/SiO$_2$ polymer hybrids. These obtained fluorinated oligomers/SiO$_2$ polymer hybrids were purified by Soxhlet extraction to afford the expected fluoroalkylated polymer hybrids in 54–76% isolated yields (Scheme 2). In the hybridization of fluoroalkyl end-capped trimethoxyvinylsilane co-oligomers with TEOS, aqueous HCl is a suitable catalyst for the preparation of fluorinated polymer hybrids. This would be due to the higher amphiphilic characteristic of fluorinated co-oligomers, although the corresponding R_F-(VM-Si)$_n$-R_F oligomers exhibit a strong hydrophobic character.

Elementary analyses of fluorine in the fluorinated polymer hybrids illustrated in Scheme 2 were performed to clarify the presence of the fluorinated oligomers in the hybrids, and the results are listed in Table I.

As shown in Table I, the contents of fluorine in the fluorinated hybrids after the purification of the obtained products by Soxhlet extraction were detected by elementary analyses, which were relatively lower than the theoretical values. These results indicate that fluorinated oligomers could be tightly bound to the silica matrix.

It was demonstrated that a variety of fluoroalkyl end-capped oligomers/SiO$_2$ polymer hybrids are produced through the hydrolysis and condensation reactions of TEOS and fluoroalkyl end-capped trimethoxyvinylsilane homo- or co-oligomers involved in

R_F-(CH$_2$-CH)$_x$-(CH$_2$-CH)$_y$-R$_F$ +   Si(OEt)$_4$ $\xrightarrow[\text{EtOH/2 day}]{\text{1N HCl}}$
         | O=C–R   **[TEOS]**
      Si(OMe)$_3$

                                                                 R_F-(CH$_2$-CH)$_x$-(CH$_2$-CH)$_y$-R$_F$ / SiO$_2$ Polymer Hybrids
[R$_F$-(VM-Si)$_x$-(DMAA)$_y$-R$_F$, |
or R$_F$-(VM-Si)$_x$-(ACMO)$_y$-R$_F$]   O=C–R
                                                                         Si(OMe)$_3$
R$_F$ = CF(CF$_3$)OC$_3$F$_7$ **[R$_F$-(VM-SiO$_2$)$_x$-(DMAA)$_y$-R$_F$/SiO$_2$**
R = NMe$_2$ (DMAA), N◯O (ACMO)   **or R$_F$-(VM-Si)$_x$-(ACMO)$_y$-R$_F$/SiO$_2$]**

Run	R$_F$-[CH$_2$-CH]$_x$-[CH$_2$-CH]$_y$-R$_F$ O=C–R (g) Si(OMe)$_3$	TEOS (g)	1N HCl (g)	Product Yield[a] (%)
R = NMe$_2$ [Mn(Mw/Mn): 2180 (1.87); x: y (feed ratio) = 7 : 93]				
3	0.4	2.0 (9.6 mmol)	0.4	62
4	0.8	2.0	2.0	76
5	1.2	2.0	3.0	69
R = N◯O [Mn(Mw/Mn): 15690 (1.23); x: y (feed ratio) = 5 : 90]				
6	0.4	2.0	0.4	54
7	0.8	2.0	2.0	62
8	1.2	2.0	3.0	57

a) Isolated yield based on R$_F$-(CH$_2$CHSi(OMe)$_3$)$_x$-(CH$_2$CHCOR)$_y$-R$_F$ (0.4 ~ 1.2 g)
   and SiO$_2$ [9.6 mmol (0.58 g)].

Scheme 2

the sol–gel process under acidic conditions. In view of the development of new fluorinated oligomers/silica gel polymer hybrids, it is of particular interest to explore a novel sol–gel process by the use of fluoroalkyl end-capped oligomers possessing no trialkoxysilyl segments, which could be incorporated into silica networks. Hitherto, it was reported that organic polymers containing amido groups such as polyvinylpyrrolidone and poly(N,N-dimethylacrylamide) should be incorporated homogeneously into the silica gel, utilizing hydrogen bonding interaction between the silanol groups and amido groups of organic polymers.[16] Thus, we tried to react fluoroalkyl end-capped N,N-dimethylacrylamide homooligomers [R$_F$-(DMAA)$_n$-R$_F$], acryloylmorpholine homooligomers [R$_F$-(ACMO)$_n$-R$_F$], N-(1,1-dimethyl-3-oxobutyl)acrylamide oligomer [R$_F$-(DOBAA)$_n$-R$_F$] with TEOS under the same

conditions as those illustrated in Scheme 2. These results are shown in Scheme 3.

As shown in Scheme 3, hybridizations of TEOS with R$_F$-(DMAA)$_n$-R$_F$, R$_F$-(ACMO)$_n$-R$_F$, and R$_F$-(DOBAA)$_n$-R$_F$ oligomers were found to proceed smoothly to afford the corresponding fluorinated oligomers/silica gel polymer hybrids in 10–85% of isolated yields after the purification of the crude products with Soxhlet extraction. It is well known that the incorporation of organic commodity polymers into a silica glass causes phase separation and the composite glass becomes turbid. However, our present fluoroalkyl end-capped DMAA and ACMO oligomers/silica gel polymer hybrids are transparent as well as R$_F$-(VM-SiO$_2$)$_n$- R$_F$/SiO$_2$ polymer hybrids, R$_F$-(VM-SiO$_2$)$_x$-(ACMO)$_y$-R$_F$/SiO$_2$ polymer hybrids, and R$_F$-(VM-SiO$_2$)$_x$-(DMAA)$_y$-R$_F$/SiO$_2$ polymer hybrids[16],

TABLE I
Elementary Analyses for Fluorine in R$_F$-Oligomers/SiO$_2$ Polymer Hybrids

Run[a]	R$_F$-Oligomer [R$_F$ = CF(CF$_3$)OC$_3$F$_7$] [Fluorine atom (%)]	R$_F$-Oligomer/SiO$_2$ hybrid [Fluorine atom (%)]	
	Found	Found	Theoretical
	R$_F$-[CH$_2$CHSi(OMe)$_3$]$_x$-(DMAA)$_y$-R$_F$		
3	19.91	1.79	8.12
4	19.91	6.52	11.54
5	19.91	6.43	13.42
	R$_F$-[CH$_2$CHSi(OMe)$_3$]$_x$-(ACMO)$_y$-R$_F$		
6	18.89	3.72	7.71
7	18.89	9.64	11.03
8	18.89	6.82	8.82

[a] Each different from those of Scheme 2.

R$_F$-(CH$_2$-CH)$_n$-R$_F$ +   Si(OEt)$_4$ $\xrightarrow[\text{EtOH /2 day}]{\text{1N HCl}}$ R$_F$-(CH$_2$-CH)$_n$-R$_F$/ SiO$_2$ Polymer Hybrids
    | [TEOS] |
  O=C-R   O=C-R

R$_F$ = CF(CF$_3$)O[CF$_2$CF(CF$_3$)O]$_m$C$_3$F$_7$;   R = NMe$_2$: DMAA; R = N◯O; ACMO
m = 0, 1, 2

R = NHCMe$_2$CH$_2$C(=O)Me: DOBAA

Run	R$_F$-[CH$_2$-CHC(=O)R]$_n$-R$_F$ (g)	TEOS (g)	1N-HCl (g)	Product Yield[a] (%)
R$_F$ = CF(CF$_3$)OC$_3$F$_7$; R = NMe$_2$ [Mn (Mw/Mn): 2020 (1.12)]				
9	0.4	2.0 (9.6 mmol)	1.0	21
10	0.8	2.0	2.0	85
11	1.2	2.0	3.0	10
12 R$_F$ = CF(CF$_3$)OC$_3$F$_7$; R = N◯O [Mn (Mw/Mn): 12500 (1.26)]				
	0.4	2.0	1.0	74
13 R$_F$ = CF(CF$_3$)OC$_3$F$_7$; R = NHCMe$_2$CH$_2$C(=O)Me [Mn (Mw/Mn): 3710 (2.32)]				
	0.4	2.0	2.0	68
14 R$_F$ = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$; R = DOBAA [Mn (Mw/Mn): 6770 (2.02)]				
	0.4	2.0	2.0	61
15 R$_F$ = CF(CF$_3$)OCF$_2$CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$; R = DOBAA [Mn (Mw/Mn): 9390 (1.81)]				
	0.4	2.0	2.0	85

a) Isolated yield based on R$_F$-(CH$_2$CHCOR)$_n$-R$_F$ (0.4 ~ 1.2 g) and SiO$_2$ (9.6 mmol (0.58 g).

Scheme 3

and have no phase separation. Furthermore, the carbonyl stretching band of R$_F$-(DMAA)$_n$-R$_F$ oligomer was shifted from 1632 to 1624 cm^{-1} by the hybridization. This lower wavelength number region shift of the carbonyl stretching band was observed in other fluoroalkyl end-capped oligomers (data not shown). These findings suggest th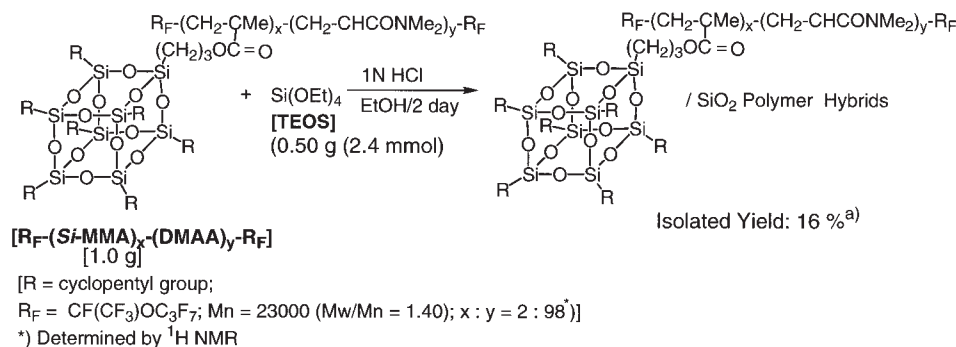at molecular-level combination, which is due to the interaction between the amido groups in oligomers and residual silanol groups through the intermolecular hydrogen bonding, was accomplished. Elementary analyses of fluorine for some fluoroalkyl end-capped oligomers in Scheme 3 indicate that the contents of fluorine were slightly decreased even after the hybridization with TEOS as shown in the following:

	R$_F$-oligomer [fluorine atom (%)]	R$_F$-oligomer/SiO$_2$ polymer hybrid [fluorine atom (%)]	
Run 9 in Scheme 3 R$_F$-(DMAA)$_n$-R$_F$			
	Found	Found	Theoretical
	24.56	6.70	10.02
Run 12 in Scheme 3 R$_F$-(ACMO)$_n$-R$_F$			
	Found	Found	Theoretical
	21.26	6.03	8.68

Therefore, the hybridization of fluoroalkyl end-capped DMAA, ACMO, and DOBAA homo-oligomers with TEOS through a sol–gel process should result from the physical entrapment of fluoroalkyl end-capped oligomers in forming silica gel networks with the intermolecular hydrogen bonding interaction between the amido segments in oligomers and the residual silanol groups in silica gels.

Previously, we reported that fluoroalkyl end-capped DMAA co-oligomers containing silsesquioxane segments were prepared by the reactions of fluoroalkanoyl peroxides with DMAA and the corresponding methacrylate monomer bearing silsesquioxane unit (*Si*-MMA), the structure of which is similar as that of the obtained siloxane network after the hydrolysis and subsequent condensation of TEOS.[13] Therefore, because this fluorinated *Si*-MMA co-oligomer [R$_F$-(*Si*-MMA)$_x$-(DMAA)$_y$- R$_F$] is expected to have a high affinity for TEOS, a novel fluorinated *Si*-MMA co-oligomer/silica gel polymer hybrid should be obtained through the sol–gel process with TEOS under acidic conditions. In fact, as shown in Scheme 4, the hybridization of R$_F$-(*Si*-

R_F-(CH$_2$-ĊMe)$_x$-(CH$_2$-CHCONMe$_2$)$_y$-R$_F$
(CH$_2$)$_3$OĊ=O

+ Si(OEt)$_4$ $\xrightarrow[\text{EtOH/2 day}]{\text{1N HCl}}$

[TEOS]
(0.50 g (2.4 mmol)

/ SiO$_2$ Polymer Hybrids

Isolated Yield: 16 %[a)]

[R_F-(*Si*-MMA)$_x$-(DMAA)$_y$-R$_F$]
[1.0 g]

[R = cyclopentyl group;
R_F = CF(CF$_3$)OC$_3$F$_7$; Mn = 23000 (Mw/Mn = 1.40); x : y = 2 : 98[*])]
*) Determined by ^{1}H NMR

a) Isolated yield based on R_F-(*Si*-MMA)$_x$-(DMAA)$_y$-R$_F$ and SiO$_2$ (2.4 mmol: 0.14 g).

Scheme 4

MMA)$_x$-(DMAA)$_y$-R$_F$ co-oligomer was proceeded to afford R_F-(*Si*-MMA)$_x$-(DMAA)$_y$-R$_F$ co-oligomer/silica gel polymer hybrid under acidic conditions.

Elementary analyses for fluorine in R_F-(*Si*-MMA)$_x$-(DMAA)$_y$-R$_F$ co-oligomer/silica gel polymer hybrid are as follows:

R_F-(*Si*-MMA)$_x$-(DMAA)$_y$-R$_F$ cooligomer	R_F-(*Si*-MMA)$_x$-(DMAA)$_y$-R$_F$ cooligomer/SiO$_2$ polymer hybrid	
[fluorine atom (%)]	[fluorine atom (%)]	
Found	Found	Theoretical
10.42	6.66	4.27

This result shows that R_F-(*Si*-MMA)$_x$-(DMAA)$_y$-R$_F$ co-oligomer could be tightly incorporated into the siloxane networks, which are obtained after the hydrolysis and subsequent condensation of TEOS under acidic conditions to afford the corresponding fluorinated co-oligomer/silica gel polymer hybrid. However, the content (6.66%) of fluorine in the obtained hybrid is higher than that of theoretical one (4.27%). This indicates that the hydrolysis and condensation of TEOS was not proceeded sufficiently under Scheme 4's conditions.

The contents of a variety of fluoroalkyl end-capped oligomers in the hybrids illustrated in Schemes 1–4 were also estimated by the use of thermogravimetric analyses (TGA), in which the weight loss of these hybrids was measured by raising the temperature to around 800°C; the results are shown in Table II.

As shown in Table II, of particular interest, R_F-(VM-SiO$_2$)$_n$-R$_F$ oligomers/SiO$_2$ polymer hybrids lost 10% of their weight around 344°C [R_F = CF(CF$_3$)OC$_3$F$_7$] and 404°C [R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$] under nitrogen. In contrast, thermal stability: T_{dec} (163–315°C: defined by a 10% mass loss at a 10°C/min heating rate under nitrogen) of other fluorinated oligomers/SiO$_2$ polymer hybrids in Table II were found to decrease significantly compared to those of R_F-(VM-SiO$_2$)$_n$- R$_F$ oligomer/SiO$_2$ polymer hybrids. Thus, our present fluorinated trimethoxyvinylsilane oligomers/SiO$_2$

polymer hybrids are attractive functional materials possessing excellent thermal stability. On the other hand, as shown in Table II, in a variety of fluorinated homo- and co-oligomers/SiO$_2$ polymer hybrids (Runs 9–11, Runs 3 and 5, and Runs 6 and 8), the weight loss of each fluorinated polymer hybrid by TGA was found to decrease with a decrease of the feed ratio of fluoroalkyl end-capped oligomer based on TEOS. This finding suggests that fluoroalkyl end-capped oligomers could be incorporated homogeneously into the silica gel by utilizing hydrogen bonding interaction between the silanol groups and amido segments of fluorinated oligomers including a sol–gel reaction between TEOS and trimethoxysilyl segments in fluorinated oligomers. In R_F-(DOBAA)$_n$-R$_F$ oligomers/SiO$_2$ polymer hybrids, the weight loss of fluorinated hybrids by TGA was found to increase with an increase of the fluoroalkyl chains in the fluorinated polymer hybrids, which were prepared under the same feed ratios of TEOS and fluorinated DOBAA oligomers (see Scheme 3). This finding suggests that fluoroalkyl end-capped oligomers could be incorporated homogeneously into the silica gel by utilizing hydrogen bonding.

Specific surface area and particle size of the fluorinated polymer hybrids listed in Schemes 1–3 were determined by the BET method,[17] and the results are shown in Table III. Our present fluorinated oli-

TABLE II
Thermal Stability (T_{dec})[a] of A Variety of Fluoroalkyl End-capped Oligomers/SiO$_2$ Polymer Hybrids

Run[b]	Type of oligomer contained in polymer hybrid	T_{dec}(°C)
1	R_F-(VM-Si)$_n$-R_F [R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$]	404
2	[R_F = CF(CF$_3$)OC$_3$F$_7$]	344
15	R_F-(DOBAA)$_n$-R_F [R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$]	224
14	[R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$]	243
13	[R_F = CF(CF$_3$)OC$_3$F$_7$]	273
9	R_F-(DMAA)$_n$-R_F [R_F = CF(CF$_3$)OC$_3$F$_7$]	254
10	[R_F = CF(CF$_3$)OC$_3$F$_7$]	215
11	[R_F = CF(CF$_3$)OC$_3$F$_7$]	163
3	R_F-(VM-Si)$_x$-(DMAA)$_y$-R_F [R_F = CF(CF$_3$)OC$_3$F$_7$]	273
5	[R_F = CF(CF$_3$)OC$_3$F$_7$]	171
6	R_F-(VM-Si)$_x$-(ACMO)$_y$-R_F [R_F = CF(CF$_3$)OC$_3$F$_7$]	315
8	[R_F = CF(CF$_3$)OC$_3$F$_7$]	245
—[c]	R_F-(Si-MMA)$_x$-(DMAA)$_y$-R_F [R_F = CF(CF$_3$)OC$_3$F$_7$]	235

[a] Defined by a 10% mass loss at a 10°C/min heating rate.
[b] Each different from those of Schemes 1, 2, and 3.
[c] See Scheme 4.

gomers/SiO$_2$ polymer hybrids were found to have a relatively large surface area ($\approx$143 m^2/g). In fluoroalkyl end-capped trimethoxyvinylsilane homo- and co-oligomers/SiO$_2$ polymer hybrids, their primary particle sizes are submicron levels (170–541 nm). This is due to the acid-catalyzed sol–gel reactions between TEOS and trimethoxysilyl segments in fluorinated oligomers, in which the hydrolysis step is faster than the condensation step, resulting in a more extended silica network structure.[18] On the other hand, fluoroalkyl end-capped DMAA and DOBAA homooligomers/SiO$_2$ polymer hybrids could afford nanometer size-controlled particles (84–99 nm). This interesting finding would depend upon whether fluoroalkyl end-capped DMAA and DOBAA oligomers can form the nanometer size-controlled molecular aggregates in so-

lutions,[19] and these fluorinated aggregate cores should interact with TEOS to afford very fine hybrid nanoparticles.

Interestingly, it was clarified that the sol solutions, which are obtained by the reactions of TEOS with R_F-(VM-Si)$_x$-(ACMO)$_y$-R_F, R_F-(DMAA)$_n$-R_F, and R_F-(ACMO)$_x$-R_F [R_F = CF(CF$_3$)OC$_3$F$_7$] oligomers in ethanol under acidic conditions for 4 h at room temperature, can be applied to the surface modifications of the glass. In fact, these fluorinated oligomers/silica gel polymer hybrids were tested for surface activity as a new type of surface modification agent.

As shown in Table IV, the contact angles for dodecane on the modified glass with fluorinated oligomers/silica gel polymer hybrids showed a significantly large value (27–42°) compared with that (0°) of

TABLE III
Specific Surface Area and Particle Size of Fluoroalkyl End-Capped Oligomers/SiO$_2$ Polymer Hybrids Calculated by BET Method

Run[a]	Type of oligomer contained in polymer hybrid	Specific surface area (m^2/g)	Particle Size (nm)
1	R_F-(VM-Si)$_n$-R_F [R_F = CF(CF$_3$)OC$_3$F$_7$]	50	227
2	R_F-(VM-Si)$_n$-R_F [R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$]	75	170
13	R_F-(DOBAA)$_n$-R_F [R_F = CF(CF$_3$)OC$_3$F$_7$]	143	88
14	R_F-(DOBAA)$_n$-R_F [R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$]	108	97
15	R_F-(DOBAA)$_n$-R_F [R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$]	102	99
9	R_F-(DMAA)$_n$-R_F [R_F = CF(CF$_3$)OC$_3$F$_7$]	129	84
3	R_F-(VM-Si)$_x$-[CH$_2$CHC(=O)NMe$_2$]$_y$-R_F [R_F = CF(CF$_3$)OC$_3$F$_7$]	27	541
6	R_F-(VM-Si)$_X$-(CH$_2$CH)$_y$-R_F [R_F = CF(CF$_3$)OC$_3$F$_7$] O=C–N(morpholine)	115	69
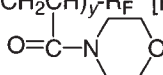
[a] Each different from those of Schemes 1, 2, and 3.

TABLE IV
Contact Angles of Dodecane and Water on Glasses Treated with Fluoroalkyl End-Capped Oligomers/SiO$_2$ Polymer Hybrids, Fluoroalkyl End-Capped Oligomers, and SiO$_2$ before and after These Modified Glasses Were Dipped into Chloroform [R$_F$ = CF(CF$_3$)OC$_3$F$_7$]

	R$_F$-Oligomer	Contact angle (Degree)							
			Water						
Run[a]	Dip time	Dodecane	0 min	5 min	10 min	15 min	20 min	25 min	30 min
9	R$_F$-(DMAA)$_x$-R$_F$/SiO$_2$ polymer hybrid								
	Before dipping	42	44	38	32	25	20	15	9
	After 1 day	42	44	39	32	27	20	17	0
	R$_F$-(DMAA)$_x$-R$_F$								
	Before Dipping	42	14	0	0	0	0	0	0
	After 1 day	16	14	0	0	0	0	0	0
12	R$_F$-(ACMO)$_x$-R$_F$/SiO$_2$ polymer hybrid								
	Before dipping	27	36	33	26	20	15	11	5
	After 1 day	27	36	27	17	11	8	0	0
	R$_F$-(ACMO)$_x$-R$_F$								
	Before dipping	27	29	27	23	15	12	6	0
	After 1 day	0	29	23	20	11	7	0	0
6	R$_F$-(VM-Si)$_x$-(ACMO)$_y$-R$_F$/SiO$_2$ polymer hybrid								
	Before dipping	41	75	66	64	58	47	41	31
	After 1 day	41	48	42	36	32	23	13	0
	R$_F$-(VM-Si)$_x$-(ACMO)$_y$-R$_F$								
	Before dipping	43	75	72	64	45	38	28	22
	After 1 day	15	33	32	29	25	23	19	17
	SiO$_2$								
	Before dipping	0	29	29	29	29	29	29	29
	After 1 day	0	29	29	29	29	29	29	29

[a] Each different from those of Schemes 2 and 3.

the glass treated with only TEOS (in the absence of the fluorinated oligomers). In contrast, R$_F$-(VM-Si)$_x$-(ACMO)$_y$-R$_F$, R$_F$-(DMAA)$_n$-R$_F$, and R$_F$-(ACMO)$_y$-R$_F$ oligomers also showed the same large values (27–43°) as those of fluorinated oligomers/silica gel hybrids on their surface. In each hybrid or oligomer, time dependence of contact angle of dodecane was not observed. However, the contact angles of dodecane were found to decrease extremely on the glass surface after these modified glasses were dipped into chloroform solution, which exhibits good solubility for these parent fluorinated oligomers, for 1 day at room temperature, although the decrease of the contact angles could not be observed at all in the case of modified glasses with the fluorinated oligomers/silica gel polymer hybrids. This finding would be due to the covalent modification on glass surface through the condensation process between the residual silanol groups in the polymer hybrids and the silanol groups on the glass surface.

More interestingly, a steep time dependence of contact angle of water was observed in these fluorinated oligomers/silica gel polymer hybrids as shown in Table III. The contact angles were found to decrease significantly from 75° (or 44°, 36°) to 31°(or 9°, 5°) over 30 min with each hybrid, although the R$_F$-(VM-Si)$_n$-R$_F$ oligomer/silica gel polymer hybrids had strong oleophobic and hydrophobic properties.[Contact angles of dodecane and water on the glass treated with this fluorinated hybrid (R$_F$ = CF(CF$_3$)OC$_3$F$_7$) are 44° and 90°, respectively, and time dependence for the contact angles of dodecane and water was not observed.] This finding suggests that at the interface with water, hydrophobic fluoroalkyl segments in fluorinated oligomers are easily replaced by the strongly hydrophilic dimethyamino carbonyl segments [—C(=O)NMe$_2$] or morpholino segments in fluorinated oligomers, and these hydrophilic segments should be arranged more regularly at the water interface. It takes about 30 min to replace the fluoroalkyl segments by the hydrophilic segments when the environment is changed from air to water. These modified glasses were found to possess not only strong oleophobic but also good hydrophilic characteristics on their surface even after dipping these glasses into the chloroform solution for 1 day at room temperature.

To clarify the surface arrangement of fluoroalkyl groups in fluorinated hybrids on the glass surface, we analyzed the glass surface modified by fluorinated oligomers/silica gel polymer hybrids by the use of the X-ray photoelectron spectroscopy (XPS) technique, and the relative area ratios of fluorine (F$_{1s}$), nitrogen (N$_{1s}$), carbon (C$_{1s}$), and oxygen (O$_{1s}$) based on silicon (Si$_{2p}$) at the surface were also estimated. These results are shown in Table V.

As shown in Table V, interestingly, the relative area of fluorine was in general found to become higher in

TABLE V
Relative Area Ratios of F_{1s} for Si_{2p} Peaks of the X-ray Photoelectron Spectroscopy Spectra of R_F-Oligomer/SiO_2 Polymer Hybrids

Run[a]	R_F-oligomer in polymer hybrid	F : 1s	O : 1s	C : 1s	Si : 2p	N : 1s
—[b]	R_F-(Si-MMA)$_x$-(DMAA)$_y$-R_F	1.62	2.47	5.13	1.00	0.85
3	R_F-(CH$_2$CHSi(OMe)$_3$)$_x$-(DMAA)$_y$-R_F	0.82	2.17	1.67	1.00	0.16
9	R_F-(DMAA)$_x$-R_F	2.19	1.99	2.10	1.00	0.20
12	R_F-(ACMO)$_x$-R_F	2.34	2.33	3.34	1.00	0.35

[a] Each different from those of Schemes 2 and 3.
[b] See Scheme 4.

R_F-(DMAA)$_n$-R_F and R_F-(ACMO)$_n$-R_F oligomers/silica gel polymer hybrids. This would be due to the higher surface arrangement of fluoroalkyl groups in fluoroalkyl end-capped homo-oligomers/silica gel polymer hybrids above the glass surface, because these fluorinated hybrids should be prepared by the physical entrapment of fluorinated homo-oligomers into the siloxane network.

In conclusion, it was verified that fluoroalkyl end-capped trimethoxyvinylsilane oligomers, trimethoxyvinylsilane–DMAA cooligomers, and trimethoxyvinylsilane–ACMO cooligomers are convenient preoligomers for the preparation of new fluorinated oligomers/silica gel polymer hybrids by the sol–gel reactions including hydrolysis and subsequent condensation between TEOS and trimethoxysilyl segments in oligomers under acidic conditions. Additionally, fluoroalkyl end-capped DMAA oligomers, ACMO oligomers, and DMAA co-oligomer containing silsesquioxane segments are also found to react with TEOS under acidic conditions to afford fluorinated oligomers/silica gel polymer hybrids. In these fluorinated hybrids, fluorinated trimethoxyvinylsilane oligomers/silica gel polymer hybrids have a higher thermal stability compared to those of other fluorinated polymer hybrids. Fluorinated sol solutions especially which are prepared by the sol–gel reactions of fluorinated homo- and co-oligomers with TEOS under acidic conditions, are applicable to a novel surface modification agent of a variety of common materials such as glass to exhibit not only strong oleophobicity imparted by fluorine but also a good hydrophilicity on their surface.

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