Synthesis and Properties of Novel Fluoroalkyl End-Capped Oligomers Containing Silsesquioxane Segments

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ABSTRACT: Fluoroalkyl end-capped homo- and co-oligomers containing silsesquioxane segments were prepared by the reactions of fluoroalkanoyl peroxides with the corresponding methacrylate monomer-bearing silsesquioxane unit (*Si*-MMA) and comonomers such as N,N-dimethylacrylamide (DMAA) and acrylic acid (ACA). These new fluorinated *Si*-MMA oligomers were easily soluble in various organic solvents and were able to reduce the surface tension of *m*-xylene effectively. The modified poly(methyl methacrylate) [PMMA] and glass surface treated with fluorinated *Si*-MMA homo-oligomers exhibited a strong oleophobicity, although these fluorinated oligomers possess high oleophilic silsesquioxane segments. In contrast, the modified PMMA surface treated with fluorinated *Si*-MMA–DMAA cooligomers exhibited a good hydrophilicity with a strong oleophobicity. In a series of fluorinated *Si*-MMA oligomers, fluorinated *Si*-MMA homo-oligomers had a relatively high thermal stability. Therefore, these fluoroalkyl end-capped *Si*-MMA oligomers are suggested to have high potential for new functional materials through their unique properties such as a high solubility and surface active properties. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3486–3493, 2002

Key words: fluoropolymers; functionalization of polymers; silicones; surfactants; thermogravimetric analysis

INTRODUCTION

There has been great interest in partially fluorinated polymers, especially fluoroalkyl end-capped polymer, because they exhibit various unique properties such as a high solubility, surface active properties, and biological activities that cannot be achieved by the perfluorinated polymers and randomly fluoroalkylated polymers.[1] In fact, fluoroalkyl end-capped acrylic acid oligomers [R_F-($CH_2CHCOOH$)$_n$-R_F; R_F = fluoroalkyl groups] have a good solubility in water and polar organic solvents such as MeOH, EtOH, and dimethyl sulfoxide and were able to reduce the surface tension of water quite effectively with a clear break point resembling a CMC (critical micelle concentration).[2] However, it is well-known that organosilicon compounds are attractive functional materials in the field of material science and that these compounds exhibit good hydrophobic properties but not oleophobic properties.[3] In contrast, organofluorine compounds bearing relatively longer fluoroalkyl groups have both hydrophobic and oleophobic properties. Therefore, there has been a need for the development of new functional materials possessing the excellent properties imparted by both silicon and fluorine.[4] From this suspective, we have already reported on the synthesis and applications of various fluoroalky end-capped oligomers containing silicon segments.[5] For example, it was demonstrated that fluoroalkyl end-capped acrylic acid–trimethylvinylsilane cooligomers [R_F–($CH_2CHCOOH$)$_x$–($CH_2CHSiMe_3$)$_y$–R_F; R_F = fluoroalkyl groups] are easily soluble in water, and nonpolar organic solvents such as benzene and *m*-xylene, and these co-oligomers can reduce the surface tension of these solvents quite effectively.[6] Furthermore, these fluoroalkyl end-capped co-oligomers were clarified to form self-assembled molecular aggregates with the aggregations of terminal fluoroalkyl segments in aqueous and organic media.[7] Interestingly, these fluorinated molecular aggregates were found to interact with HIV-1 viruses to exhibit a potent anti-HIV-1 activity.[8] Therefore, it is very important to develop new fluoroalkyl end-capped oligomers containing a variety of silicon segments. Hitherto, much attention has been focused on functionalized polyhedral siloxanes, also called silsesquioxanes, as models for the investigation of surface-modified silica gels, precursors to silicates, their applications in catalysts, and polymerizable reagents.[9] Therefore, it is deeply desirable to synthesis

$$R_F = CF(CF_3)O[CF_2CF(CF_3)O]_mC_3F_7; \quad m = 0, 1$$
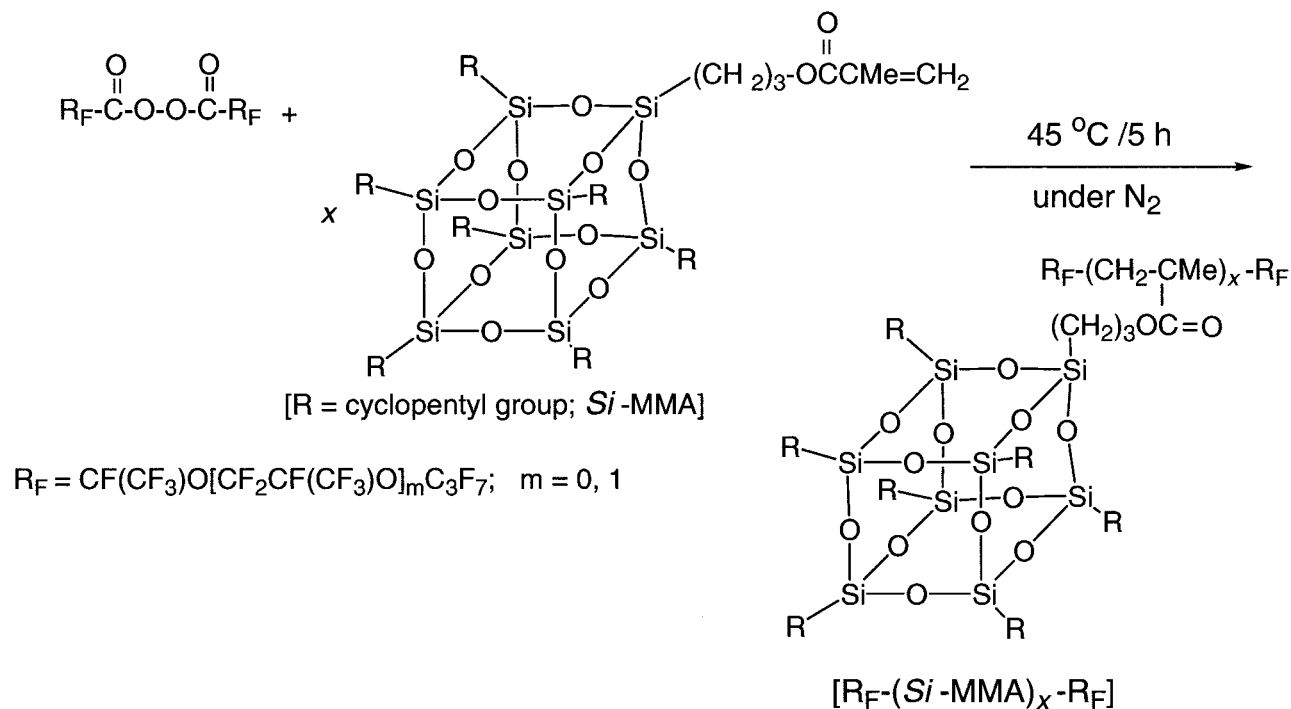
Scheme 1

novel fluoroalkyl end-capped oligomers containing silsesquioxane segments with the view of developing new functional materials with qualities imparted by both fluorine and silicon. In this article we report on the synthesis and properties of novel fluoroalkyl end-capped oligomers containing silsesquioxane segments.

RESULTS AND DISCUSSION

We were initially interested in methacrylate-functionalized polyhedral oligomeric silsesquioxane (*Si*-MMA) as a radical polymerizable monomer in the synthesis of fluoroalkyl end-capped oligomers con-

taining silsesquioxane segments. Thus, we tried to react *Si*-MMA with fluoroalkanoyl peroxides, and the results for these reactions are shown in Scheme 1 and Table I.

As shown in Scheme 1 and Table I, the reactions of *Si*-MMA with fluoroalkanoyl peroxides were found to proceed smoothly under very mild conditions, to afford fluoroalkyl end-capped *Si*-MMA homo-oligomers in 40% ~ 71% isolated yields. The fluoroalkyl end-capped *Si*-MMA homooligomers thus obtained are insoluble in water; however, these oligomers are easily soluble in common organic solvents such as chloroform, 1,2-dichloroethane, tetrahydrofuran, benzene, toluene, *m*-xylene, ethyl acetate, acetone, hexane, N,N-dimethyl-

TABLE I
Reactions of Fluoroalkanoyl Peroxides with *Si*-MMA

No.	R_F in Peroxide (mmol)	*Si*-MMA (mmol)	Product $R_F\text{-}(Si\text{-MMA})_x\text{-}R_F{}^a$	
			Yield (%)	$\overline{M}_n\ (\overline{M}_w/\overline{M}_n)$
1	$CF(CF_3)OC_3F_7$			
	1	1	44	2060 (1.37)
2	$CF(CF_3)OC_3F_7$			
	1	2	66	1200 (1.25)
3	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$			
	1	1	40	1080 (1.14)
4	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$			
	1	2	71	1460 (1.50)

[a] The yields are based on the starting materials (*Si*-MMA and the decarboxylated peroxide unit [R_F–R_F]). Molecular weights were determined by gel permeation chromatography analyses.
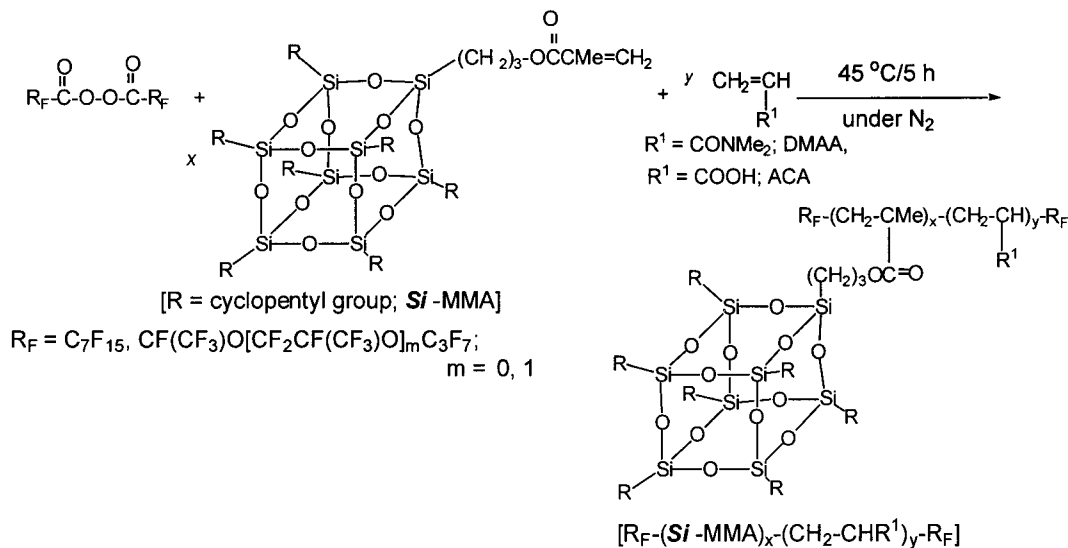
Scheme 2

formamide, and a fluorinated solvent (1 : 1 mixed solvents of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane). The molecular weights of fluoroalkyl end-capped *Si*-MMA homooligomers listed in Table I were measured by GPC (gel permeation chromatography) calibrated with standard polystyrenes by using tetrahydrofuran as the eluent, and the molecular weights of the oligomers obtained were a few thousand levels. In addition, negative peaks at higher molecular regions were observed in each oligomer. This result is not clarified at present; however, this finding would depend on the that fluoroalkyl end-capped *Si*-MMA homo-oligomers are likely to form molecular aggregates derived from the synergistical interaction of the aggregations of end-capped fluoroalkyl groups and on the intermolecular interaction between the silsesquoixane segments. In fact, in fluoroalkyl end-capped oligomers containing betaine segments, we have already reported that these fluorinated oligomers could cause a gelation derived from the synergistical interaction of the aggregations of fluoroalkyl segments and the ionic interactions of the betaine segments.[10]

We have also tried to synthesize a variety of fluoroalkyl end-capped *Si*-MMA cooligomers by the use of fluoroalkanoyl peroxide as a key intermediate, and the reaction scheme and the results were as follows:

As shown in Scheme 2 and Table II, the reactions of fluoroalkanoyl peroxides with *Si*-MMA and comonomers such as N,N-dimethylacrylamide (DMAA) and acrylic acid (ACA) were found to proceed smoothly to afford fluoroalkyl end-capped *Si*-MMA cooligomers. Co-oligomerization ratios (x : y) of the obtained co-oligomers were determined by ^{1}H NMR (proton nuclear magnetic resonance), and the ratios of silsesquioxane segments were 1% ∼ 5%. The molecular weights of the co-oligomers in Table II were determined by GPC under similar conditions as those of fluoroalkyl end-capped *Si*-MMA homo-oligomers. In the measurements of the molecular weights of these fluoroalkyl end-capped *Si*-MMA cooligomers by GPC, we had a tendency similar to that of the homo-oligomers in Table I, and a negative peak in each co-oligomer was observed. A series of fluoroalkyl end-capped *Si*-MMA–DMAA co-oligomers showed no solubility in water, but these fluorinated co-oligomers possessed a good solubility in common organic solvents such as MeOH, EtOH, tetrahydrofuran, chloroform, 1,2-dichloroethane, toluene, benzene, ethyl acetate, dimethyl sulfoxide, N,N-dimethylformamide, and acetone. Fluoroalkyl end-capped *Si*-MMA–ACA co-oligomers exhibited a slightly poor solubility compared with that of the corresponding DMAA co-oligomers and were insoluble in ethyl acetate and acetone. Although these fluoroalkyl end-capped *Si*-MMA co-oligomers possess hydrophilic segments such as carboxydimethylamide [–C(=O)NMe$_2$] and carboxy groups, these fluorinated co-oligomers could not show a hydrophilic property. This finding would result from the presence of silsesquioxane segments, which exhibit a highly oleophilic character.

The relatively high solubility of our fluoroalkyl end-capped *Si*-MMA oligomers in organic solvents should open a new route to the development of the field of new functional fluorinated silicon materials. Thus, it is very interesting to develop these fluorinated *Si*-MMA oligomers to new fluorinated polymeric surfactants. The surface properties of our present fluoroalkyl end-capped *Si*-MMA–DMAA cooligomers were evaluated by measuring the reduction in surface tensions of *m*-xylene solutions by these co-oligomers using the

TABLE II
Reactions of Fluoroalkanoyl Peroxides with *Si*-MMA and Comonomers

No.	R_F in Peroxide (mmol)	*Si*-MMA (mmol)	$CH_2 = CHR^1$ (mmol)	Product R_F-(*Si*-MMA)$_x$-(CH$_2$-CHR^1)$_y$-R$_F$		
				Yield (%)[a]	$\overline{Mn}(\overline{Mw}/\overline{Mn})$[b]	x : y[c]
R^1 = CONMe$_2$:						
5	CF(CF$_3$)OC$_3$F$_7$ 1	0.5	20	23	23000 (1.49)	2:98
6	CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$ 2	0.5	20	11	5730 (1.55)	1:99
7	CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$ 2	1	20	26	7130 (1.91)	3:97
8	CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$ 2	1	20	19	31000 (4.60)	5:95
9	C$_7$F$_{15}$ 1	0.5	10	43	3880 (1.49)	1:99
R^1 = CO$_2$H:						
10	CF(CF$_3$)OC$_3$F$_7$ 2	1	20	36	4790 (1.36)	2:98
11	CF(CF$_3$)OC$_3$F$_7$ 1	0.5	20	53	4370 (1.29)	2:98

[a] The yields are based on the starting materials (*Si*-MMA, co-monomer, and the decarboxylated peroxide unit [R_F–R_F]).
[b] Molecular weights were determined by gel permeation chromatography analyses.
[c] Co-oligomerization ratios of the co-oligomers were determined by proton nuclear magnetic resonance.

Wilhelmy plate method at 30°C. These results are shown in Figure 1.

As Figure 1 shows, a significant decrease in the surface tension of *m*-xylene, around 22 mN/m, was found for longer perfluorooxaalkyl end-capped *Si*-MMA co-oligomers, compared with shorter fluoroalkylated and nonfluorinated *Si*-MMA co-oligomers. This finding suggests that longer perfluorooxaalkyl chains in co-oligomers are likely to be arranged regularly above the *m*-xylene surface, although this co-oligomer possesses a highly oleophilic silsesquioxane segment.

Fluoroalkyl end-capped *Si*-MMA oligomers are expected to become surface-active to the common organic materials such as poly(methyl methacrylate) (PMMA), because these fluorinated *Si*-MMA oligomers possess a good solubility in common organic solvents and a surfactant property, as shown in Figure 1. Thus, we have measured the contact angles for water and dodecane on the PMMA surface treated with these fluorinated *Si*-MMA oligomers (1% (*m/m*) based on PMMA), and the results are shown in Table III.

As shown in Table III, significantly large values (15° ~ 36°) of the contact angles of dodecane were ob-
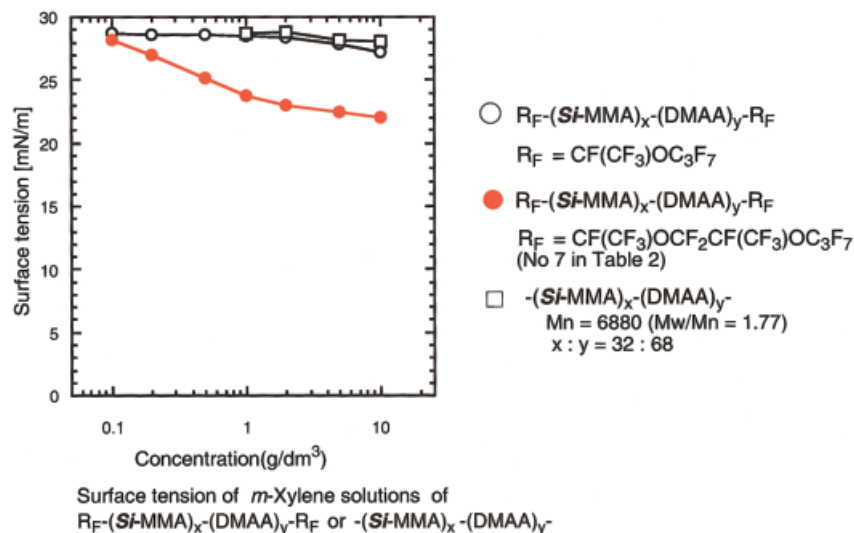

Surface tension of *m*-Xylene solutions of
R_F-(*Si*-MMA)$_x$-(DMAA)$_y$-R_F or -(*Si*-MMA)$_x$-(DMAA)$_y$-

Figure 1 Surface tension of *m*-xylene solutions of R_F–(*Si*-MMA)$_x$–(DMAA)$_y$–R_F or–(*Si*-MMA)$_x$–(DMAA)$_y$–.

TABLE III
Contact Angles of Dodecane and Water on PMMA Films Treated with R_F–(Si-MMA)$_x$–R_F and
R_F–(Si-MMA)$_x$–(CH$_2$CHR^1)$_y$–R_F[a]

			Contact Angle (Degree)							
						Water				
No.[b]	Oligomer	Dodecane	0 min	5 min	10 min	15 min	20 min	25 min	30 min	
1	R_F–(Si-MMA)$_x$–R_F [R_F = CF(CF$_3$)OC$_3$F$_7$]	35	92							
4	R_F–(Si-MMA)$_x$–R_F [R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$]	36	97							
	–(Si-MMA)$_x$–(Mn = 3800)	0	87							
	R_F–(Si-MMA)$_x$–(CH$_2$CHR^1)$_y$–R_F									
5	R^1 = CO$_2$NMe$_2$ [R_F = CF(CF$_3$)OC$_3$F$_7$]	15	92	64	56	44	32	27	26	
7	R^1 = CO$_2$NMe$_2$ [R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$]	34	60	39	37	36	35	34	30	
	–(Si-MMA)$_x$–(CH$_2$CHCONMe$_2$)$_y$– Mn = 6880 (x : y = 32 : 68)	0	45	45	45	45	45	45	45	
	PMMA	0	68							

[a] Concentration of oligomer based on PMMA is 1% (m/m).
[b] Each different from those of Tables I and II.

served on the PMMA surface treated with fluoroalkyl end-capped Si-MMA homo- and co-oligomers, especially longer fluoroalkylated oligomers, compared with those (0°) of the corresponding nonfluorinated Si-MMA homo-oligomers, co-oligomers and nontreated PMMA, indicating that fluorinated Si-MMA oligomers possess a strong oil repellency. The contact angles of water for R_F–(Si-MMA)$_x$–R_F were found to increase compared with that of the corresponding nonfluorinated oligomer (–[Si-MMA]–) or nontreated PMMA. However, interestingly, a steep time dependence of contact angles of water was observed in R_F–(Si-MMA)$_x$–(DMAA)$_y$–R_F as in Table III, and the contact angles of water for R_F–(Si-MMA)$_x$–(DMAA)$_y$–R_F decreased dramatically from 92° (or 60°) to 26° (or 30°) over 30 min, although the contact angles of water for the corresponding nonfluorinated–(Si-MMA)$_x$–(DMAA)$_y$–,–(Si-MMA)$_x$–, and R_F–(Si-MMA)$_x$–R_F were constant (45°, 87°, and 92° [or 97°]), respectively, over 30 min. Therefore, our fluorinated Si-MMA–DMAA co-oligomers were clarified to show a good hydrophilicity with a strong oil repellency above their surface, though these co-oligomers have both fluoroalkyl groups and hydrophobic silsesquioxane segments. These findings suggests that at the interface with water, hydrophobic fluoroalkyl segments are replaced by the hydrophilic carboxydimethylamido segments and that it takes about 30 min to replace the fluoroalkyl segments by carboxydimethylamido segments when the environment is changed from air to water.

Our present fluoroalkyl end-capped Si-MMA oligomers are also expected to become the surface-active materials to inorganic compounds such as glass, 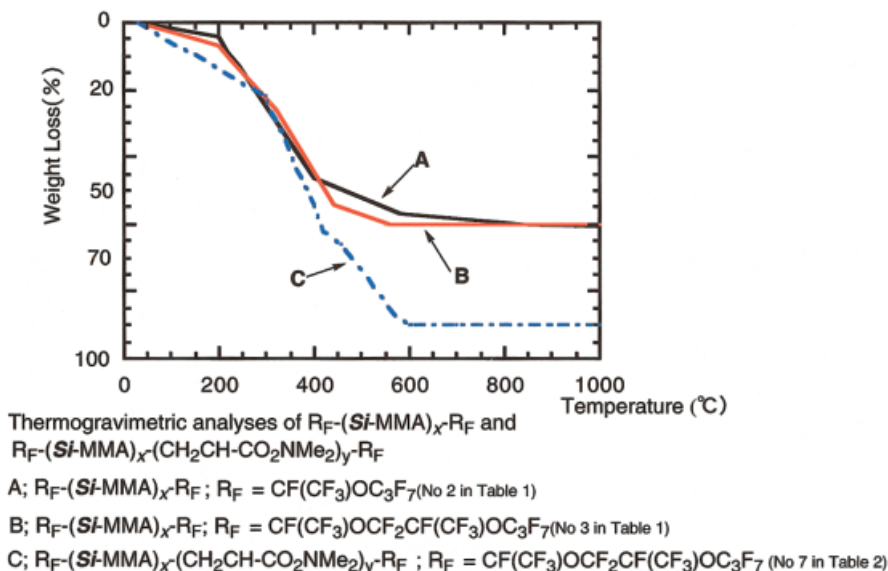as these oligomers possess silsesquioxane units, which are useful for the models of surface modified silica gels. In fact, R_F–(Si-MMA)$_x$–R_F could interact with glass to form stable film on the glass surface. Contact angles for water on glass surface treated with R_F–(Si-MMA)$_x$–R_F are shown in Table IV.

As shown in Table IV, contact angles for water and dodecane on the glass treated with fluorinated Si-MMA oligomers, especially longer fluoroalkylated Si-MMA oligomers were found to increase significantly compared with those of the corresponding nonfluorinated Si-MMA homo-oligomer and nontreated glass, indicating that longer fluoroalkyl segments in oligomers are likely to be arranged regularly above the glass surface to exhibit the strong oleophobic and hydrophobic properties.

The thermal stability of some fluoroalkyl end-capped Si-MMA homo- and co-oligomers in Tables I and II were investigated by thermogravimetric analysis (TGA), and the results were shown in Figure 2.

TABLE IV
Contact Angles of Dodecane and Water on Glass Surface
Treated With R_F–(Si-MMA)$_x$–R_F

		Contact Angle (Degree)	
No.	Oligomer	Dodecane	Water
1	R_F–(Si-MMA)$_x$–R_F [R_F = CF(CF$_3$)OC$_3$F$_7$]	18	51
3	R_F–(Si-MMA)$_x$–R_F [R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$	21	128
	–(Si-MMA)$_x$– (Mn = 3800)	0	32
	nontreated glass	0	30

Thermogravimetric analyses of R_F-(Si-MMA)$_x$-R_F and
R_F-(Si-MMA)$_x$-(CH$_2$CH-CO$_2$NMe$_2$)$_y$-R_F

A; R_F-(Si-MMA)$_x$-R_F ; R_F = CF(CF$_3$)OC$_3$F$_7$(No 2 in Table 1)

B; R_F-(Si-MMA)$_x$-R_F ; R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$(No 3 in Table 1)

C; R_F-(Si-MMA)$_x$-(CH$_2$CH-CO$_2$NMe$_2$)$_y$-R_F ; R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$ (No 7 in Table 2)

Figure 2 Thermogravimetric analyses of R_F–(Si-MMA)$_x$–R_F and R_F–(Si-MMA)$_x$–(CH$_2$CH-CONMe$_2$)$_y$–R_F A; R_F–(Si-MMA)$_x$–R_F; R_F = CF(CF$_3$)OC$_3$F$_7$(No 2 in Table 1) B; R_F–(Si-MMA)$_x$–R_F; R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$(No 3 in Table 1) C; R_F–(Si-MMA)$_x$–(CH$_2$CH-CONMe$_2$)$_y$–R_F; R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$ (No 7 in Table II).

As shown in Figure 2, fluoroalkyl end-capped Si-MMA homooligomers were found to possess a high thermal stability (T_{dec} [defined by a 10% mass loss at a 10°C/min heating rate under nitrogen]: ca. 240°C) compared with that of (T_{dec}: ca. 160°C) of R_F–(Si-MMA$_x$–(DMAA)$_y$–R_F. Previously, Lichtenhan et al. reported that nonfluorinated Si-MMA (R in Si-MMA is cyclohexyl group) homopolymer (Mn = 117000) exhibited an excellent thermal stability (T_{dec}: 388°C) compared with that of our present fluoroalkyl end-capped Si-MMA oligomers.[11] However, our results for thermal stability are reasonable because the molecular weights of our present R_F–(Si-MMA)$_x$–R_F are oligomeric regions.

In conclusion, it was demonstrated that fluoroalkanoyl peroxide is a useful tool for the synthesis of novel fluoroalkyl end-capped Si-MMA homo- and co-oligomers under very mild conditions. Furthermore, these fluorinated Si-MMA oligomers are found to possess a high solubility in common organic solvents and were able to reduce the surface tension of water effectively. Moreover, these fluorinated oligomers can be applied to new polymeric surface modifiers to exhibit a strong oleophobicity on the PMMA and glass surfaces, although these oligomers have oleophilic silsesquioxane segments. Interestingly, in fluoroalkyl end-capped Si-MMA–DMAA co-oligomers, the modified PMMA surface with these fluorinated co-oligomers was shown to possess a good hydrophilicity with a strong oleophobicity. Fluoroalkyl end-capped Si-MMA homo-oligomers had a relatively high thermal stability compared with that of the corresponding co-oligomer. These findings suggest that our present fluoroalkyl end-capped Si-MMA oligomers should be-

come useful intermediates for the development of new fluorinated organic–inorganic polymer hybrids, and reports on the synthesis and applications of these novel fluorinated hybrids will be forthcoming.

EXPERIMENTAL

Measurements

NMR spectra were measured using a Varian Unityplus 500 (500 MHz) spectrometer, while infrared (IR) spectra were recorded on a HORIBA FT-300 FTIR (Fourier transform infrared) spectrophotometer. Molecular weights were measured using a Shodex DS-4 (pomp, Tokyo, Japan) and Shodex RI-71 (Detector, Tokyo, Japan) GPC-calibrated with standard polystyrenes by using tetrahydrofuran as the eluent. Thermal analyses were recorded on a RIGAKU DENKI TG8101 D differential thermobalance.

Materials

A series of fluoroalkanoyl peroxides [(R$_F$COO)$_2$] were prepared by the method described in the literature.[12,13] DMAA was used as received from Kohjin Co., Ltd. (Tokyo, Japan). Acrylic acid and Si-MMA were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan) and Sigma Aldrich Japan Co. (Tokyo, Japan), respectively.

General procedure for the synthesis of fluoroalkyl end-capped Si-MMA homooligomers

Perfluoro-2-methyl-3-oxahexanoyl peroxide (1.0 mmol) in 1 : 1 mixed solvents (AK-225) of 1,1-dichloro-2,2,3,3,3-

pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane (15 g) was added to a mixture of *Si*-MMA (1.0 mmol) and AK-225 (50 g). The solution was stirred at 45°C for 5 hours under nitrogen. After evaporating the solvent, the obtained crude products were reprecipitated from the chloroform–methanol system to give bis(perfluoro-1-methyl-2-oxapentylated) *Si*-MMA homo-oligomer [R_F–(*Si*-MMA)$_x$–R_F: R_F = CF(CF$_3$)OC$_3$F$_7$: 0.69 g). This oligomer showed the following spectral data: IR v/cm^{-1} 1638 (C=O), 1325 (CF$_3$), 1242 (CF$_2$), 1117 (–O–); ^{1}H NMR (CDCl$_3$) δ 0.52 ~ 0.72 (SiCH), 0.89 ~ 2.42 (CH$_2$, CH$_3$), 3.88 ~ 4.22 (CH$_2$); ^{19}F NMR(CDCl$_3$, ext. CF$_3$CO$_2$H) δ −5.53 ~ −7.79 (16F), −53.51 ~ −54.18 (6F); average molar mass (M$_n$) = 2060, M$_w$/M$_n$ = 1.37 (GPC calibrated with standard polystyrenes by using tetrahydrofuran as the eluent).

The other products obtained exhibited the following spectral characteristics: R_F–(*Si*-MMA)$_x$–R_F: R_F = CF(CF$_3$)-C$_3$F$_7$ (no. 2 in Table I): IR v/cm^{-1} 1637 (C=O), 1319 (CF$_3$), 1242 (CF$_2$), 1151 (–O–); ^{1}H NMR (CDCl$_3$) δ 0.52 ~ 0.70 (SiCH), 0.79 ~ 2.12 (CH$_2$, CH$_3$), 3.89 ~ 4.21 (CH$_2$); ^{19}F NMR(CDCl$_3$, ext. CF$_3$CO$_2$H) δ −5.53 ~ −7.79 (16F), −53.51 ~ −54.13 (6F).

R_F–(*Si*-MMA)$_x$–R_F: R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$ (no. 3 in Table I): IR v/cm^{-1} 1643 (C=O), 1302 (CF$_3$), 1198 (CF$_2$), 1151 (–O–); ^{1}H NMR(CDCl$_3$) δ 0.52 ~ 2.49 (SiCH, CH$_2$, CH$_3$), 3.83 ~ 4.35 (CH$_2$); ^{19}F NMR(CDCl$_3$, ext. CF$_3$CO$_2$H) δ −4.34 ~ −8.05 (26F), −54.05 (6F), −69.60 (2F).

R_F–(*Si*-MMA)$_x$–R_F: R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$ (no. 4 in Table I): IR v/cm^{-1} 1639 (C=O), 1306 (CF$_3$), 1200 (CF$_2$), 1151 (–O–); ^{1}H NMR(CDCl$_3$) δ 0.48 ~ 2.52 (SiCH, CH$_2$, CH$_3$), 3.82 ~ 4.22 (CH$_2$); ^{19}F NMR(CDCl$_3$, ext. CF$_3$CO$_2$H) δ −9.25 ~ −13.10 (26F), −58.51 ~ −59.33 (6F), −74.53 ~ −74.71 (2F).

R_F–(*Si*-MMA)$_x$–(DMAA)$_y$–R_F: R_F = CF(CF$_3$)OC$_3$F$_7$ (no. 5 in Table II): IR v/cm^{-1} 1605 (C=O), 1340 (CF$_3$), 1220 (CF$_2$), 1110 (–O–); ^{1}H NMR (CDCl$_3$) δ 0.50 ~ 2.15 (SiCH, CH$_2$, CH$_3$), 2.22 ~ 3.68 (CH, CH$_3$), 3.70 ~ 3.98 (CH$_2$); ^{19}F NMR(CDCl$_3$, ext. CF$_3$CO$_2$H) δ −5.44 ~ −12.45 (16F), −59.13 ~ −60.12 (6F).

R_F–(*Si*-MMA)$_x$–(DMAA)$_y$–R_F: R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$ (no. 6 in Table II): IR v/cm^{-1} 1605 (C=O), 1330 (CF$_3$), 1230 (CF$_2$), 1110(–O–); ^{1}H NMR (CDCl$_3$) δ 0.46 ~ 2.19 (SiCH, CH$_2$, CH$_3$), 2.22 ~ 3.52 (CH, CH$_3$), 3.72 ~ 4.19 (CH$_2$); ^{19}F NMR (CDCl$_3$, ext. CF$_3$CO$_2$H) δ −9.46 ~ −12.85 (26F), −59.13 ~ −60.51 (6F), −74.84 ~ −75.00 (2F).

R_F–(*Si*-MMA)$_x$–(DMAA)$_y$–R_F: R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$ (no. 7 in Table II): IR v/cm^{-1} 1630 (C=O), 1334 (CF$_3$), 1246 (CF$_2$), 1119 (–O–); ^{1}H NMR(CDCl$_3$) δ 0.50 ~ 2.18 (SiCH, CH$_2$, CH$_3$), 2.22 ~ 3.39 (CH, CH$_3$), 3.72 ~ 4.17 (CH$_2$); ^{19}F NMR(CDCl$_3$, ext. CF$_3$CO$_2$H) δ −9.44 ~ −12.76 (26F), −59.13 ~ −59.81 (6F), −74.84 ~ −74.94 (2F).

R_F–(*Si*-MMA)$_x$–(DMAA)$_y$–R_F: R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$ (no. 8 in Table II): IR v/cm^{-1} 1605 (C=O), 1335 (CF$_3$), 1195 (CF$_2$), 1080 (–O–); ^{1}H NMR (CDCl$_3$) δ 0.50 ~ 2.20 (SiCH, CH$_2$, CH$_3$), 2.21 ~ 3.30 (CH, CH$_3$), 3.72 ~ 4.21 (CH$_2$); ^{19}F NMR(CDCl$_3$, ext. CF$_3$CO$_2$H) δ −9.46 ~ −12.79 (26F), −59.16 ~ −59.50 (6F), −74.74 ~ −75.02 (2F).

R_F–(*Si*-MMA)$_x$–(DMAA)$_y$–R_F: R_F = C$_7$F$_{15}$ (no. 9 in Table II): IR v/cm^{-1} 1605 (C=O), 1345 (CF$_3$), 1200 (CF$_2$), 1095 (–O–); ^{1}H NMR(CDCl$_3$) δ 0.50 ~ 2.19 (SiCH, CH$_2$, CH$_3$), 2.22 ~ 3.30 (CH, CH$_3$), 3.78 ~ 4.09 (CH$_2$); ^{19}F NMR(CDCl$_3$, ext. CF$_3$CO$_2$H) δ −10.22 (6F), −47.92 (4F), −51.21 (4F), −51.55 (4F), −52.23 (8F), −55.63 (4F).

R_F–(*Si*-MMA)$_x$–(ACA)$_y$–R_F: R_F = CF(CF$_3$)OC$_3$F$_7$ (no. 10 in Table II): IR v/cm^{-1} 1690 (C=O), 1325 (CF$_3$), 1210 (CF$_2$), 1070 (–O–); ^{1}H NMR(CDCl$_3$) δ 0.50 ~ 3.00 (SiCH, CH$_2$, CH$_3$), 3.70 ~ 4.22 (CH$_2$); ^{19}F NMR(CDCl$_3$, ext. CF$_3$CO$_2$H) δ −12.11 ~ −14.81 (16F), −60.20 ~ −61.00 (6F).

R_F–(*Si*-MMA)$_x$–(ACA)$_y$–R_F: R_F = CF(CF$_3$)OC$_3$F$_7$ (no. 11 in Table II): IR v/cm^{-1} 1700 (C=O), 1335 (CF$_3$), 1230 (CF$_2$), 1100 (–O–); ^{1}H NMR(CDCl$_3$) δ 0.50 ~ 2.90 (SiCH, CH$_2$, CH$_3$), 3.70 ~ 4.12 (CH$_2$); ^{19}F NMR(CDCl$_3$, ext. CF$_3$CO$_2$H) δ −12.14 ~ −14.29 (16F), −60.20 ~ −61.89 (6F).

Surface tension measurements

The surface tensions of *m*-xylene solutions of the fluorinated *Si*-MMA oligomers were measured at 30°C using a Wilhelmy-type surface tensiometer (ST-1, Shimadzu Co., Kyoto, Japan) with a glass plate.

Contact angle measurements

The contact angles were measured with the use of the goniometer-type contact angle meter (Erma G-1-1000) according to our previously reported method.[14] Briefly, a PMMA film containing fluoroalkyl endcapped *Si*-MMA oligomer (1% [*m/m*]) was prepared by the cast coating method with 1,2-dichloroethane as solvent, and the contact angles of water and dodecane for this PMMA film were measured. In the contact angle measurements for glass, the glass plates (10 × 10 mm^2 pieces) were dipped into the 1% (*m/m*) ethanol solutions of fluoroalkyl end-capped *Si*-MMA oligomers 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 150°C, After the heat treatment, the contact angles of water and dodecane for these glass plates were measured.

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