Synthesis and Applications of Silicone Oil–Soluble Fluoroalkyl End-Capped Cooligomers

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ABSTRACT: Fluoroalkyl end-capped cooligomers containing polydimethylsiloxane and polyoxyethylene segments were prepared under very mild conditions by the cooligomerizations of fluoroalkanoyl peroxides with methacrylate monomers containing the corresponding segments and comonomers such as dimethylacrylamide and acryloylmorpholine. These obtained fluorinated cooligomers exhibited amphipathic characteristics and became soluble in water and common organic solvents. In particular interest, fluoroalkyl end-capped cooligomers containing polyoxyethylene units were soluble not only in poly(methylphenylsiloxane) (silicone oil) but also in water, including common organic solvents except for hexane. Additionally, these fluorinated cooligomers were able to reduce the surface tension of water and *m*-xylene quite effectively, to around 15 and 20 mN/m levels, respectively. In these fluorinated cooligomers, fluoroalkyl end-capped acryloylmorpholine cooligomers containing polyoxyethylene segments were applicable as a novel emulsifying agent against water and silicone oil. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1467–1476, 2005

Key words: coatings; fluoropolymers; silicones; solution properties; surfactants

INTRODUCTION

There continues to be a growing interest in organosilicon compounds as functional materials in a variety of fields as well as organofluorine compounds.[1] From the perspective of developing novel functional materials possessing excellent properties imparted by both silicon and fluorine, various fluorine-containing silicon compounds have been prepared and their interesting properties have also been reported in detail.[2] The increasing interest in applications of a series of fluorine-containing silicon compounds has recently been focused in various fields because of their good surfactant properties.[3] These fluorinated silicon compounds generally have good solubility in silicone oil; however, these compounds exhibit poor solubility in both water and common organic solvents.[4] Therefore, it has been of surpassing interest to explore novel fluorinated silicon compounds that possess good solubility not only in silicone oil but also in water, including organic solvents. In our comprehensive studies on the development of highly soluble fluoroalkyl end-capped oligomeric surfactants,[5] we have found that fluoroalkyl end-capped *N,N*-dimethylacrylamide and acryloylmorpholine cooligomers, containing polydimethylsiloxane or polyoxyethylene segments, show good solubility toward these solvents, and the results are reported herein.

EXPERIMENTAL

Measurements

FTIR spectra were measured using a Shimadzu FTIR-8400 spectrophotometer (Shimadzu, Kyoto, Japan). NMR spectra and molecular weights were measured using a Unity-plus 500 (500 MHz) spectrometer (Varian Associates, Palo Alto, CA) and a Shodex (Tokyo, Japan) DS-4 (pump) and Shodex RI-71 (detector) size-exclusion chromatograph (SEC), calibrated with polystyrene standard using tetrahydrofuran as the eluent. The surface tensions of aqueous and *m*-xylene solutions of the fluoroalkyl end-capped MMA-*Si* and PME-*m* cooligomers were measured at 30°C using a

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Wilhelmy-type surface tensiometer (ST-1, Shimadzu Co.) with a glass plate. Contact angles were measured by the use of the goniometer-type contact angle meter (ERMA G-1-1000) according to our previously reported method.[6]

Materials

MMA-*Si* and PME-*m* were used as received from Chisso Corp. (Tokyo, Japan) and NOF Corp. (Tokyo, Japan), respectively. *N,N*-Dimethylacrylamide (DMAA) and acryloylmorpholine (ACMO) were used as received from Kohjin Co., Ltd. (Tokyo, Japan). Silicone oil was purchased from Shin-Etsu Chemical Co., Ltd. (Tokyo, Japan). A series of fluoroalkanoyl peroxides [(R_FCOO)$_2$] were prepared by the method described in the literature.[7]

General procedure for the synthesis of fluoroalkyl end-capped cooligomers

Perfluoro-2-methyl-3-oxahexanoyl peroxide (27 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 (350 g) was added to MMA-*Si* (1.47 mmol) and DMAA (377 mmol). The homogeneous solution was stirred at 45°C for 5 h under nitrogen. After evaporating the solvent, the obtained oily crude products were reprecipitated from hexane to give an α,ω-bis(perfluoro-1-methyl-2-oxapentylated) MMA-*Si*–DMAA cooligomer (4.19 g). This cooligomer exhibited the following characteristic spectra:

IR (ν/cm^{-1}) 1628 [C(═O)], 1339 (CF$_3$), 1242 (CF$_2$), 1096 (Si—O); ^{1}H-NMR (CDCl$_3$) δ −0.10 to 0.18, 0.93 (CH$_3$), 1.10–1.83 (CH$_2$, CH$_3$), 2.21–3.19 (CH, CH$_2$), 3.72 (CH$_2$); ^{19}F-NMR (CDCl$_3$, ext. CF$_3$CO$_2$H) δ −3.86 to −7.41 (16F), −54.60 (6F).

The other products obtained exhibited the following spectral characteristics:

- R_F-(MMA-*Si*)$_x$-(DMAA)$_y$-R_F
- R_F = CF(CF$_3$)OC$_6$F$_{13}$ (No. 2 in Table I)

IR (ν/cm^{-1}); 1620 [C(═O)], 1331 (CF$_3$), 1245 (CF$_2$). 1099 (Si—O); ^{1}H-NMR (CDCl$_3$) δ −0.10 to 0.12, 0.92 (CH$_3$), 1.13–1.85 (CH$_2$, CH$_3$), 2.23–3.32 (CH, CH$_2$); ^{19}F-NMR (CDCl$_3$, ext. CF$_3$CO$_2$H) δ −5.18 to −9.18 (16F), −46.56 (4F), −49.60 (4F), −49.70 (4F), −50.61 (6F).

- R_F-(MMA-*Si*)$_x$-(DMAA)$_y$-R_F
- R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$ (No. 3 in Table I)

IR (ν/cm^{-1}) 1620 [C(═O)], 1310 (CF$_3$), 1245 (CF$_2$), 1099 (Si—O); ^{1}H-NMR (CDCl$_3$) δ −0.10 to 0.21, 0.82 (CH$_3$), 1.10–1.82 (CH$_2$, CH$_3$), 2.22–3.18 (CH, CH$_2$), 3.60 (CH$_2$); ^{19}F-NMR (CDCl$_3$, ext. CF$_3$CO$_2$H) δ −5.80 to −8.76 (26F), −54.09 to −54.43 (6F), −69.95 (2F).

- R_F-(MMA-*Si*)$_x$-(ACMO)$_y$-R_F
- R_F = CF(CF$_3$)OC$_3$F$_7$ (No. 4 in Table I)

IR (ν/cm^{-1}) 1628 [C(═O)], 1310 (CF$_3$), 1254 (CF$_2$), 1111 (Si—O), 1030 (–O–); ^{1}H-NMR (CDCl$_3$) δ −0.10 to 0.19, 0.83 (CH$_3$), 1.01–1.90 (CH$_2$, CH$_3$), 2.31–2.73 (CH), 2.92–3.93 (CH$_2$); ^{19}F-NMR (CDCl$_3$, ext. CF$_3$CO$_2$H) δ −5.60 to 7.47 (16F), −54.08 (6F).

- R_F-(MMA-*Si*)$_x$-(ACMO)$_y$-R_F
- R_F = CF(CF$_3$)OC$_3$F$_7$ (No. 4 in Table I)

IR (ν/cm^{-1}) 1628 [C(═O)], 1310 (CF$_3$), 1254 (CF$_2$), 1111 (Si—O), 1030 (–O–); ^{1}H-NMR (CDCl$_3$) δ −0.10 to 0.19, 0.83 (CH$_3$), 1.01–1.90 (CH$_2$, CH$_3$), 2.31–2.73 (CH), 2.92–3.93 (CH$_2$); ^{19}F-NMR (CDCl$_3$, ext. CF$_3$CO$_2$H) δ −5.60 to 7.47 (16F), −54.08 (6F).

- R_F-(MMA-*Si*)$_x$-(ACMO)$_y$-R_F
- R_F = CF(CF$_3$)OC$_3$F$_7$ (No. 5 in Table I)

IR (ν/cm^{-1}) 1624 [C(═O)], 1305 (CF$_3$), 1242 (CF$_2$), 1111 (Si—O), 1030 (–O–); ^{1}H-NMR (CDCl$_3$) δ −0.10 to 0.19, 0.86 (CH$_3$), 1.09–1.88 (CH$_2$, CH$_3$), 2.32–2.83 (CH), 3.12–3.95 (CH$_2$); ^{19}F-NMR (CDCl$_3$, ext. CF$_3$CO$_2$H) δ −5.60 to 7.44 (16F), −54.04 (6F).

- R_F-(MMA-*Si*)$_x$-(ACMO)$_y$-R_F
- R_F = CF(CF$_3$)OC$_6$F$_{13}$ (No. 6 in Table I)

IR (ν/cm^{-1}) 1632 [C(═O)], 1310 (CF$_3$), 1248 (CF$_2$), 1111 (Si—O), 1038 (–O–); ^{1}H-NMR (CDCl$_3$) δ −0.10 to 0.20, 0.85 (CH$_3$), 1.10–1.91 (CH$_2$, CH$_3$), 2.32–2.73 (CH), 3.08–3.88 (CH$_2$); ^{19}F-NMR (CDCl$_3$, ext. CF$_3$CO$_2$H) δ −6.58 to 7.57 (16F), −46.94 (4F), −47.29 (4F), −49.78 (4F), −50.24 (6F).

- R_F-(MMA-*Si*)$_x$-(ACMO)$_y$-R_F
- R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$ (No. 7 in Table I)

IR (ν/cm^{-1}) 1636 [C(═O)], 1310 (CF$_3$), 1250 (CF$_2$), 1111 (Si—O), 1030 (–O–); ^{1}H-NMR (CDCl$_3$) δ −0.10 to 0.20, 0.83 (CH$_3$), 1.12–1.93 (CH$_2$, CH$_3$), 2.34–2.72 (CH), 3.18–3.92 (CH$_2$); ^{19}F-NMR (CDCl$_3$, ext. CF$_3$CO$_2$H) δ −5.65 to 6.74 (26F), −54.01 to 54. (6F), −69.84 (2F).

- R_F-(MMA-*Si*)$_x$-(DOBAA)$_y$-R_F
- R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$ (No. 8 in Table I)

IR (ν/cm^{-1}) 1712, 1666 [C(═O)], 1310 (CF$_3$), 1248 (CF$_2$), 1099 (Si—O); ^{1}H-NMR (CDCl$_3$) δ −0.10 to 0.22, 0.81 (CH$_3$), 1.02–2.21 (CH$_2$, CH$_3$), 2.42–3.75 (CH, CH$_2$); ^{19}F-NMR (CDCl$_3$, ext. CF$_3$CO$_2$H) δ −6.75 to 9.08 (26F), −56.46 to 56.59 (6F), −72.14 (2F).

TABLE I
Reactions of Fluoroalkanoyl Peroxides with MMA-*Si* (or PME-*m*) with Comonomers

Run	R_F in $(R_FCO_2)_2$ (mmol)	MMA-*Si*[a] [or PME-*m*] (mmol)	Co-M (mmol)	Product		
				Yield[b] (%)	M_n (M_w/M_n)[c]	$[x : y]$
1	$CF(CF_3)OC_3F_7$		DMAA	R_F-(MMA-*Si*)$_x$-(DMAA)$_y$-R_F		
	27.0	1.47	377	23	5560 (2.90)	[0.5 : 140][d]
2	$CF(CF_3)OC_6F_{13}$					
	6.30	0.18	91.6	45	5070 (1.69)	[0.3 : 145][d]
3	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$					
	8.84	0.26	129	64	6860 (3.65)	[0.3 : 145][d]
	$CF(CF_3)OC_3F_7$		ACMO	R_F-(MMA-*Si*)$_x$-(ACMO)$_y$-R_F		
4	7.22	0.82	189	91	12,770 (1.29)	[1.1 : 262][d]
5	7.22	0.76	337	61	5550 (1.66)	[1.1 : 467][d]
6	6.56	0.75	104	48	7070 (3.05)	[1.1 : 159][d]
7	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$					
	8.84	1.01	140	83	8710 (2.64)	[1.1 : 159][d]
8	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$			R_F-(MMA-*Si*)$_x$-(DOBAA)$_y$-R_F		
			DOBAA			
	21.0	1.28	252	69	9160 (1.77)	[0.6 : 120][d]
9	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$			R_F-(PME-*4*)$_x$-(DMAA)$_y$-R_F		
		$m = 4$	DMAA			
	26.1	26.1	366	89	4880 (1.97)	[8 : 92][e]
10	$CF(CF_3)OC_6F_{13}$			R_F-(PME-*4*)$_x$-(ACMO)$_y$-R_F		
		$m = 4$	ACMO			
	6.56	19.7	32.8	40	4830 (2.60)	[42 : 58][e]
11	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$			R_F-(PME-*4*)$_x$-(ACMO)$_y$-R_F		
		$m = 4$	ACMO			
	8.84	26.6	50.0	79	4190 (1.99)	[46 : 54][e]
12	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$			R_F-(PME-*8*)$_x$-(DMAA)$_y$-R_F		
		$m = 8$	DMAA			
	11.0	33.0	55.1	95	3800 (2.26)	[37 : 63][e]
13	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$			R_F-(PME-*8*)$_x$-(ACMO)$_y$-R_F		
		$m = 8$	ACMO			
	11.0	33.0	55.1	69	9480 (1.25)	[45 : 55][e]
14	$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$			R_F-(PME-*8*)$_x$-(DOBAA)$_y$-R_F		
		$m = 8$	DOBAA			
	11.0	33.0	55.1	82	5760 (2.30)	[25 : 75][e]

[a] Molecular weight: 10,000 g/mol.
[b] The yield was based on the starting materials [MMA-*Si* (or PME-*m*) and comonomer] and the decarboxylated peroxide unit (R_F–R_F).
[c] Molecular weight was determined by SEC by using THF as the eluent (polystyrene standard).
[d] Feed molar ratio.
[e] Cooligomerization ratio was determined by ^{1}H-NMR.

- R_F-(PME-*4*)$_x$-(DMAA)$_y$-R_F
- $R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (No. 9 in Table I)

IR (ν/cm^{-1}) 3452 (OH), 1720, 1628 [C(=O)], 1310 (CF_3), 1242 (CF_2), 1153 (–O–); ^{1}H-NMR ($CDCl_3$) δ 0.85–1.99 (CH_2, CH_3), 2.28–3.21 (CH, CH_2), 3.51–3.83 (CH_2), 3.90–4.27 (CH_2), 4.43–4.60 (CH_2); ^{19}F-NMR ($CDCl_3$, ext. CF_3CO_2H) δ −6.38 to 9.21 (26F), −56.43 to 57.94 (6F), −72.22 (2F).

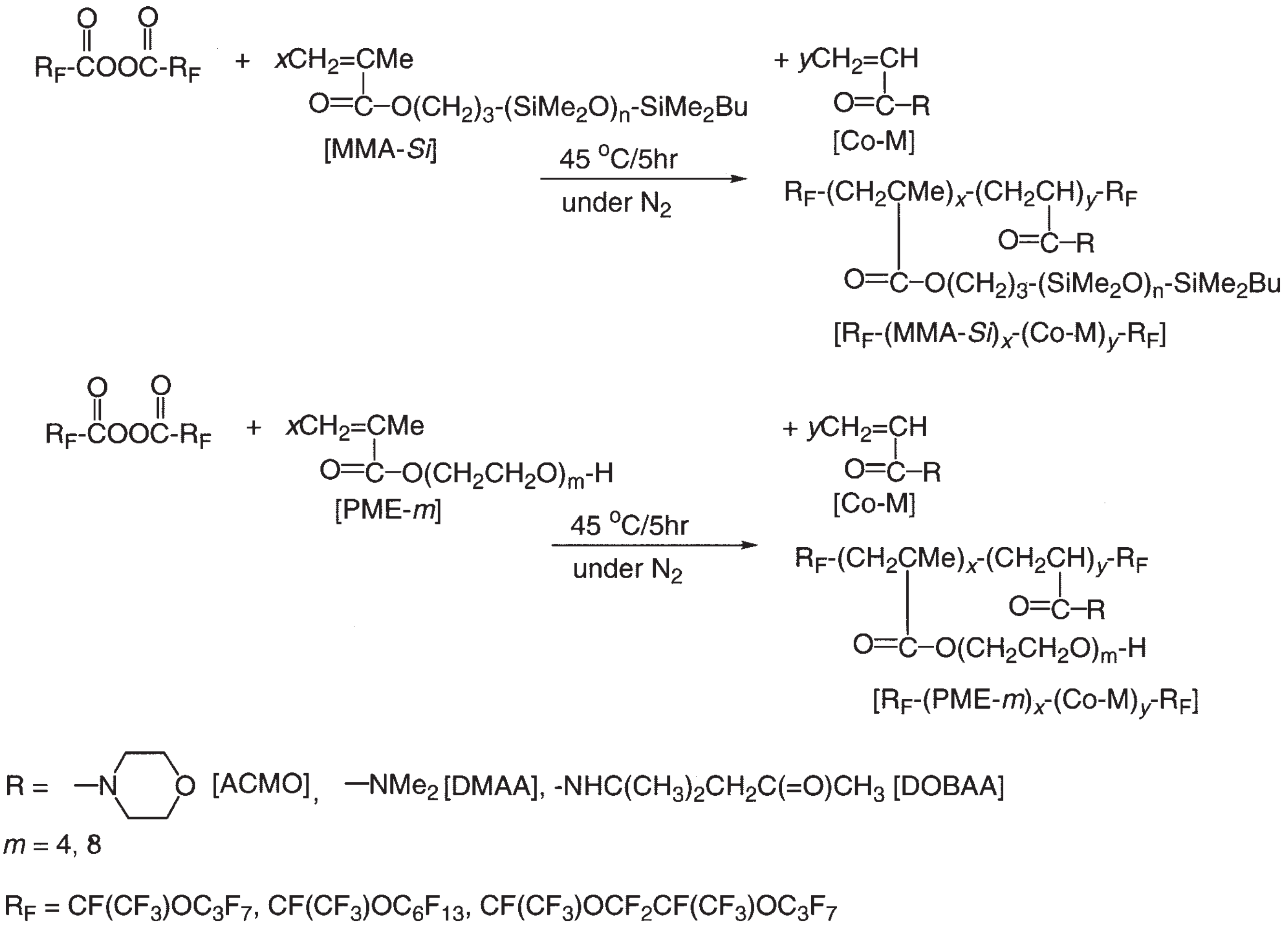
- R_F-(PME-*4*)$_x$-(ACMO)$_y$-R_F
- $R_F = CF(CF_3)OC_6F_{13}$ (No. 10 in Table I)

IR (ν/cm^{-1}) 3422 (OH), 1720, 1628 [C(=O)], 1312 (CF_3), 1242 (CF_2), 1115, 1034 (–O–); ^{1}H-NMR ($CDCl_3$) δ 0.80–3.00 (CH_2, CH, CH_2), 3.18–3.90 (CH_2), 3.92–4.43 (CH_2); ^{19}F-NMR ($CDCl_3$, ext. CF_3CO_2H) δ −5.18 to −7.49 (16F), −47.13 (4F), −47.29 (4F), −49.42 (4F), −50.27 (6F).

- R_F-(PME-*4*)$_x$-(ACMO)$_y$-R_F
- $R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (No. 11 in Table I)

IR (ν/cm^{-1}) 3445 (OH), 1724, 1636 [C(=O)], 1300 (CF_3), 1242 (CF_2), 1119, 1034 (–O–); ^{1}H-NMR ($CDCl_3$) δ 0.80–2.92 (CH_2, CH, CH_2), 3.18–3.91 (CH_2), 3.97–4.38 (CH_2); ^{19}F-NMR ($CDCl_3$, ext. CF_3CO_2H) δ −4.32 to −7.73 (26F), −52.27 to −56.24 (6F), −69.66 (2F).

- R_F-(PME-*8*)$_x$-(DMAA)$_y$-R_F
- $R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (No. 12 in Table I)



Scheme 1

IR (ν/cm^{-1}) 3422 (OH), 1724, 1636 [C(═O)], 1331 (CF_3), 1242 (CF_2), 1119 (–O–); ^{1}H-NMR ($CDCl_3$) δ 0.78–2.21 (CH_2, CH_2), 2.39–3.90 (CH, CH_3, CH_2), 3.92–4.40 (CH_2); ^{19}F-NMR ($CDCl_3$, ext. CF_3CO_2H) δ −7.94 to −12.15 (26F), −58.51 to −60.67 (6F), −74.27 (2F).

- R_F-(PME-8)$_x$-(ACMO)$_y$-R_F
- $R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (No. 13 in Table I)

IR (ν/cm^{-1}) 3420 (OH), 1724, 1639 [C(═O)], 1310 (CF_3), 1242 (CF_2), 1115, 1034 (–O–); ^{1}H-NMR ($CDCl_3$) δ 0.80–2.92 (CH_2, CH, CH_2), 3.18–3.90 (CH_2), 3.95–4.30 (CH_2); ^{19}F-NMR ($CDCl_3$, ext. CF_3CO_2H) δ −8.33 to −12.09 (26F), −58.49 to −58.59 (6F), −74.17 (2F).

- R_F-(PME-8)$_x$-(DOBAA)$_y$-R_F
- $R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (No. 14 in Table I)

IR (ν/cm^{-1}) 1713, 1659 [C(═O)], 1310 (CF_3), 1246 (CF_2), 1115 (–O–); ^{1}H-NMR ($CDCl_3$) δ 0.80–2.21 (CH_2, CH_3), 2.42–3.90 (CH, CH_2), 3.98–4.42 (CH_2); ^{19}F-NMR ($CDCl_3$, ext. CF_3CO_2H) δ −8.30 to −11.70 (26F), −58.49 to −58.57 (6F), −74.25 (2F).

Emulsification of water and silicone oil in the presence of fluorinated cooligomer

In a 30-mL vial, 1 mL of a silicone solution of fluoroalkyl end-capped cooligomer (0.2 g/dm^3) and 9 mL of water were mixed vigorously for 3 min at room temperature. After standing at room temperature, the separation time of this emulsion solution was measured.

RESULTS AND DISCUSSION

The reactions of fluoroalkanoyl peroxides with methacrylate monomers containing polydimethylsiloxane segments (MMA-*Si*) and comonomers such as *N*,*N*-dimethylacrylamide (DMAA), acryloylmorpholine (ACMO), and *N*-(1,1-dimethyl-3-oxobutyl)acrylamide (DOBAA) in 1 : 1 mixed solvents (AK-225) of 1,1-dichloro-2,2,3,3,3-pentafluoropropane–1,3-dichloro-1,2,2,3,3-pentafluoropropane were carried out by heat-

TABLE II
Solubilities of R_F-(MMA-*Si*)$_x$-(CoM)$_y$-R_F

		Solvent														
Run[a]	R_F in cooligomer	H_2O	MeOH	EtOH	THF	$CHCl_3$	Ph-H	Ph-CH_3	AcOEt	AK-225[b]	DMSO	DMF	*n*-Hexane	Acetone	CH_2Cl_2	KF-56[c]
R_F-(MMA-*Si*)$_x$-(DMAA)$_y$-R_F																
1	$CF(CF_3)OC_3F_7$	○[d]	○	○	○	○	○	○	○	○	○	○	X[e]	○	○	Δ[f]
2	$CF(CF_3)OC_6F_{13}$	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
3	$CF(CF_3)CF_2CF(CF_3)OC_3F_7$	○	○	○	○	○	○	○	○	○	○	○	×	○	○	×
R_F-(MMA-*Si*)$_x$-(ACMO)$_y$-R_F																
4	$CF(CF_3)OC_3F_7$	×	×	×	○	○	○	○	○	○	○	○	×	○	○	○
5	$CF(CF_3)OC_3F_7$	×	×	×	○	○	○	○	○	○	○	○	×	○	○	○
6	$CF(CF_3)OC_6F_{13}$	○	×	×	○	○	○	○	○	○	×	○	×	○	○	Δ
7	$CF(CF_3)CF_2CF(CF_3)OC_3F_7$	○	×	×	○	○	○	○	○	○	×	○	×	○	○	Δ
R_F-(MMA-*Si*)$_x$-(DOBAA)$_y$-R_F																
8	$CF(CF_3)CF_2CF(CF_3)OC_3F_7$	×	○	○	○	○	○	○	○	○	○	○	×	○	○	×

[a] Each different from those of Table I.
[b] AK-225, mixed solvents (1 : 1) of $CF_3CF_2CHCl_2$ and $CClF_2CF_2CHClF$.
[c] KF-56, methyl phenyl silicone oil.
[d] ○, transparent solution.
[e] ×, insoluble. [f] Δ, turbid solution.

TABLE III
Solubilities of R_F-(PME-*m*)$_x$-(CoM)$_y$-R_F

		Solvent														
Run[a]	R_F in cooligomer	H_2O	MeOH	EtOH	THF	$CHCl_3$	Ph-H	Ph-CH_3	AcOEt	AK-225[b]	DMSO	DMF	*n*-Hexane	Acetone	CH_2Cl_2	KF-56[c]
R_F-(PME-*m*)$_x$-(DMAA)$_y$-R_F ($m = 4$)																
9	$CF(CF_3)CF_2CF(CF_3)OC_3F_7$	○[d]	○	○	○	○	○	○	○	○	○	○	×[e]	○	○	×
R_F-(PME-*m*)$_x$-(ACMO)$_y$-R_F ($m = 4$)																
11	$CF(CF_3)CF_2CF(CF_3)OC_3F_7$	○	○	○	○	○	○	○	○	○	○	○	×	○	○	Δ[f]
R_F-(PME-*m*)$_x$-(DMAA)$_y$-R_F ($m = 8$)																
12	$CF(CF_3)CF_2CF(CF_3)OC_3F_7$	○	○	○	○	○	○	○	○	○	○	○	×	○	○	Δ
R_F-(PME-*m*)$_x$-(ACMO)$_y$-R_F ($m = 8$)																
13	$CF(CF_3)CF_2CF(CF_3)OC_3F_7$	○	○	○	○	○	○	○	○	○	○	○	×	○	○	○
R_F-(PME-*m*)$_x$-(DOBAA)$_y$-R_F ($m = 8$)																
14	$CF(CF_3)CF_2CF(CF_3)OC_3F_7$	×	○	○	○	○	○	○	○	○	○	○	×	○	○	Δ

[a] Each different from those of Table I.
[b] AK-225, mixed solvents (1 : 1) of $CF_3CF_2CHCl_2$ and $CClF_2CF_2CHClF$.
[c] KF-56, methyl phenyl silicone oil.
[d] ○, transparent solution.
[e] ×, insoluble.
[f] Δ, turbid solution.

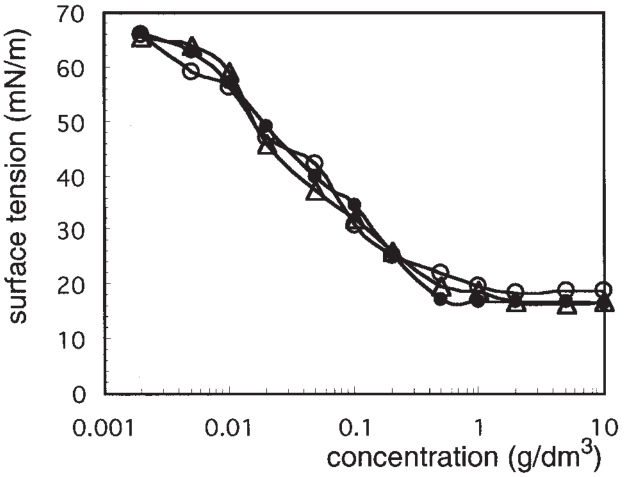


Figure 1 Surface tension of aqueous solutions of R_F–(MMA–*Si*)$_x$–(DMAA)$_y$–R_F at 30°C: △—△ Run 1, R_F = $CF(CF_3)OC_3F_7$; ○—○ Run 2, R_F = $CF(CF_3)OC_6F_{13}$; ●—● Run 3, R_F = $CF(CF_3)OCFCF_2(CF_3)OC_3F_7$.

ing the reaction mixtures at 45°C for 5 h under nitrogen. Furthermore, we tried to react fluoroalkanoyl peroxides with methacrylate monomers containing polyoxyethylene segments (PME-*m*) and comonomers such as DMAA, ACMO, and DOBAA under similar conditions. These processes are shown in Scheme 1.

As shown in Scheme 1, MMA-*Si* and PME-*m* were found to react with fluoroalkanoyl peroxides, under very mild conditions, to afford fluoroalkyl end-capped MMA-*Si* and PME-*m* cooligomers in 23–95% isolated yields. These results are listed in Table I.

The obtained fluoroalkyl end-capped MMA-*Si*–DMAA cooligomers in Table I have good solubility in water and common organic solvents except for hexane; however, fluoroalkyl end-capped MMA-*Si*–ACMO and MMA-*Si*–DOBAA cooligomers have poor solubility in water. On the other hand, fluoroalkyl end-capped PME-*m*–DMAA and PME-*m*–ACMO cooligomers have good solubility not only in water but also in common organic solvents. More interestingly, fluoroalkyl end-capped PME-*8*–ACMO cooligomers were found to be soluble not only in these solvents but also in silicone oil [poly(methylphenylsiloxane)]. These solubility results are summarized in Tables II and III. Thus, fluoroalkyl (Tables II and III) end-capped cooligomers, especially fluoroalkyl end-capped PME-*8*–ACMO cooligomers, are predicted to be developed into novel fluorinated polysurfactants that possess excellent solubility in various solvents including silicone oil.

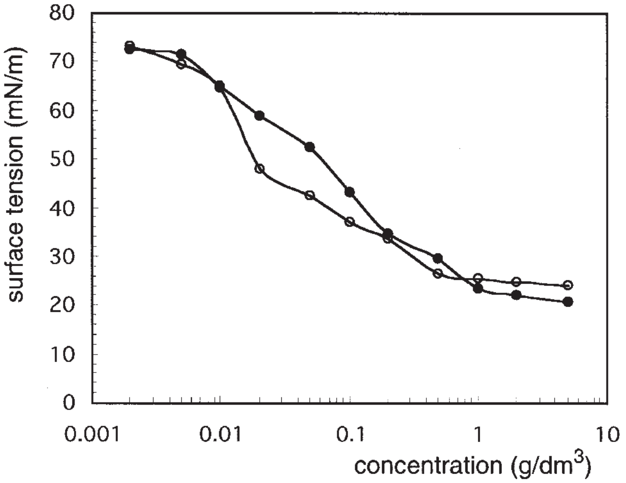


Figure 2 Surface tension of aqueous solutions of R_F–(MMA–*Si*)$_x$–(ACMO)$_y$–R_F at 30°C: ○—○ Run 6, R_F = $CF(CF_3)OC_6F_{13}$; ●—● Run 7, R_F = $CF(CF_3)OCFCF_2(CF_3)OC_3F_7$.

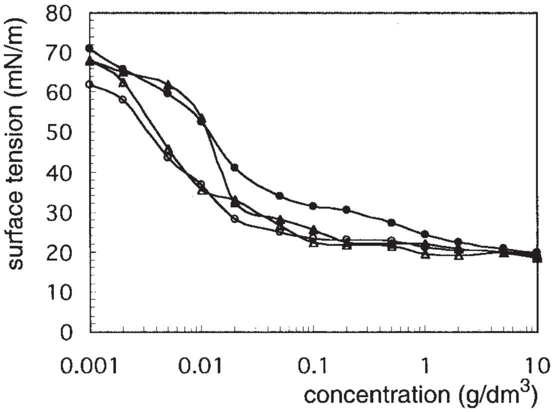


Figure 3 Surface tension of aqueous solutions of R_F–(PME-*m*)$_x$–$[CH_2CHC({=}O)R]_y$–R_F at 30°C. R = NMe_2: △—△ Run 12, *m* = 8, $CF(CF_3)OCFCF_2(CF_3)OC_3F_7$; R = [morpholino group]: ●—● Run 10, *m* = 4, R_F = $CF(CF_3)OC_6F_{13}$; ▲—▲ Run 11, *m* = 4, R_F = $CF(CF_3)OCFCF_2(CF_3)OC_3F_7$; ○—○ Run 13, *m* = 8, R_F = $CF(CF_3)OCFCF_2(CF_3)OC_3F_7$.

To clarify the surfactant properties of these fluoroalkyl end-capped MMA-*Si* and PME-*m* cooligomers, we measured the surface tensions of their aqueous solutions using the Wilhelmy plate method at 30°C. The results are shown in Figures 1–3.

As shown in Figures 1–3, fluoroalkyl end-capped MMA-*Si*–DMAA cooligomers (see Fig. 1), MMA-*Si*–ACMO cooligomers (see Fig. 2), PME-*m*–DMAA, and PME-*m*–ACMO cooligomers (see Fig. 3) were effectively able to reduce the surface tension of water, to around 15–20 mN/m. In particular, fluoroalkyl end-capped MMA-*Si*–DMAA cooligomers were more effective in reducing the surface tension of water with a clear break point resembling a critical micelle concentration (cmc). These findings suggest that these cooligomers could form self-assembled molecular aggregates in aqueous solutions. In addition, we measured the surface tension of *m*-xylene solutions of our present fluoroalkyl end-capped cooligomers under similar conditions (see Figs. 4 and 5).

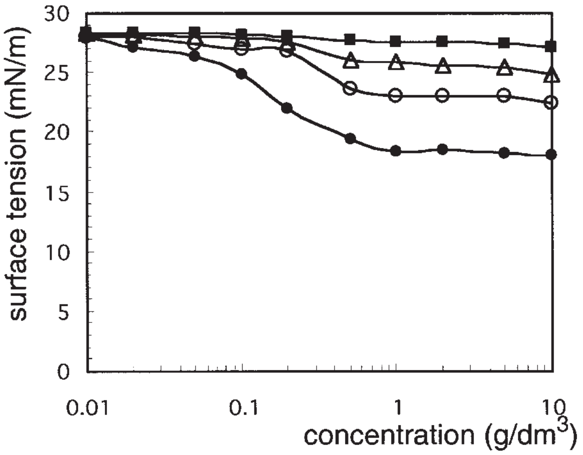


Figure 4 Surface tension of *m*-xylene solutions of R_F–(MMA–*Si*)$_x$–(DMAA)$_y$–R_F at 30°C: △—△ Run 1, R_F = $CF(CF_3)OC_3F_7$; ○—○ Run 2, R_F = $CF(CF_3)OC_6F_{13}$; ●—● Run 3, R_F = $CF(CF_3)OCFCF_2(CF_3)OC_3F_7$; ■—■ –(MMA-*Si*)$_x$–(DMAA)$_y$ –[M_n = 17,500 g/mol (M_w/M_n = 1.61); $x:y$ = 0.8 : 189, feed molar ratio].

Figures 4 and 5 show that fluoroalkyl end-capped MMA-*Si*–DMAA cooligomers and MMA-*Si*–ACMO cooligomers were effectively able to reduce the surface tension of *m*-xylene. In particular, fluoroalkyl end-capped MMA-*Si* cooligomers, having longer fluoroalkyl groups (Runs 3 and 7), were more effective in reducing the surface tension of *m*-xylene from 28 to around 18–20 mN/m levels, although the corresponding nonfluorinated cooligomers [-(MMA-*Si*)$_x$-(DMAA)$_y$-; -(MMA-*Si*)$_x$-(ACMO)$_y$-] were not able to effectively reduce the surface tension of *m*-xylene. Similarly, fluoroalkyl end-capped PME-4–DMAA cooligomer (Run 9 in Table I) was able to reduce the surface tension of *m*-xylene to around 20 mN/m level (data not shown).

As mentioned above, our present fluoroalkyl end-capped MMA-*Si* and PME-*m* cooligomers are characterized not only by good solubility in a variety of solvents including water and silicone oil but also by a good surfactant property. Thus, these fluorinated cooligomers are candidates for development into new fluorinated surface-active compounds for common polymeric materials such as polystyrene (PSt) and poly(methyl methacrylate) (PMMA). In fact, fluoroalkyl end-capped MMA-*Si* and PME-*m* cooligomers were tested for surface activity as a new type of surface modification agents. These results are shown in Tables IV and V.

Contact angles for dodecane on the cast films of PSt treated with fluoroalkyl end-capped MMA-*Si* and PME-*m* cooligomers (each concentration of cooligomer based on PSt is 1 wt %) showed a significantly large value (22–48°) compared with that (0°) of the corresponding nonfluorinated cooligomers or that (0°) of the nontreated PSt. These values were found to increase with increasing length of end-capped fluoroalkyl groups in cooligomers (see Tables IV and V). In each oligomer, a time dependency of contact angle of dodecane was not observed. These results suggest that end-capped fluoroalkyl segments in cooligomers should be arranged regularly above the PSt surface to exhibit a markedly strong oleophobicity imparted by fluorine, although these cooligomers possess highly oleophilic dimethylsilicone and poly(oxyethylene) units.

Of particular interest, we obtained extremely low values (~ 0°) in measurements of contact angles for water on the PSt surface treated with fluoroalkyl end-capped PME-*m* cooligomers, which exhibited a strong hydrophilicity on their surface (see Table V). On the other hand, the corresponding fluorinated MMA-*Si* cooligomers exhibited the highest values (129°: see Table IV). A steep time dependency of contact angle of water was observed in fluoroalkyl end-capped PME-*m* cooligomers as in Table V. The contact angles of water were found to sharply decrease from 11 ~ 14 to 0°. In contrast, the fluorinated MMA-*Si* cooligomers and the corresponding nonfluorinated MMA-*Si* cooligomers were not able to effectively decrease the contact angle of water. Thus, fluorinated PME-*m* cooligomers were shown to possess a significantly strong hydrophilicity above their surface, even though these cooligomers have a strong hydrophobic fluoroalkyl group. These results suggest that at the interface with water, hydrophobic fluoroalkyl segments are easily replaced by the strongly hydrophilic groups such as polyoxyethylene groups. The hydrophilic groups in cooligomers should be arranged regularly above the PSt surface. It

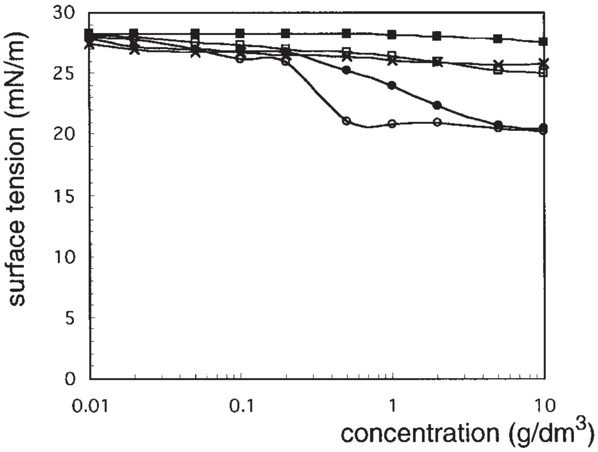


Figure 5 Surface tension of *m*-xylene solutions of R_F–(MMA–*Si*)$_x$–(ACMO)$_y$–R_F at 30°C: *—* Run 4, R_F = $CF(CF_3)OC_3F_7$; □—□ Run 5, R_F = $CF(CF_3)OC_3F_7$; ●—● Run 6, R_F = $CF(CF_3)OC_6F_{13}$; ○—○ Run 7, R_F = $CF(CF_3)OCFCF_2(CF_3)OC_3F_7$; ■—■ –(MMA-*Si*)$_x$–(ACMO)$_y$ –[M_n = 7110 g/mol (M_w/M_n = 1.59); $x:y$ = 0.3 : 100, feed molar ratio].

TABLE IV
Contact Angles of Dodecane and Water on PSt Films Treated with R_F-(MMA-*Si*)$_x$-(Co-M)$_y$-R_F[a)]

R_F in Oligomer Run[b]	Contact angle (degree)							
		Water						
	Dodecane	0 min	5 min	10 min	15 min	20 min	25 min	30 min
Co-M: DMAA								
$CF(CF_3)OC_3F_7$								
1	22	119	118	116	115	111	110	109
$CF(CF_3)OC_6F_{13}$								
2	35	111	110	108	107	107	106	106
$CF(CF_3)OCFCF_2(CF_3)OC_3F_7$								
3	43	126	125	124	123	122	121	121
—(MMA-*Si*)$_x$-(DMAA)$_y$–[M_n = 17,500 g/mol (M_w/M_n = 1.61)], [x : y = 0.8 : 189][c]								
	0	97	97	95	94	94	93	92
Co-M: ACMO								
$CF(CF_3)OC_3F_7$								
4	26	110	110	109	108	107	106	106
5	23	109	109	108	107	107	105	105
$CF(CF_3)OC_6F_{13}$								
6	34	126	126	125	124	124	123	122
$CF(CF_3)OCFCF_2(CF_3)OC_3F_7$								
7	37	129	129	127	125	124	123	122
Co-M: DOBAA								
$CF(CF_3)OCFCF_2(CF_3)OC_3F_7$								
8	41	82	78	75	68	66	55	52

[a] Concentration of oligomer based on PSt is 1 wt %.
[b] Each different from those in Table I.
[c] Feed molar ratio.

takes about 5 or 25 min to replace the fluoroalkyl groups by the hydrophilic segments when the environment is changed from air to water. In fluorinated MMA-*Si* cooligomers, highly hydrophobic polydimethylsiloxane segments should be arranged regularly above the PSt surface in response to the environmental change (from air to water) to exhibit a highly hydrophobic character.

TABLE V
Contact Angles of Dodecane and Water on PSt Films Treated with R_F-(PME-*m*)$_x$-(Co-M)$_y$-R_F[a]

R_F in Oligomer Run[b]	Contact angle (degree)							
		Water						
	Dodecane	0 min	5 min	10 min	15 min	20 min	25 min	30 min
R_F-(PME-*m*)$_x$-(DMAA)$_y$-R_F								
$CF(CF_3)OCF_2CF(CF_3)C_3F_7$								
9 $m = 4$	48	0	0	0	0	0	0	0
R_F-(PME-*m*)$_x$-(ACMO)$_y$-R_F								
$CF(CF_3)OC_3F_7$								
10 $m = 4$	35	14	12	9	6	4	2	0
$CF(CF_3)OCF_2CF(CF_3)C_3F_7$								
11 $m = 4$	40	12	5	0	0	0	0	0
R_F-(PME-*m*)$_x$-(DMAA)$_y$-R_F								
$CF(CF_3)OCF_2CF(CF_3)C_3F_7$								
12 $m = 8$	42	11	5	0	0	0	0	0
R_F-(PME-*m*)$_x$-(ACMO)$_y$-R_F								
$CF(CF_3)OCF_2CF(CF_3)C_3F_7$								
13 $m = 8$	40	11	9	5	0	0	0	0
R_F-(PME-*m*)$_x$-(DOBAA)$_y$-R_F								
$CF(CF_3)OCF_2CF(CF_3)C_3F_7$								
14 $m = 8$	35	11	0	0	0	0	0	0

[a] Concentration of oligomer based on PSt is 1 wt %.
[b] Each different from those in Table I.

TABLE VI
Emulsification of Water and Silicone Oil in the Presence of Fluorinated Cooligomers at Room Temperature

Run[a]	R_F in cooligomer	Separation time (min)
R_F-(MMA-*Si*)$_x$-(DMAA)$_y$-R_F		
1	$CF(CF_3)OC_3F_7$	3
R_F-(MMA-*Si*)$_x$-(ACMO)$_y$-R_F		
4	$CF(CF_3)OC_3F_7$	11
5	$CF(CF_3)OC_3F_7$	9
–(MMA-*Si*)$_x$-(ACMO)$_y$–		2
R_F-(MMA-*Si*)$_x$-(DOBAA)$_y$-R_F		
8	$CF(CF_3)OCFCF_2(CF_3)OC_3F_7$	5
R_F-(PME-*m*)$_x$-(ACMO)$_y$-R_F		
$CF(CF_3)OCFCF_2(CF_3)OC_3F_7$		
13 $m = 8$		>3 days
No oligomer		0

[a] Each different from those in Table I.

In addition, it is very interesting to apply our present fluorinated cooligomers to the novel emulsifying agents for water and silicone oil because these fluorinated cooligomers have good solubility in silicone oil. In fact, we investigated the emulsification of water and silicone oil (volume ratio: 9 : 1) in the presence of fluorinated cooligomers at room temperature, results of which study are shown in Table VI.

As shown in Table VI, fluoroalkyl end-capped MMA-*Si* cooligomers were not able to effectively emulsify the mixture of water and silicone oil. However, of particular interest, fluoroalkyl end-capped PME-*m*–ACMO cooligomer was clearly shown to have good emulsification with respect to this mixed solvent. In particular, the mixed solvent of water and silicone oil in the presence of this fluorinated cooligomer was very stable, without separation, over 3 days under similar conditions. This finding would be dependent on its excellent solubility of water and silicone oil, including common organic solvents except for hexane, compared to that of other fluorinated cooligomers.

CONCLUSIONS

We succeeded in preparing a variety of fluoroalkyl end-capped MMA-*Si* and PME-*m* cooligomers by the use of fluoroalkanoyl peroxide as a key intermediate. In these fluoroalkyl end-capped cooligomers thus obtained, fluoroalkyl end-capped MMA-*Si*–ACMO cooligomers have relatively good solubility in silicone oil compared to that of the corresponding DMAA and DOBAA cooligomers. In particular, fluoroalkyl end-capped PME-*m* cooligomers were characterized by a superior solubility, not only in water but also in common organic solvents including silicone oil, to that of the MMA-*Si* cooligomers. In our present fluorinated cooligomers, fluoroalkyl end-capped PME-*m*–ACMO cooligomer [$m = 8$, $R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$] has the highest solubility from a variety of solvents compared to that of other fluorinated cooligomers, and it was demonstrated that this cooligomer became soluble in water and silicone oil including common organic solvents except for hexane. Moreover, these fluorinated MMA-*Si* and PME-*m* cooligomers were quite effectively able to reduce the surface tension of water and *m*-xylene to around 20 mN/m levels to exhibit a clear break point resembling a cmc. This finding suggests that these fluorinated cooligomers can form the self-assembled molecular aggregates in these solvents. Our present fluorinated cooligomers were applied to novel surface modification agents, and the modified PSt surface treated with these cooligomers exhibited good oleophobicity imparted by fluorine. Of particular interest, the modified PSt films with fluorinated PME-*m* cooligomers were characterized by extremely high surface hydrophilicity, whereas the fluorinated MMA-*Si* cooligomers were characterized by high surface hydrophobicity. In our present fluorinated cooligomers, fluorinated PME-*m*–ACMO cooligomer, which exhibited a higher solubility in a variety of solvents including silicone oil, was applicable as a novel polymeric-type emulsifying agent. Therefore, it was verified that our fluorinated MMA-*Si* and PME-*m* cooligomers have high potential for new fluorinated functional materials because of their higher solubility in silicone oil and good surfactant properties.

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