Synthesis of Fluoroalkyl End-Capped Preoligomers Containing Succinimidyl Segments—Application to Novel Fluorinated Oligomers Possessing Surface Antibacterial Activity

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ABSTRACT: Fluoroalkyl end-capped *N*-acryloxysuccinimide (ASuI) cooligomers were prepared under very mild conditions by the cooligomerizations of fluoroalkanoyl peroxides with ASuI and comonomers such as *N*,*N*-dimethylacrylamide (DMAA) and acryloylmorpholine (ACMO). These fluorinated ASuI cooligomers thus obtained were in general easily soluble in water and common organic solvents. These fluorinated ASuI cooligomers were also able to reduce the surface tension of water quite effectively to around 20 mN/m with a clear break point resembling a critical micelle concentration (CMC), although the corresponding nonfluorinated ASuI cooligomers were not effective for reducing the surface tension of water. Fluorinated ASuI cooligomers were applicable to new fluorinated precooligomers, and these precooligomers could react with several amino compounds such as aniline, cytosine, and cyclohexylamine to afford fluorinated cooligomer-bound aromatic and cyclohexyl segments under mild conditions. Of particular interest, these fluorinated precooligomers were able to react with low molecular weight biocides such as sulfathiazole (STZ) and 3-amino-5-hydroxypyrazole (AHP) to give the corresponding fluorinated cooligomers containing antibacterial segments under similar conditions. These cooligomers were shown to have not only a good oleophobicity imparted by fluorine but also surface antibacterial activity against *Staphylococcus aureus*. Therefore, our present fluorinated cooligomers containing antibacterial segments are suggested to have high potential for new fluorinated functional materials through their surface active property and surface antibacterial activity. J Appl Polym Sci 92: 3874–3880, 2004

Key words: biomaterials; fluoropolymers; self-assembly; surfaces; surfactants

INTRODUCTION

It is well known that fluoroalkyl end-capped oligomers exhibit a wide variety of unique properties such as good solubility, surface active property, and the formation of self-assembled molecular aggregates imparted by the aggregations of fluorine which cannot be achieved by the corresponding randomly fluoroalkylated polymers and block-type fluoroalkylated polymers.[1] In these fluoroalkyl end-capped oligomers, we have already reported that fluoroalkyl end-capped oligomers containing dimethyloctylammonium segments possess not only a surface active property but also a good antibacterial activity.[2] However, due to the difficulty of the preparation of radical polymerizable monomers containing bioactive units,[3] the development of new fluorinated oligomeric biocides possessing both an antibacterial activity and a surface activity imparted by fluorine have hitherto been very limited. From the point of the development of such fluorinated oligomeric biocides, it is very interesting to synthesize fluoroalkyl end-capped preoligomers containing the protected reactive segments such as succinimidyl groups. These fluorinated preoligomers containing the protected segments are expected to react easily with commercially available low molecular weight biocides bearing amino groups. In fact, the preparation of poly(vinyl alcohol) partially functionalized with monosuccinate groups has been reported, and high degrees of modification were achieved in the coupling of model bioactive amino compounds to this

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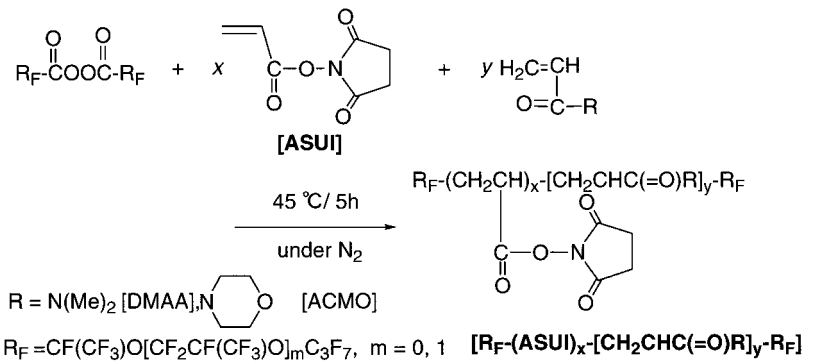


Scheme 1 Synthesis of fluoroalkyl end-capped preoligomer.

monosuccinylated poly(vinyl alcohol).[4] In this article, we report on the synthesis of fluoroalkyl end-capped oligomers containing succinimidyl groups as the protected reactive segments, with particular emphasis on the applications to the novel fluorinated polymeric biocides possessing not only the surface antibacterial activity but also the surface activity imparted by fluorine.

RESULTS AND DISCUSSION

First, we tried to react fluoroalkanoyl peroxides with *N*-acryloxysuccinimide (ASuI) and comonomers such as *N,N*-dimethylacrylamide (DMAA) and acryloylmorpholine (ACMO). The reaction scheme and the results are shown in Scheme 1 and Table I, respectively.

As shown in Scheme 1 and Table I, fluoroalkanoyl peroxides were found to react with ASuI and comonomers to afford fluoroalkyl end-capped ASuI cooligomers in 60–98% isolated yields under very mild conditions. The molecular weights of fluoroalkyl end-capped ASuI cooligomers were measured by gel permeation chromatography (GPC) with tetrahydrofuran as the eluant and the obtained molecular weights were oligomeric areas (3000–6000).

We tested fluoroalkyl end-capped ASuI cooligomers in Table I for the solubility. R_F-$(ASuI)_x$-$(ACMO)_y$-R_F cooligomers were soluble in water. These cooligomers exhibited a solubility in common organic solvents such as tetrahydrofuran, chloroform, acetone, dichloroethane, dimethylsulfoxide, and *N,N*-dimethylformamide (DMF) except for hexane. On the other hand, R_F-$(ASuI)_x$-$(DMAA)_y$-R_F cooligomers were easily soluble not only in water but also in common organic solvents except for hexane. This good solubility of our present fluorinated ASuI cooligomers is suggested to be applicable to novel fluorinated polymeric surfactants. In fact, we have measured the surface tension of aqueous solutions of fluorinated ASuI cooligomers by the Wilhelmy plate methods, and the results are shown in Figures 1 and 2.

As shown in Figures 1 and 2, R_F-$(ASuI)_x$-$(DMAA)_y$-R_F and R_F-$(ASuI)_x$-$(ACMO)_y$-R_F cooli-

TABLE I
Reactions of Fluoroalkanoyl Peroxides with ASul and Comonomers

No.	R_F in $(R_FCO_2)_2$ (mmol)	ASul (mmol)	R in CH_2=CHCOR (mmol)	Products: Yield[a] (%)	Products: M_n (M_W/M_n)[b]	Products: [x : y][c]
1	$C_3F_7OCF(CF_3)$		R = NMe_2 [DMAA]			
	12	12	120	60	3360 (1.38)	10 : 90
2	$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$					
	3	3	30	98	6280 (1.66)	22 : 78
3	$C_3F_7OCF(CF_3)$		R =  [ACMO]			
	2	2	15	80	4830 (2.19)	17 : 83
4	$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$					
	3	3	30	96	5420 (1.90)	13 : 87

[a] The yields were based on the strating materials (ASul and comonomers), and the decarboxylated peroxide unit (R_F-R_F).
[b] Molecular weights of cooligomers were determined by GPC.
[c] Cooligomerization ratio was determined by ^{1}H-NMR.

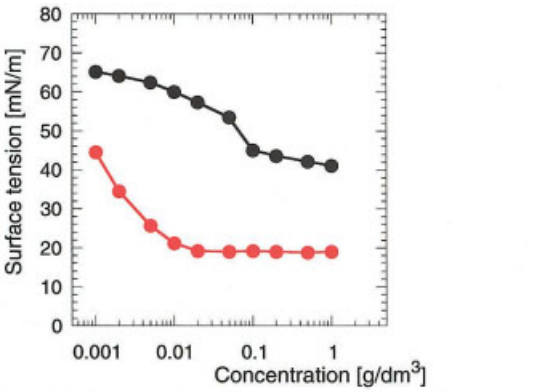


Fig. 1 Surface tension of aqueous solutions of R_F-$(ASuI)_x$-$(DMAA)_y$-R_F

Figure 1 Surface tension of aqueous solutions of R_F-$(ASuI)_x$-$(DMAA)_y$-R_F.

gomers were effective for reducing the surface tension of water with a clear break point resembling a critical micelle concentration (CMC). In contrast, the corresponding nonfluorinated ASuI cooligomers were not able to reduce effectively the surface tension of water and exhibited no clear break point resembling a CMC. This finding suggests that fluoroalkyl end-capped ASuI cooligomers are likely to form the self-assembled molecular aggregates in aqueous solutions.

To develop our present fluoroalkyl end-capped ASuI cooligomers to novel fluorinated polymeric biocides which possess not only a good surface active property imparted by fluorine but also a surface antibacterial activity, it is very important to study the reactions of these fluorinated ASuI cooligomers with some low molecular weight amino compounds such as aniline, cyclohexylamine, and cytosine. The reactions of fluorinated ASuI cooligomers with amino compounds are shown in Scheme 2.

As shown in Scheme 2, the reactions of fluorinated ASuI cooligomers with amino compounds proceeded smoothly to give fluoroalkyl end-capped cooligomer-bound aniline, cyclohexylamine, and cytosine units in excellent to moderate isolated yields (43–80%). It is strongly expected that our present fluorinated precooligomers containing succinimidyl segments could react with low molecular weight biocides bearing amino group. Thus, we tried to react these precooligomers with the well-known biocides such as sulfathiazole (STZ) and 3-amino-5-hydroxypyrazole (AHP)[5] as shown in Schemes 3 and 4.

As shown in Schemes 3 and 4, the reactions of fluorinated precooligomers with STZ and AHP were found to proceed under the same conditions as in Scheme 2, and the expected fluoroalkyl end-capped cooligomers containing STZ and AHP segments were obtained. The isolated yields of fluorinated cooligomers were 34–77%, and the yields of fluorinated cooligomers containing STZ segments were almost the same as those of the corresponding AHP cooligomers. Additionally, the molecular weights of the obtained cooligomers containing STZ and AHP segments measured by GPC were oligomeric areas (M_n = 2000–9000). We studied the solubility of fluorinated cooligomers containing STZ and AHP segments. The solubility of these fluorinated cooligomers were found to be, in general, inferior to those of the parent fluorinated ASuI cooligomers, and these cooligomers were soluble in water, methanol, tetrahydrofuran, chloroform, 1,2-dichloroethane, acetone, dimethylsulfoxide, and DMF.

In this way, it was clarified that fluoroalkyl end-capped cooligomers containing STZ and AHP were soluble in water, chloroform, and dichloroethane. Therefore, these fluorinated cooligomers were expected to apply new fluorinated polymeric surfactants containing antibacterial segments. We measured the surface tension of aqueous solutions of fluorinated cooligomers containing AHP segments. The surface tension of aqueous solutions of the corresponding nonfluorinated cooligomer was also measured for comparison. These results are shown in Figure 3.

As shown in Figure 3, fluorinated cooligomers containing AHP segments were able to reduce the surface tension of water quite effectively to around 20 mN/m with a clear break point resembling a CMC, despite the fact that the corresponding nonfluorinated cooligomer was not effective for reducing the surface tension of water. Such a good surfactant property indi-

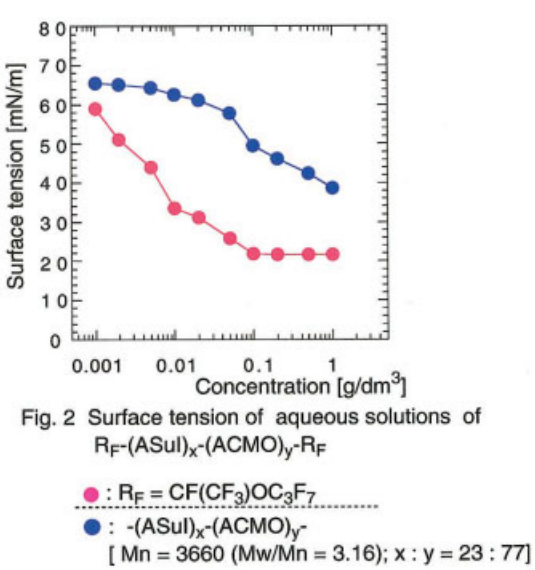
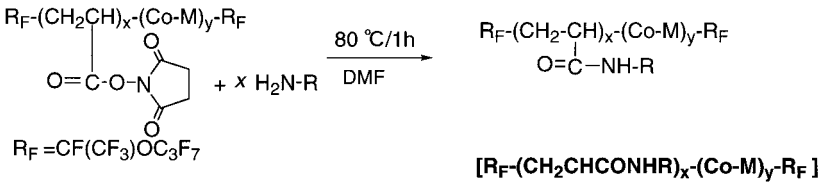


Fig. 2 Surface tension of aqueous solutions of R_F-$(ASuI)_x$-$(ACMO)_y$-R_F

Figure 2 Surface tension of aqueous solutions of R_F-$(ASuI)_x$-$(ACMO)_y$-R_F.



$[R_F\text{-}(ASul)_x\text{-}(Co\text{-}M)_y\text{-}R_F]$	R in H_2N-R	$[R_F\text{-}(CH_2CHCONHR)_x\text{-}(Co\text{-}M)_y\text{-}R_F]$ Yield (%)	Mn (Mw/Mn) [x : y][a]
0.29 mmol[Co-M: DMAA]	(1.5 mmol)	43	3210 (2.75) [1 : 99]
0.25 mmol[Co-M: ACMO]	(1.2 mmol)	73	4840 (1.80) [3 : 97]
0.18 mmol[Co-M: DMAA]	(1.5 mmol)	67	6890 (1.54) [14 : 86]
0.06 mmol[Co-M: ACMO]	(0.28 mmol)	73	9240 (1.34) [7 : 93]
0.20 mmol[Co-M: DMAA]	NH (1.0 mmol)	80	3410 (1.32) [8 : 92]

a) cooligomerization was determined by ^{1}H NMR

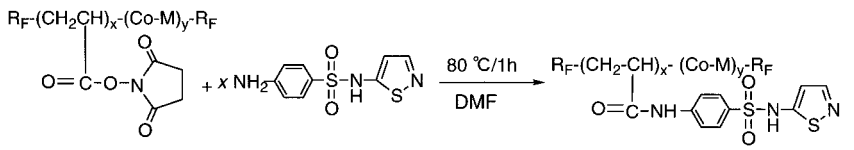
Scheme 2 Reactions of fluoroalkyl end-capped precooligomers with some amino compounds.

cates that our present fluorinated cooligomers are applicable to novel fluorinated surface active compounds for common organic polymeric materials such as poly(methyl methacrylate) (PMMA) and polystyrene (PSt). Fluorinated cooligomers were tested for surface activity as a new type of surface modification agents. These results are shown in Table II.

As shown in Table II, the contact angles of dodecane on the cast films of PMMA and PSt treated with fluorinated cooligomers containing STZ and AHP segments were found to show significantly large values (PMMA: 10–20°; PSt: 20–55°) compared with those of nontreated PMMA (0°) and PSt (0°). From this finding, these fluorinated cooligomers were clarified to exhibit a markedly strong oleophobicity imparted by fluorine above the PMMA or PSt surface, although these oligomers possess highly oleophilic moieties such as STZ and AHP segments. Therefore, fluoroalkyl groups in cooligomers are likely to be arranged above the PMMA or PSt surface. STZ or AHP segments in cooligomers should also be arranged regularly above the PMMA and PSt surfaces to exhibit a surface antibacterial activity.

In fact, fluorinated cooligomers containing STZ and AHP segments have been evaluated for the surface antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* by the viable cell-counting method. About 10^6 or 10^5 cells/mL of bacteria were exposed to each small circular piece (67 mm in diameter) of the modified PMMA films treated with the fluorinated cooligomers. These results are shown in Table III.

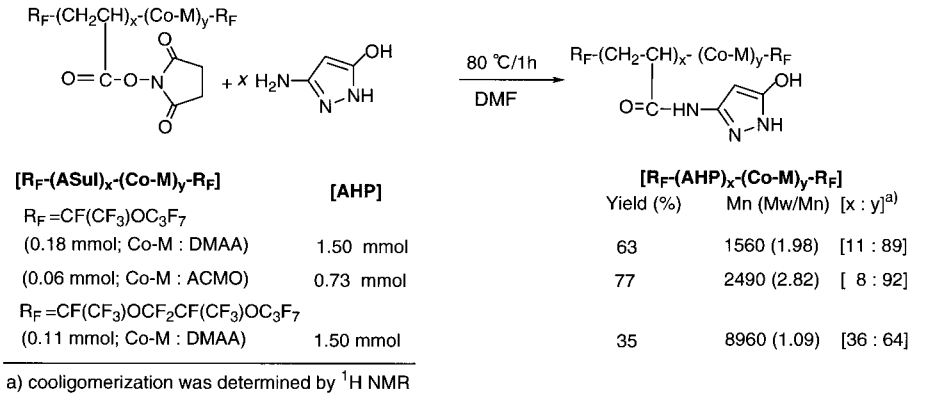
As shown in Table III, fluorinated cooligomers containing STZ and AHP segments were inactive against *E. coli*. However, these fluorinated cooligomers were capable of killing the bacterial cells (*S. aureus*) after 24 h of contact under 37°C. The modified PMMA films treated with these fluorinated cooligomers were found to exhibit high antibacterial activity against *S. aureus*. R_F-$(AHP)_x$-$(ACMO)_y$-R_F [R_F = $CF(CF_3)OC_3F_7$] cooligomer especially was capable of killing completely the



$[R_F\text{-}(ASul)_x\text{-}(Co\text{-}M)_y\text{-}R_F]$	[STZ]	$[R_F\text{-}(STZ)_x\text{-}(Co\text{-}M)_y\text{-}R_F]$ Yield (%)	Mn (Mw/Mn) [x : y][a]
R_F =$CF(CF_3)OC_3F_7$			
(0.17 mmol; Co-M : DMAA)	1.50 mmol	73	9240 (1.41) [4 : 96]
(0.06 mmol; Co-M : ACMO)	0.72 mmol	34	3170 (2.15) [3 : 97]
R_F =$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$			
(0.10 mmol; Co-M : DMAA)	1.50 mmol	52	1710 (1.95) [4 : 96]
(0.11 mmol; Co-M : ACMO)	1.50 mmol	77	6380 (1.59) [3 : 97]

a) cooligomerization was determined by ^{1}H NMR

Scheme 3 Reactions of fluoroalkyl end-capped precooligomers with sulfathiazole.



Scheme 4 Reactions of fluoroalkyl end-capped precooligomers with 3-amino-5-hydroxypyrazole.

bacterial cells from 10^5 to 0 CFU. This high antibacterial activity would depend on whether the bacteria are unable to colonize the PMMA surface treated with the fluorinated AHP-ACMO cooligomer, because AHP segments as well as fluoroalkyl segments in cooligomers should be arranged regularly above the PMMA surface, although the PMMA film contains only 1% (wt %) fluorinated cooligomer.

In conclusion, we succeeded in preparing fluoroalkyl end-capped cooligomers containing succinimidyl segments by the reactions of fluoroalkanoyl peroxides with ASuI and comonomers such as DMAA and ACMO. These obtained fluorinated ASuI cooligomers were applicable to novel fluorinated preoligomers containing the protected reactive groups. In fact, these cooligomers were found to react smoothly with low molecular weight biocides bearing amino group to afford new fluoroalkyl end-capped cooligomers containing antibacterial segments. It was clarified that these fluorinated cooligomers containing antibacterial segments possess not only a good oleophobicity imparted by fluorine but also a high surface antibacterial activity.

EXPERIMENTAL

Measurements

Fourier transform infrared (FTIR) spectra were measured by using a Horiba FT-300 FTIR spectrophotometer (Kyoto, Japan). NMR spectra and molecular weights were measured by using a Varian Unity-plus 500 (500 MHz) spectrometer (Palo Alto, CA) and a Shodex DS-4 (pomp) and Shodex RI-71 (Detector) gel permeation chromatography (GPC, Tokyo, Japan) calibrated with standard PSt by using tetrahydrofuran as the eluant, respectively. The surface tensions of aqueous solutions of the fluoroalkyl end-capped cooligomers were measured at 30°C by using a Wilhelmy-type surface tensiometer (ST-1, Shimadzu Co., Kyoto,

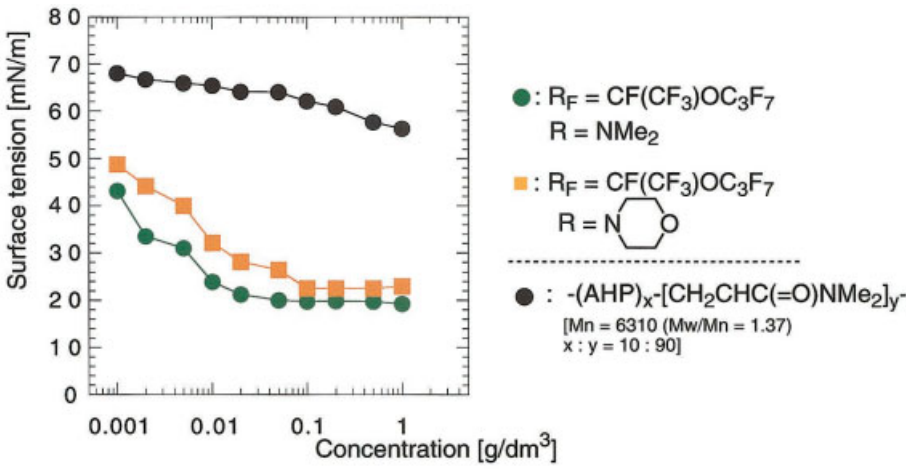


Fig. 3 Surface tension of aqueous solutions of R_F-(AHP)$_x$-[$CH_2CHC(=O)R]_y$-R_F

Figure 3 Surface tension of aqueous solutions of R_F-(AHP)$_x$-[$CH_2CHC(=O)R]_y$-R_F.

TABLE II
Contact Angle of Dodecane on PMMA and PSt Films Treated with R_F-(STZ)$_x$-[Co-M]$_y$-R_F[a] and R_F-(AHP)$_x$-[Co-M]$_y$-R_F[a]

Oligomer	Contact angle (°) PMMA	Pst
R_F-(STZ)$_x$-(Co-M)$_y$-R_F		
R_F = CF(CF$_3$)OC$_3$F$_7$; Co-M: DMAA	20	25
R_F = CF(CF$_3$)OC$_3$F$_7$; Co-M: ACMO	10	35
R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$: DMAA	—	55
R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$: ACMO	—	45
R_F-(AHP)$_x$-(Co-M)$_y$-R_F		
R_F = CF(CF$_3$)OC$_3$F$_7$; Co-M: DMAA	10	30
R_F = CF(CF$_3$)OC$_3$F$_7$; Co-M: ACMO	19	20
R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$: ACMO	—	30
Nontreated	0	0

[a] Concentration of oligomer based on PMMA (or Pst) is 1% (m/m).

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

Materials

ASuI was purchased from Acros Organics (Geel, Belgium). DMAA and ACMO were used as received from Kohjin Co., Ltd. (Tokyo, Japan). STZ and AHP were purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). A series of fluoroalkanoyl peroxides [(R_F-COO)$_2$] were prepared by the method described in the literature.[7]

General procedure for the synthesis of fluoroalkyl end-capped ASuI cooligomers

Perfluoro-2-methyl-3-oxahexanoyl peroxide (11.8 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 (200 g) was added to ASuI (11.8 mmol) and DMAA (118 mmol). The homogeneous solution was stirred at 45°C for 5 h under nitrogen. After evaporating the solvent, the crude products obtained were dialyzed with 50% methanol solution to give an α,ω-bis(perfluoro-1-methyl-2-oxapentylated) ASuI–DMAA cooligomer (12.4 g). This cooligomer exhibited the following spectra characteristics:

IR (ν/cm^{-1}) 1627 [C(═O)], 1351 (CF$_3$), 1238 (CF$_2$); ^{1}H-NMR (D$_2$O) δ 1.18–1.79 (CH$_2$), 2.18–3.01 (CH, CH$_2$, CH$_3$); ^{19}F-NMR (D$_2$O, ext. CF$_3$CO$_2$H) δ −5.69 to −7.43 (16F), −54.1 to −54.2 (6F).

Similarly, a series of fluoroalkyl end-capped ASuI cooligomers were prepared by the reactions with fluoroalkanoyl peroxides. These exhibited the following spectral characteristics:

R_F-(ASuI)$_x$-(DMAA)$_y$-R_F [R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$];
IR (ν/cm^{-1}) 1630 [C(═O)], 1350 (CF$_3$), 1240 (CF$_2$);
^{1}H-NMR (D$_2$O) δ 1.09–1.97 (CH$_2$), 2.18–3.20 (CH, CH$_2$, CH$_3$);
^{19}F-NMR (D$_2$O, ext. CF$_3$CO$_2$H) δ −5.45 to −8.20 (26F), −5461 to −56.0 (6F), −71.2 (2F).

R_F-(ASuI)$_x$-(ACMO)$_y$-R_F [R_F = CF(CF$_3$)OC$_3$F$_7$]
IR (ν/cm^{-1}) 1629 [C(═O)], 1383 (CF$_3$), 1238 (CF$_2$);
^{1}H-NMR (D$_2$O) δ 0.98–1.98 (CH$_2$), 2.12–2 0.98 (CH, CH$_2$), 3.02–3.91 (CH$_2$);
^{19}F-NMR (D$_2$O, ext. CF$_3$CO$_2$H) δ −5.30 to −7.89 (16F), −54.20 to −54.60 (6F).

R_F-(ASuI)$_x$-(ACMO)$_y$-R_F [R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$]
IR (ν/cm^{-1}) 1720 [C(═O)], 1350 (CF$_3$), 1230 (CF$_2$);
^{1}H-NMR (D$_2$O) δ 0.95–2.12 (CH$_2$), 2.22–4.25 (CH, CH$_2$);
^{19}F-NMR(D$_2$O, ext. CF$_3$CO$_2$H) δ −5.84 to −8.93 (26F), −54.40 to -55.90 (6F), −70.7 (2F).

General procedure for the reactions of fluoroalkyl end-capped precooligomers with amino compounds

A solution of R_F-(ASuI)$_x$-(DMAA)$_y$-R_F [R_F = CF(CF$_3$)OC$_3$F$_7$] (0.17 mmol: 0.58 g) and aniline (1.5 mmol) in DMF (10 g) was stirred at 80°C for 1 h. After the solvent was evaporated off under reduced pressure, the crude products were dialyzed against 50% methanol solution to give R_F-[CH$_2$CHC(═O)NHPh]$_x$-(DMAA)$_y$-R_F (0.32 g).

This cooligomer showed the following spectral data:

IR (ν/cm^{-1}) 1620 [C(═O)], 1361 (CF$_3$), 1254 (CF$_2$);
^{1}H-NMR (D$_2$O) δ 1.00–1.85 (CH$_2$), 2.20–3.15 (CH, CH$_2$, CH$_3$), 7.10–7.58 (aromatic protons, 5H);
^{19}F-NMR (D$_2$O, ext. CF$_3$CO$_2$H) δ −5.74 to −7.76 (16F), −54.10 to −56.50 (6F).

Similarly, fluoroalkyl end-capped cooligomer-bound aromatic and cyclohexyl segments were pre-

TABLE III
Surface Antibacterial Activity of PMMA Films Treated with R_F-(STZ)$_x$-(Co-M)$_y$-R_F and R_F-(AHP)$_x$-(Co-M)$_y$-R_F [R_F = CF(CF$_3$)OC$_3$F$_7$)] against *Escherichia coli* and *Staphylococcus aureus*

Oligomer	*E. coli* (CFU)[a] (cell/ml)	*S. aureus* (CFU)[a] (cell/ml)
Control	1.2×10^6	1.1×10^5
R_F-(STZ)$_x$-(ACMO)$_y$-R_F	2.5×10^5	1.8×10^3
R_F-(AHP)$_x$-(DMAA)$_y$-R_F	7.4×10^5	9.1×10^3
R_F-(AHP)$_x$-(ACMO)$_y$-R_F	3.1×10^5	0

[a] CFU indicates colony forming units.

pared by the use of R_F-(ASuI)$_x$-(Co-M)$_y$-R_F. These exhibited the following spectral characteristics:

R_F-[$CH_2CHC(=O)NHPh]_x$-(ACMO)$_y$-R_F [R_F = $CF(CF_3)OC_3F_7$]
IR (ν/cm^{-1}) 1629 [C(=O)], 1361 (CF_3), 1242 (CF_2);
^{1}H-NMR (D_2O) δ 1.10–2.00 (CH_2), 2.18–4.20 (CH, CH_2), 7.10–7.79 (aromatic protons, 5H);
^{19}F-NMR (D_2O, ext. CF_3CO_2H) δ −4.10 to −7.76 (16F), −54.10 to −55.60 (6F).

R_F-[$CH_2CHC(=O)NH$-R]$_x$-(DMAA)$_y$-R_F [H-R = cyclohexylamine; R_F = $CF(CF_3)OC_3F_7$]
IR (ν/cm^{-1}) 1620 [C(=O)], 1361 (CF_3), 1254 (CF_2);
^{1}H-NMR (D_2O) δ 1.01–1.95 (CH_2), 2.10–3.60 (CH, CH_3), 3.05–4.21 (CH_2);
^{19}F-NMR (D_2O, ext. CF_3CO_2H) δ −4.00 to −7.76 (16F), −54.20 to −55.50 (6F).

R_F-[$CH_2CHC(=O)NH$-R]$_x$-(ACMO)$_y$-R_F [H-R = cyclohexylamine; R_F = $CF(CF_3)OC_3F_7$]
IR (ν/cm^{-1}) 1628 [C(=O)], 1361 (CF_3), 1242 (CF_2);
^{1}H-NMR (D_2O) δ 0.98–2.01 (CH_2), 2.03–2.99 (CH, CH_2), 3.05–4.21 (CH_2);
^{19}F-NMR (D_2O, ext. CF_3CO_2H) δ −4.08 to −7.76 (16F), −54.10 to −55.60 (6F).

R_F-[$CH_2CHC(=O)NH$-R]$_x$-(DMAA)$_y$-R_F [H-R = cytosine; R_F = $CF(CF_3)OC_3F_7$]
IR (ν/cm^{-1}) 1620 [C(=O)], 1359 (CF_3), 1240 (CF_2);
^{1}H-NMR (D_2O) δ 1.15–1.80 (CH_2), 2.25–3.13 (CH, CH_3), 5.87 (aromatic proton, 1H), 7.41 (aromatic proton, 1H);
^{19}F-NMR (D_2O, ext. CF_3CO_2H) δ −4.33 to −7.79 (16F), −54.20 to −55.70 (6F).

R_F-(STZ)$_x$-(DMAA)$_y$-R_F [R_F = $CF(CF_3)OC_3F_7$]
IR (ν/cm^{-1}) 1627 [C(=O)], 1249 (CF_2);
^{1}H-NMR (D_2O) δ 1.08–1.69 (CH_2), 2.18–3.01 (CH, CH_3), 6.62 (aromatic proton, 1H), 6.71 (aromatic protons, 2H), 7.03 (aromatic proton, 1H), 7.55 (aromatic protons, 2H);
^{19}F-NMR (D_2O, ext. CF_3CO_2H) δ −4.05 to −7.76 (16F), −54.20 to −55.70 (6F).

R_F-(STZ)$_x$-(DMAA)$_y$-R_F [R_F = $CF(CF_3)OCF_2CF(CF_3)OC_3F_7$]
IR (ν/cm^{-1}) 1627 [C(=O)], 1260 (CF_2);
^{1}H-NMR (D_2O) δ 1.12–2.01 (CH_2), 2.29–3.10 (CH, CH_3), 6.58 (aromatic proton, 1H), 6.68 (aromatic protons, 2H), 6.99 (aromatic proton, 1H), 7.51 (aromatic protons, 2H);
^{19}F NMR (D_2O, ext. CF_3CO_2H) δ −5.08 to −8.78 (26F), −54.50 to −55.70 (6F), −71.20 (2F).

R_F-(STZ)$_x$-(ACMO)$_y$-R_F [R_F = $CF(CF_3)OC_3F_7$]
IR (ν/cm^{-1}) 1629 [C(=O)], 1247 (CF_2);
^{1}H-NMR (D_2O) δ 0.95–2.10 (CH_2), 2.21–3.82 (CH, CH_2), 6.63 (aromatic proton, 1H), 6.71 (aromatic protons, 2H), 7.03 (aromatic proton, 1H), 7.55 (aromatic protons, 2H);
^{19}F-NMR (D_2O, ext. CF_3CO_2H) δ −5.09 to −7.76 (16F), −54.20 to −55.80 (6F).

R_F-(STZ)$_x$-(ACMO)$_y$-R_F [R_F = $CF(CF_3)OCF_2CF(CF_3)OC_3F_7$]
IR (ν/cm^{-1}) 1720 [C(=O)], 1350 (CF_3), 1240 (CF_2);
^{1}H-NMR (D_2O) δ 1.05–2.02 (CH_2), 2.30–3.00 (CH), 3.02–4.10 (CH_3), 6.62 (aromatic proton, 1H), 6.70 (aromatic protons, 2H), 7.01 (aromatic proton, 1H), 7.54 (aromatic protons, 2H);
^{19}F-NMR (D_2O, ext. CF_3CO_2H) δ −5.84 to −8.93 (26F), −55.90 (6F), −70.90 (2F).

R_F-(AHP)$_x$-(DMAA)$_y$-R_F [R_F = $CF(CF_3)OC_3F_7$]
IR (ν/cm^{-1}) 1627 [C(=O)], 1351 (CF_3), 1249(CF_2);
^{1}H-NMR (D_2O) δ 1.18–1.62 (CH_2), 2.12–3.04 (CH, CH_3), 7.79 (aromatic proton, 1H);
^{19}F-NMR (D_2O, ext. CF_3CO_2H) δ −4.31 to −7.76 (16F), −54.20 to −56.50 (6F).

R_F-(AHP)$_x$-(ACMO)$_y$-R_F [R_F = $CF(CF_3)OC_3F_7$]
IR (ν/cm^{-1}) 1627 [C(=O)], 1243 (CF_2);
^{1}H-NMR (D_2O) δ 0.98–2.03 (CH_2), 2.12–2.93 (CH), 3.02–3.88 (CH_2), 7.80 (aromatic proton, 1H);
^{19}F-NMR (D_2O, ext. CF_3CO_2H) δ −4.10 to −7.76 (16F), −54.10 to −55.10 (6F).

R_F-(AHP)$_x$-(ACMO)$_y$-R_F [R_F = $CF(CF_3)OCF_2CF(CF_3)OC_3F_7$]
IR (ν/cm^{-1}) 1690 [C(=O)], 1349 (CF_3), 1251 (CF_2);
^{1}H-NMR (D_2O) δ 0.98–2.03 (CH_2), 2.22–4.21 (CH, CH_3), 7.71 (aromatic proton, 1H);
^{19}F-NMR (D_2O, ext. CF_3CO_2H) δ −5.84 to −8.88 (26F), −54.30 to −55.80 (6F), −70.60 (2F).

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