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Synthesis and antibacterial activity of novel fluoroalkyl end-capped oligomers containing ammonium segments: application to new fluorinated gelling materials with antibacterial activity

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New fluoroalkyl end-capped 2-aminoethyl methacrylate hydrochloride (AEM) co-oligomers containing triol or tetraol segments were prepared by reaction of fluoroalkanoyl peroxides with AEM and the corresponding triol or tetraol monomer under very mild conditions. Fluoroalkyl end-capped AEM co-oligomers thus obtained had no solubility in water and DMSO. However, these co-oligomers could cause gelation in these solvents under non-crosslinked conditions, although the corresponding AEM homo-oligomers had good solubility in these solvents, and were able to reduce the surface tension of water quite effectively. Interestingly, fluoroalkyl end-capped AEM co-oligomers exhibited as extremely high antibacterial activity against *Staphylococcus aureus* and *Pseudomonas aeruginosa* as the corresponding fluorinated AEM homo-oligomers. In addition, fluoroalkyl end-capped AEM co-oligomer gels are applicable to new fluorinated gelling polymer electrolytes, and these cationic gels containing lithium ions exhibited a considerably high ionic conductivity of the level of 10^{-3} S cm^{-1} at room temperature.

Introduction

Recently, polymer gels have received increasing attention owing to their high potential in various industrial, biological, and environmental applications.[1] For example, polymer gels, such as poly[*N*-tris(hydroxymethyl)methylacrylamide] gels crosslinked by *N*,*N*′-methylenebisacrylamide, have been widely used as anticonvective media for electrophoretic separation of biomolecules, and their derivatives have been applied to a drug-delivery system.[2] On the other hand, partially fluoroalkylated polymeric compounds are attractive functional materials because they exhibit various unique properties such as high solubility, surface active properties and the formation of self-assembled molecular aggregates which cannot be achieved by the corresponding randomly fluoroalkylated polymers and fluoroalkylated block polymers.[3] From this point of view, we have already reported on the synthesis and properties of partially fluoroalkylated oligomers, that is, a variety of fluoroalkyl end-capped oligomers by the use of fluoroalkanoyl peroxides as key intermediate.[4] In these fluoroalkyl end-capped oligomers, it was demonstrated that fluoroalkyl end-capped oligomers containing cationic segments such as trimethylammonium,[5] pyridinium,[6] allylammonium,[7] and diallylammonium[7] segments were easily soluble in water and were able to reduce the surface tension of water as effectively as the low-molecular cationic surfactants. These fluorinated oligomers were also found to exhibit antibacterial activity to some extent.[5–7]

Therefore, it is very interesting to explore fluoroalkyl end-capped cationic polymer gels possessing an excellent antibacterial activity; however, although the preparation and application of these novel fluorinated materials have hitherto been very limited, these compounds have been the subject of considerable research of both a fundamental and an applied nature. In addition, great interest is also focused on the application of these partially fluorinated cationic polymer gels to gelled polymer electrolyte-based rechargeable lithium batteries which can offer liquid-like values for conductivity.[8] It is expected that these fluorinated cationic polymer gels could exhibit a very high ionic conductivity owing to the electrostatic repulsion between the cationic segments and lithium ions. In this paper, we would like to report on the synthesis and antibacterial activity of novel fluoroalkyl end-capped cationic co-oligomer gels including those of the corresponding water-soluble cationic homo-oligomers, with emphasis on the applications to new fluorinated functional materials possessing biological properties and ionic conductivity.

Results and discussion

It is well-known that chlorhexidine dihydrochloride {1,1′-hexamethylenebis[(5-(4-chlorophenyl)biguanide) dihydrochloride] is a derivative of guanidine and this compound is a potent low-molecular weight biocide.[9] Therefore, an ammonium segment would be very effective as a functional group which could exhibit high antibacterial activity, since this segment is similar to a guanidine unit. In view of the development of new fluoroalkyl end-capped cationic co-oligomer gels possessing a good antibacterial activity, firstly, it is very important to study the synthesis, and properties such as surfactant properties and antibacterial activity, of water-soluble fluoroalkyl end-capped homo-oligomers containing ammonium segments. Thus, we tried to synthesize fluoroalkyl end-capped homo-oligomers

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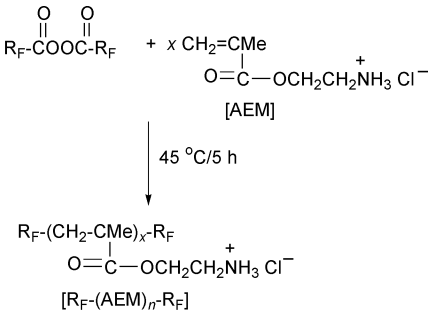
containing ammonium segments by using fluoroalkanoyl peroxide as a key intermediate.

The reactions of fluoroalkanoyl peroxides with 2-aminoethyl methacrylate hydrochloride (AEM) were carried out in heterogeneous solvent systems [1 : 1 mixture (AK-225) of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane and water] by stirring vigorously at 45 °C for 5 h under nitrogen. The reaction scheme is as follows.

As shown in Scheme 1 and Table 1, fluoroalkanoyl peroxides were found to react with AEM under very mild conditions to afford fluoroalkyl end-capped AEM homo-oligomers in 28–42% isolated yields. The molecular weights of these fluorinated AEM homo-oligomers were measured by GPC (gel permeation chromatography) by using 0.2 mol dm^{-3} Na_2HPO_4 solution as the eluent, and the obtained values (M_n) were of the order of 4000–8000. The concentrations of fluoroalkanoyl peroxides used were higher than that of AEM (molar ratio of AEM/peroxide = 5), in contrast to the usual case for radical polymerization. Under these conditions, mainly AEM homo-oligomers with two fluoroalkyl end-groups would be obtained *via* primary radical termination or radical chain transfer to the peroxide, as well as by our previously reported methods for the synthesis of two fluoroalkyl end-capped acrylic acid oligomers and methyl methacrylate oligomers.[10]

Fluoroalkyl end-capped AEM homo-oligomers thus obtained were easily soluble in water and dimethyl sulfoxide (DMSO). Thus, we applied these AEM homo-oligomers to new fluorinated cationic oligosurfactants. The surface properties of our fluoroalkyl end-capped AEM homo-oligomers were evaluated by measuring the reduction in surface tension of aqueous solutions by these oligomers using the Wilhelmy plate method at 30 °C. These results were shown in Fig. 1.

As shown in Fig. 1, fluoroalkyl end-capped AEM homo-oligomers were able to reduce the surface tension of water, quite effectively. Especially, the longest perfluorooxaalkyl end-capped AEM homo-oligomer was more effective in reducing



R_F = C_3F_7, $CF(CF_3)O[CF_2CF(CF_3)O]_mC_3F_7$; m = 0, 1, 2

Scheme 1

Table 1 Reactions of fluoroalkanoyl peroxide with AEM

R_F in peroxide (mmol)	AEM/ mmol	Product	
		Yield (%)[a]	M_n (M_w/M_n)
C_3F_7 (5.2)	25	37	5240 (1.24)
$CF(CF_3)OC_3F_7$ (5.1)	25	42	4710 (1.26)
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (1.8)	9.0	38	6530 (1.13)
$CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (1.5)	7.4	28	8180 (1.16)

[a]The yield is based on the starting materials [AEM and the decarboxylated peroxide unit (R_F–R_F)].

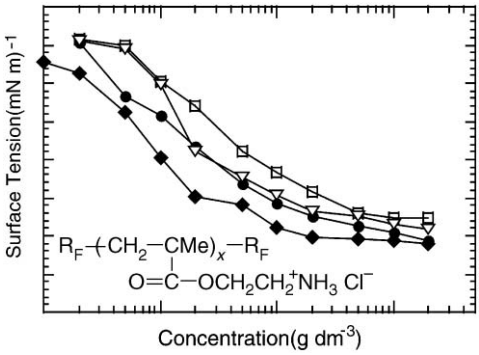


Fig. 1 Surface tension of aqueous solutions of fluoroalkyl end-capped AEM oligomers at 30 °C. □: R_F = C_3F_7; ●: R_F = $CF(CF_3)OC_3F_7$; ▽: R_F = $CF(CF_3)OCF_2CF(CF_3)OC_3F_7$; ◆: R_F = $CF(CF_3)OCF_2$-$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$.

the surface tension of water to around the 18 mN m^{-1} level with a clear break point resembling a CMC (critical micelle concentration). Usually, it is well-known that no CMC or break point resembling a CMC is observed in nonfluorinated polymeric surfactants or randomly fluoroalkylated polymeric surfactants.[11] From this point of view, our present fluorinated AEM homo-oligomers are expected to become new fluorinated cationic oligosurfactants.

Polymeric drugs are well known to possess superior properties, such as high local density of active groups, that set them apart from low-molecular weight analogues.[12] Recently, considerable interest has also been devoted to polycationic biocides, and synthesis and antibacterial activity of numerous polycationic biocides such as polymeric quaternary ammonium salts and phosphonium salts have been reported.[13] However, the exploration of new polycationic biocides possessing unique properties imparted by fluorine such as surface active properties has hitherto been very limited. Therefore, it is very interesting to test our present fluoroalkyl end-capped AEM homo-oligomers for their antibacterial activity. In fact, we investigated the antibacterial activity of these fluorinated AEM homo-oligomers against *S. aureus* and *P. aeruginosa* by the vial cell counting method. About 10^8 cells per ml of *S. aureus* and *P. aeruginosa* were exposed to 1000 μg ml^{-1} (or 100 μg ml^{-1}, or 1 μg ml^{-1}) of the oligomers in saline, and Table 2 shows the colony-forming units (cfu) *versus* exposure of these fluorinated homo-oligomers against *S. aureus* and *P. aeruginosa*.

As shown in Table 2, each fluoroalkyl end-capped AEM homo-oligomer was found to exhibit extremely high antibacterial activity against *S. aureus* and *P. aeruginosa*, and these oligomers are capable of killing the bacterial cells from 10^8 to below 10^3 cfu. In general, all fluoroalkyl end-capped AEM homo-oligomers in Table 2 were active (below 10^3 cfu level) at 100 μg ml^{-1} of oligomer. Of particular interest, R_F–$(AEM)_n$–R_F [R_F = $CF(CF_3)OC_3F_7$] was active (10^4 cfu levels) against *S. aureus* and *P. aeruginosa* even at 1 μg ml^{-1} of oligomer. This finding cannot yet be explained in detail at the present time; however, one thought is that the cationic homo-oligomer with fluoroalkyl segments of moderate length [R_F = $CF(CF_3)OC_3F_7$] is likely to form suitable self-assembled molecular aggregates to interact with negatively charged bacterial cells, and the bacterial cells could act as guest molecules for these aggregates to exhibit high antibacterial activity. In fact, it is well-known that bacterial cell surfaces are negatively charged, and adsorption onto the bacterial cell surface is strongly affected by the effective positive charge density of the cationic species.[14] The compounds, which are capable of killing bacterial cells from 10^8 to 10^5 cfu, are in general considered to possess antibacterial activity. Therefore, our present R_F–$(AEM)_n$–R_F homo-oligomers, especially R_F–$(AEM)_n$–R_F [R_F = $CF(CF_3)OC_3F_7$] is considered to be a new potent fluorinated polymeric biocide. Previously, we reported

Table 2 Antibacterial activity of fluoroalkyl end-capped AEM homo-oligomers against *Staphylococcus aureus* and *Pseudomonas aeruginosa*

	Concentration of oligomer					
R_F in R_F–$(AEM)_n$–R_F	1 mg ml^{-1} *S. aureus*/ cfu ml^{-1}[a]	100 μg ml^{-1}	1 μg ml^{-1}	1 mg ml^{-1} *P. aeruginosa*/ cfu ml^{-1}[a]	100 μg ml^{-1}	1 μg ml^{-1}
Control	2.3×10^8	3.2×10^8	1.7×10^8	1.5×10^8	2.8×10^8	4.5×10^8
$R_F = C_3F_7$	$<1 \times 10^3$	$<1 \times 10^3$	7.8×10^6	$<1 \times 10^3$	$<1 \times 10^3$	3.5×10^6
$R_F = C_3F_7OCF(CF_3)$	$<1 \times 10^3$	$<1 \times 10^3$	6.3×10^6	$<1 \times 10^3$	$<1 \times 10^3$	2.4×10^6
$R_F = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$	$<1 \times 10^3$	$<1 \times 10^3$	1.5×10^6	$<1 \times 10^3$	$<1 \times 10^3$	1.7×10^6
$R_F = C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2OCF(CF_3)$	$<1 \times 10^3$	$<1 \times 10^3$	8.3×10^6	$<1 \times 10^3$	$<1 \times 10^3$	9.7×10^6

[a]cfu indicates colony-forming units.

that fluoroalkyl end-capped oligomers containing allylammonium and diallylammonium segments possess antibacterial activity against *S. aureus* and *P. aeruginosa* to some extent.[7] In contrast, our present fluoroalkyl end-capped AEM homo-oligomers were found to be considerably active polymeric biocides against *S. aureus* and *P. aeruginosa* compared with those of fluorinated allylammonium and diallylammonium oligomers. These results are not clarified in detail at present; however, it is suggested that the ammonium segments in R_F–$(AEM)_n$–R_F are likely to interact sterically with negatively charged bacterial cell surfaces, since ammonium segments are introduced into the AEM oligomer main chains through the ester moieties.

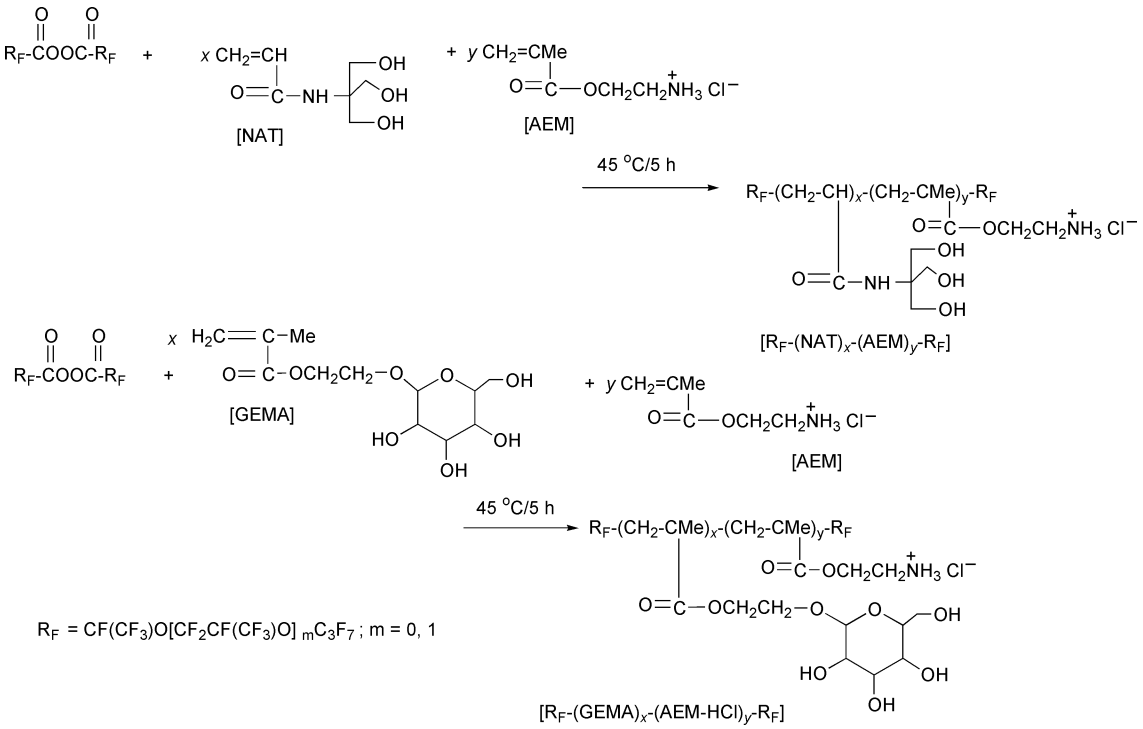
Due to the development of new fluoroalkyl end-capped cationic co-oligomer gels possessing high antibacterial activity, we tried to react fluoroalkanoyl peroxides with AEM and triol-containing monomer [*N*-tris(hydroxymethyl)methylacrylamide: NAT) or tetraol-containing monomer [2-glucosyloxyethyl methacrylate: GEMA] as co-monomer, and the reaction (Scheme 2) is as follows.

As shown in Scheme 2, the co-oligomerizations of fluoroalkanoyl peroxides with NAT (or GEMA) and AEM were found to proceed under mild conditions to afford the corresponding fluoroalkyl end-capped NAT–AEM or GEMA–NAT co-oligomers, respectively. The results for these co-oligomerizations are summarized in Table 3.

As shown in Table 3, a variety of perfluorooxaalkyl end-capped NAT–AEM and GEMA–AEM co-oligomers were obtained in 8–59% isolated yields.

Interestingly, fluoroalkyl end-capped NAT–GEMA and GEMA–AEM co-oligomers thus obtained were found to cause gelation in water and dimethyl sulfoxide (DMSO), although these co-oligomers were not soluble at all in other common organic solvents such as methanol, ethanol, tetrahydrofuran, chloroform, acetone, *N*,*N*-dimethylformamide, and a mixed fluorinated solvent (1 : 1 mixture of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane). We tried to measure the co-oligomerization ratios and the molecular weights of these fluorinated co-oligomers by using NMR and GPC (gel permeation chromatography) analyses, respectively; however, we failed to measure the ratios and the molecular weights owing to the gel formation. We have already reported that fluoroalkyl end-capped NAT homo-oligomers can cause gelation, where the aggregations of end-capped fluoroalkyl segments and hydrogen-bonding interaction are involved in establishing a physical gel network in water.[15] Thus, it is suggested that our present fluorinated NAT–AEM and GEMA–AEM co-oligomers should cause gelation as do fluorinated NAT homo-oligomers.

However, co-oligomers nos 3–7 in Table 3 caused no gelation in water and DMSO, and these fluorinated co-oligomers



Scheme 2

Table 3 Reactions of fluoroalkanoyl peroxides with NAT (or GEMA) and AEM

No	R_F in peroxide (mmol)	NAT or GEMA/ mmol NAT	AEM/mmol	Product		
				Yield[a] (%)	$x : y$[b]	$M_n(M_w/M_n)$
1	$C_3F_7OCF(CF_3)$ (2)	12	6	46	—[c]	—[c]
2	$C_3F_7OCF(CF_3)$ (3)	10	19	35	—	—
3	$C_3F_7OCF(CF_3)$ (1)	3	16	33	25 : 75	5160 (1.19)
4	$C_3F_7OCF(CF_3)$ (2)	3	16	35	18 : 82	5380 (1.17)
5	$C_3F_7OCF(CF_3)$ (2)	2	16	54	13 : 87	3620 (1.37)
6	$C_3F_7OCF(CF_3)$ (1)	2	16	32	12 : 88	2730 (1.25)
7	$C_3F_7OCF(CF_3)$ (0.8)	2	16	16	10 : 90	2990 (1.35)
8	$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$ (2)	3	10	8	—	—
9	$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$ (2)	5	10	20	—	—
		GEMA				
10	$C_3F_7OCF(CF_3)$ (2)	12	6	24	—	—
11	$C_3F_7OCF(CF_3)$ (2)	6	6	50	—	—
12	$C_3F_7OCF(CF_3)$ (3)	6	32	36	—	—
13	$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$ (2)	6	12	37	—	—
14	$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$ (2)	4	20	59	—	—

[a]The yields are based on the starting materials [NAT (or GEMA), AEM] and the decarboxylated peroxide unit (R_F–R_F). [b]Co-oligomerization was determined by ^{1}H-NMR. [c]NMR and GPC were not measured due to gelation.

became soluble in these solvents. Thus, we could measure the co-oligomerization ratios and the molecular weights of these co-oligomers by ^{1}H NMR and GPC [eluent: 5 mmol dm^{-3} tris(hydroxymethyl)aminomethane–HCl buffer (pH 7.4) solution] analyses, and the co-oligomerization ratios ($x : y$) and the molecular weights (M_n) of these co-oligomers were 10–25 : 75–90 and 2730–5380, respectively, as shown in Table 3. This would be because, as the co-oligomerization ratio (x) of R_F–$(NAT)_x$–$(AEM)_y$–R_F decreases (below 25%), hydrogen-bonding interactions between hydroxy segments in co-oligomers which cause gelation should be decreased, and these co-oligomers become soluble in water and DMSO. In contrast, each fluoroalkyl end-capped GEMA–AEM co-oligomer in Table 3 caused gelation in water and DMSO. These findings would result from the fact that the intermolecular hydrogen bonding interaction between hydroxy segments in R_F–$(GEMA)_x$–$(AEM)_y$–R_F could interact more strongly with the aggregations of end-capped fluoroalkyl segments to cause gelation, compared with those of R_F–$(NAT)_x$–$(AEM)_y$–R_F. Thus, in fluoroalkyl end-capped NAT–AEM co-oligomers, solvation should be preferred to gel formation due to the relatively weak hydrogen-bonding interaction between triol segments.

The gelation abilities of fluoroalkyl end-capped NAT–AEM and GEMA–AEM co-oligomers were studied by measuring the minimum concentration (C_{min}) of these co-oligomers necessary for gelation in water and DMSO at 30 °C according to the method reported by Hanabusa *et al.*,[16] and the results are summarized in Table 4.

As shown in Table 4, C_{min} values of a series of fluoroalkyl end-capped NAT–AEM and GEMA–AEM co-oligomers necessary to gel one litre of water–DMSO were 19–560 g dm^{-3}. In general, co-oligomers with greater molar ratios of NAT (No. 1) or GEMA (No. 10)–AEM exhibited higher gelling ability. This finding suggests that the main driving force for gelation is the synergistic interactions with the aggregations of end-capped fluoroalkyl segments in co-oligomers and intermolecular hydrogen bonding between hydroxy segments in NAT or GEMA in co-oligomers, and in particular, hydrogen bonding interactions between hydroxy segments in fluorinated co-oligomers can participate strongly in the gelator which is constructed by the aggregations of end-capped fluoroalkyl segments.

Furthermore, some fluoroalkyl end-capped AEM co-oligomers in Table 3 were tested for antibacterial activity against *S. aureus* and *P. aeruginosa* by the viable cell counting method. About 10^8 cells per ml of *S. aureus* or *P. aeruginosa* were exposed to 1 mg ml^{-1} or 100 μg ml^{-1} of the fluorinated AEM co-oligomers in saline, and Table 5 shows the colony forming units *versus* exposure of these fluorinated co-oligomers against *S. aureus* and *P. aeruginosa*.

As shown in Table 5, our present fluoroalkyl end-capped NAT–AEM and GEMA–AEM co-oligomers were found to exhibit high antibacterial activity against *S. aureus* and *P. aeruginosa* (<10 colony forming unit levels at 1 mg ml^{-1} of co-oligomers). More interestingly, these fluorinated AEM co-oligomers were also active against *S. aureus* and *P. aeruginosa* even at 100 μg ml^{-1} of co-oligomers, and were capable of killing the bacterial cells from levels of 10^8 to <10 cfu. Therefore, it was demonstrated that our present

Table 4 Critical gel concentration (C_{min}) of R_F–$(NAT)_x$–$(AEM)_y$–R_F and R_F–$(GEMA)_x$–$(AEM)_y$–R_F

No[a]	R_F in co-oligomer	C_{min}/g dm^{-3} at 30 °C	
		H_2O	DMSO
		R_F–$(NAT)_x$–$(AEM)_y$–R_F	
1	$C_3F_7OCF(CF_3)$	19	44
2	$C_3F_7OCF(CF_3)$	267	115
3	$C_3F_7OCF(CF_3)$	Soluble	Soluble
4	$C_3F_7OCF(CF_3)$	Soluble	Soluble
5	$C_3F_7OCF(CF_3)$	Soluble	Soluble
6	$C_3F_7OCF(CF_3)$	Soluble	Soluble
7	$C_3F_7OCF(CF_3)$	Soluble	Soluble
8	$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$	129	49
9	$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$	124	173
		R_F–$(GEMA)_x$–$(AEM)_Y$–R_F	
10	$C_3F_7OCF(CF_3)$	129	49
11	$C_3F_7OCF(CF_3)$	267	115
12	$C_3F_7OCF(CF_3)$	470	289
13	$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$	124	173
14	$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$	560	543

[a]Different from those in Table 3.

Table 5 Antibacterial activity of fluoroalkyl end-capped AEM co-oligomers against *Staphylococcus aureus* and *Pseudomonas aeruginosa*

		Concentration of oligomer			
No[a]	Co-oligomer	1 mg ml^{-1} *S. aureus*/ cfu ml^{-1}[b]	100 μg ml^{-1}	1 mg ml^{-1} *P. aeruginosa*/ cfu ml^{-1}[a]	100 μg ml^{-1}
	Control	3.4×10^8	2.2×10^8	3.8×10^8	3.5×10^8
R_F–$(NAT)_x$–$(AEM)_y$–R_F					
3	$R_F = C_3F_7OCF(CF_3)$	<10	90	<10	50
4	$R_F = C_3F_7OCF(CF_3)$	<10	240	<10	50
5	$R_F = C_3F_7OCF(CF_3)$	<10	110	<10	60
6	$R_F = C_3F_7OCF(CF_3)$	<10	90	<10	50
R_F–$(GEMA)_x$–$(AEM)_y$–R_F					
14	$R_F = C_3F_7COF(CF_3)CF_2OCF(CF_3)$	360	1100	<10	<10

[a]All different from those of Table 3. [b]Cfu indicates colony-forming units.

fluorinated NAT– and GEMA–AEM co-oligomers are attractive functional materials because of their gelling ability and high antibacterial activity.

In this way, our present fluorinated AEM co-oligomers were clarified to have a good gelling ability. In our present fluorinated cationic co-oligomer gels, it is expected that the ionic repulsion between the cationic segments in co-oligomers and lithium ions could be the cause of the high ionic conductivity. Thus, we applied these fluorinated gelling AEM co-oligomers to new cationic gelling fluorinated polymer electrolytes. Gelling fluorinated NAT–and GEMA–AEM co-oligomers were formed by heating DMSO solutions of the co-oligomers and lithium salt at 30 °C under ultrasonic conditions. The ionic conductivities [σ (S cm^{-1})] in fluorinated co-oligomer gels in the presence of lithium salts were measured by an AC impedance method at room temperature, and the results are shown in Table 6.

As shown in Table 6, fluoroalkyl end-capped NAT–and GEMA–AEM co-oligomer gels in the presence of lithium ions [2.7 mmol g^{-1} (co-oligomer)] were found to exhibit high ionic conductivities of 10^{-3} S cm^{-1} levels. Especially, fluorinated NAT–AEM co-oligomer gels exhibited a slightly higher ionic conductivity than that of the corresponding GEMA–AEM co-oligomer gels.

In conclusion, we succeeded in preparing a variety of water-soluble fluoroalkyl end-capped AEM homo-oligomers by the reactions of fluoroalkanoyl peroxides with the corresponding monomer (AEM) under very mild conditions. The fluorinated AEM homo-oligomers obtained were applied to new fluorinated cationic oligosurfactants possessing a high antibacterial activity. In particular, we succeeded in preparing a variety of fluoroalkyl end-capped NAT–and GEMA–AEM co-oligomers by the use of fluoroalkanoyl peroxide as a key intermediate. Interestingly, these fluorinated AEM co-oligomers could cause gelation in water and DMSO under non-crosslinked conditions and exhibited similarly high antibacterial activity to that of the corresponding fluorinated AEM homo-oligomers. Additionally, it was clarified that these fluorinated co-oligomer gels are applicable to new fluorinated cationic gelling polymer electrolytes possessing a high ionic conductivity.

Table 6 Ionic conductivity (σ/S cm^{-1}) of fluoroalkyl end-capped NAT–and GEMA–AEM co-oligomer gels in the presence of $LIN(CF_3SO_2)_2$ [2.7 mmol g^{-1} (co-oligomer) at room temperature]

No[a]	Co-oligomer	σ/S cm^{-1}
R_F–$(NAT)_x$–$(AEM)_y$–R_F		
1	$R_F = CF(CF_3)OC_3F_7$	4.3×10^{-3}
2	$R_F = CF(CF_3)OC_3F_7$	4.6×10^{-3}
R_F–$(GEMA)_x$–$(AEM)_y$–R_F		
10	$R_F = CF(CF_3)OC_3F_7$	3.0×10^{-3}
13	$R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	3.7×10^{-3}

[a]Different from those in Table 3.

Experimental

Fourier-transform infrared (FTIR) spectra were measured using a Shimadzu FTIR-8400 spectrophotometer. NMR spectra were measured using a Varian Unity-plus 500 (500 MHz) spectrometer and molecular weights were measured using a Shodex DS-4 (pump) and Shodex RI-71 (detector) gel permeation chromatography (GPC) calibrated with standard poly(ethylene glycol) using 0.2 mol dm^{-3} Na_2HPO_4 solution [or 5 mmol dm^{-3} tris(hydroxymethyl)aminomethane–HCl buffer (pH 7.4) solution] as the eluent. The ionic conductivities were determined by AC impedance measurement using a Hi Tester HIOKI-3520.

Materials

2-Aminoethyl methacrylate hydrochloride (AEM) and *N*-tris(hydroxymethyl)methylacrylamide were purchased from Acros Organics Inc. 2-Glucosyloxyethyl methacrylate (GEMA) was used as received from Nippon Fine Chemical Co. Ltd. (Hyogo, Japan). $(CF_3SO_2)_2NLi$ was purchased from Kishida Chemical Co., Ltd. (Osaka, Japan). A series of fluoroalkanoyl peroxides [$(R_FCOO)_2$] were prepared by the methods described in the literature.[17,18]

General procedure for the synthesis of fluoroalkyl end-capped AEM homo-oligomers

Perfluoro-2-methyl-3-oxahexanoyl peroxide (5.1 mmol) in a 1 : 1 mixture (AK-225) of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane (120 g) was added to an aqueous solution (50%, w/w) of AEM (25 mmol). The heterogeneous solution was stirred vigorously at 45 °C for 5 h under nitrogen. After evaporating the solvent, the crude products obtained were reprecipitated from the methanol–acetone system to give an α,ω-bis(perfluoro-1-methyl-2-oxapentylated) 2-aminoethyl methacrylate hydrochloride oligomer (2.96 g). This oligomer exhibited the following spectral characteristics: IR (cm^{-1}) 3100 (NH_3^+), 1728 (C=O), 1310 (CF_3), 1238 (CF_2); ^{1}H NMR (D_2O) δ 0.52–1.70 (CH_3, CH_2), 3.15–3.37 (CH_2), 3.95–4.50 (CH_2); ^{19}F NMR (D_2O, ext. CF_3COOH) δ −5.64 to −8.02 (16F), −52.99 to −54.10 (6F).

Similarly, a series of fluoroalkyl end-capped AEM homo- and co-oligomers were prepared by the reactions with fluoroalkanoyl peroxides. These exhibited the following spectral characteristics:

C_3F_7–$(AEM)_n$–C_3F_7: IR (cm^{-1}) 3428 (NH_3^+), 1728 (C=O),

1315 (CF_3), 1232 (CF_2); ^{1}H NMR (D_2O) δ 0.60–1.68 (CH_3, CH_2), 3.17–3.44 (CH_2), 4.00–4.42 (CH_2); ^{19}F NMR (D_2O, ext. CF_3COOH) δ −5.48 (6F), −42.94 (4F), −52.05 (4F).

$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$–$(AEM)_n$–$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$: IR($cm^{-1}$) 3480 ($NH_3^+$), 1728 (C=O), 1310 ($CF_3$), 1240 ($CF_2$); ^{1}H NMR ($D_2O$) δ 0.63–1.71(CH_3, CH_2), 3.13–3.43 (CH_2), 3.95–4.40 (CH_2); ^{19}F NMR (D_2O, ext. CF_3COOH) δ −5.56 to −11.06 (26F), −56.18 to −62.05 (6F), −71.06 (2F).

$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2OCF(CF_3)$–$(AEM)_n$–$CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$: IR ($cm^{-1}$) 3450 ($NH_3^+$), 1730 (C=O), 1302 ($CF_3$), 1242 ($CF_2$). ^{1}H NMR ($D_2O$) δ 0.65–1.70 (CH_3, CH_2), 3.14–3.40 (CH_2), 4.02–4.44 (CH_2); ^{19}F NMR (D_2O, ext. CF_3COOH) δ −4.29 to −8.21 (36F), −56.26 (6F), −69.58 to −71.11 (4F).

No 1 in Table 3: $C_3F_7OCF(CF_3)$–$(NAT)_x$–$(AEM)_y$–$CF(CF_3)OC_3F_7$: IR (cm^{-1}) 3450 (OH, NH_3^+), 1728, 1648 (C=O), 1320 (CF_3), 1240 (CF_2).

No 2 in Table 3: $C_3F_7OCF(CF_3)$–$(NAT)_x$–$(AEM)_y$–$CF(CF_3)OC_3F_7$: IR (cm^{-1}) 3410 (OH, NH_3^+), 1726, 1641 (C=O), 1310 (CF_3), 1220 (CF_2).

No 3 in Table 3: $C_3F_7OCF(CF_3)$–$(NAT)_x$–$(AEM)_y$–$CF(CF_3)OC_3F_7$: IR (cm^{-1}) 3444 (OH, NH_3^+), 1725, 1647 (C=O), 1310 (CF_3), 1240 (CF_2). ^{1}H NMR (D_2O) δ 0.52–1.22 (CH_2, CH_3), 1.38–2.41 (CH), 3.05–3.19 (CH_2), 3.38–3.72 (CH_2), 3.91–4.40 (CH_2); ^{19}F NMR (D_2O, ext. CF_3COOH) δ −10.97 to −13.07 (16F), −58.35 to −59.57 (6F).

No 4 in Table 3: $C_3F_7OCF(CF_3)$–$(NAT)_x$–$(AEM)_y$–$CF(CF_3)OC_3F_7$: IR (cm^{-1}) 3445 (OH, NH_3^+), 1724, 1632 (C=O), 1310 (CF_3), 1245 (CF_2). ^{1}H NMR (D_2O) δ 0.52–1.22 (CH_2, CH_3), 1.33–2.40 (CH), 3.09–3.41 (CH_2), 3.45–3.78 (CH_2), 3.85–4.41 (CH_2); ^{19}F NMR (D_2O, ext. CF_3COOH) δ −10.94 to −13.05 (16F), −58.35 to −59.21 (6F).

No 5 in Table 3: $C_3F_7OCF(CF_3)$–$(NAT)_x$–$(AEM)_y$–$CF(CF_3)OC_3F_7$: IR (cm^{-1}) 3429 (OH, NH_3^+), 1720, 1636 (C=O), 1308 (CF_3), 1238 (CF_2). ^{1}H NMR (D_2O) δ 0.59–1.25 (CH_2, CH_3), 1.41–2.42 (CH), 3.14–3.45 (CH_2), 3.60–3.88 (CH_2), 3.95–4.42 (CH_2); ^{19}F NMR (D_2O, ext. CF_3COOH) δ −10.94 to −12.86 (16F), −58.48 to −59.21 (6F).

No 6 in Table 3: $C_3F_7OCF(CF_3)$–$(NAT)_x$–$(AEM)_y$–$CF(CF_3)OC_3F_7$: IR (cm^{-1}) 3445 (OH, NH_3^+), 1717, 1636 (C=O), 1300 (CF_3), 1242 (CF_2). ^{1}H NMR (D_2O) δ 0.70–1.22 (CH_2, CH_3), 1.40–2.40 (CH), 3.15–3.42 (CH_2), 3.59–3.68 (CH_2), 3.98–4.39 (CH_2); ^{19}F NMR (D_2O, ext. CF_3COOH) δ −10.94 to −12.84 (16F), −58.35 to −59.21 (6F).

No 7 in Table 3: $C_3F_7OCF(CF_3)$–$(NAT)_x$–$(AEM)_y$–$CF(CF_3)OC_3F_7$: IR (cm^{-1}) 3452 (OH, NH_3^+), 1724, 1628 (C=O), 1300 (CF_3), 1243 (CF_2). ^{1}H NMR (D_2O) δ 0.62–1.21 (CH_2, CH_3), 1.18–2.32 (CH), 3.14–3.39 (CH_2), 3.58–3.71 (CH_2), 3.90–4.38 (CH_2); ^{19}F NMR (D_2O, ext. CF_3COOH) δ −9.26 to −12.84 (16F), −57.60 to −58.53 (6F).

No 8 in Table 3: $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$–$(NAT)_x$–$(AEM)_y$–$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$: IR ($cm^{-1}$) 3442 (OH, NH_3^+), 1724, 1631 (C=O), 1270 (CF_3), 1238 (CF_2).

No 9 in Table 3: $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$–$(NAT)_x$–$(AEM)_y$–$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$: IR ($cm^{-1}$) 3442 (OH, NH_3^+), 1728, 1641 (C=O), 1265 (CF_3), 1240 (CF_2).

No 10 in Table 3: $C_3F_7OCF(CF_3)$–$(GEMA)_x$–$(AEM)_y$–$CF(CF_3)OC_3F_7$: IR (cm^{-1}) 3480 (OH, NH_3^+), 1718, 1639 (C=O), 1305 (CF_3), 1275 (CF_2).

No 11 in Table 3: $C_3F_7OCF(CF_3)$–$(GEMA)_x$–$(AEM)_y$–$CF(CF_3)OC_3F_7$: IR (cm^{-1}) 3450 (OH, NH_3^+), 1724, 1635 (C=O), 1300 (CF_3), 1244 (CF_2).

No 12 in Table 3: $C_3F_7OCF(CF_3)$–$(GEMA)_x$–$(AEM)_y$–$CF(CF_3)OC_3F_7$: IR (cm^{-1}) 3420 (OH, NH_3^+), 1726, 1623 (C=O), 1310 (CF_3), 1277 (CF_2).

No 13 in Table 3: $C_3F_7OCF(CF_3)$–$(GEMA)_x$–$(AEM)_y$–$CF(CF_3)OC_3F_7$: IR (cm^{-1}) 3450 (OH, NH_3^+), 1715, 1639 (C=O), 1279 (CF_3), 1249 (CF_2).

No 14 in Table 3: $C_3F_7OCF(CF_3)$–$(GEMA)_x$–$(AEM)_y$–$CF(CF_3)OC_3F_7$: IR (cm^{-1}) 3474 (OH, NH_3^+), 1720, 1624 (C=O), 1269 (CF_3), 1246 (CF_2).

A typical procedure for gelation test

A procedure for studying the gel-formation ability was based on a method reported by Hanabusa *et al.*[16] Briefly, weighed fluoroalkyl end-capped GEMA copolymer was mixed with DMSO in a tube. The mixture was treated under ultrasonic conditions until the solid was dissolved. The resulting solution was kept at 30 °C for 1 h, and gelation was checked visually. The gel was stable and the tube could be inverted without changing the shape of the gel.

Ionic conductivity measurements

The ionic conductivities of fluorinated gel electrolytes were determined by AC impedance measurement between 40 Hz and 100 kHz using a Hi Tester HIOKI-3520. Fluorinated gels (0.98 cm in diameter) were sandwiched between two copper electrodes in a sealed cell under a dry argon atmosphere. Measurements were carried out over room temperature. Bulk resistance was derived from the Cole–Cole plot of the complex impedance data of the fluorinated gel where the imaginary impedance is zero. Conductivity was calculated from the bulk resistance according to the following equation:

$$\sigma = D/A \times R_b$$

where σ is conductivity, D is the thickness of the sample, A is the section area of the sample, and R_b is bulk resistance.

Surface tension measurements

The surface tensions of aqueous solutions of the fluoroalkyl end-capped AEM homo-oligomers were measured at 30 °C using a Wilhelmy-type surface tensiometer (ST-1, Shimadzu) with a glass plate.

Antibacterial assessment

The antibacterial activity of the oligomers were evaluated against *S. aureus* and *P. aeruginosa* by viable cell counting method as described previously.[5,6b,7c]

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