

Synthesis and Properties of Fluoroalkyl End-Capped Sulfobetaine Polymers

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ABSTRACT: A variety of fluoroalkyl end-capped 3-[N-(3-acrylamido)propyl-N,N-dimethylammonio]propanesulfonate polymers [R_F-(APDAPS)_n-R_F] were prepared by the reactions of fluoroalkanoyl peroxides with the corresponding monomer under very mild conditions. Similarly, fluoroalkyl end-capped 2-vinylpyridinio propane sulfonate polymer was obtained by the use of fluoroalkanoyl peroxide. These fluoroalkyl end-capped sulfobetaine polymers exhibited a good solubility in water; however, these polymers have a poor solubility in other solvents. In particular, R_F-(APDAPS)_n-R_F polymers caused gelation in methanol, although R_F-(VPPA)_n-R_F polymer showed no gelation in methanol. R_F-(APDAPS)_n-R_F polymers were found to form the self-assembled molecular aggregates with the aggregations of the end-capped fluoroalkyl segments and the ionic interac-

tions between sulfobetaine segments in aqueous solutions. On the other hand, it was suggested that R_F-2-vinylpyridinio propane sulfonate (VPPS)_n-R_F polymer is not likely to form the self-assemblies in aqueous solutions because of the steric hindrance of pyridiniopropyl betaine units in polymer. We also studied the surfactant properties of R_F-(APDAPS)_n-R_F and R_F-(VPPS)_n-R_F polymers compared with those of other fluoroalkyl end-capped betaine-type polymers such as 2-acrylamido-2-methylpropanesulfonic acid polymers and 2-(3-acrylamidopropyl)dimethylammonio ethanoate polymers. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1144–1153, 2004

Key words: fluoropolymers; gelation; gel permeation chromatography (GPC); self-assembly; surfactant

INTRODUCTION

There has been a great interest in poly(betaine)s that contain both a positive and a negative charge on every monomer residue with respect to their unique applications to various fields.¹ For example, Laschewsky et al.² reported on the surfactant properties of a series of permanently zwitterionic monomers and polymers based on sulfobetaines. Considerable interest has also been focused in recent years on partially fluoroalkylated polysoaps, which exhibit a wide variety of unique properties such as high dispersing, aggregate, and emulsion properties, although the corresponding low molecular weight surfactants do not exhibit such unique properties.³ Thus, it is very interesting to develop partially fluoroalkylated betaine-type polysoaps

possessing unique properties imparted by fluorine. From this standpoint, we previously reported that fluoroalkyl end-capped 2-acrylamido-2-methylpropanesulfonic acid polymers can cause a gelation derived from the synergistic interaction of the aggregation of fluoroalkyl groups and the ionic interaction of the betaine segments under noncrosslinked conditions.⁴ In view of the development of novel partially fluorinated polysoaps, we investigated the synthesis and properties of novel fluoroalkyl end-capped sulfobetaine polymers, and report the results in this article.

EXPERIMENTAL

Measurements

FTIR spectra were measured using a Horiba FT-300 FTIR spectrophotometer (Kyoto, Japan). NMR spectra and molecular weights were measured using a Varian Unity-plus 500 (500 MHz) spectrometer (Varian Associates, Palo Alto, CA) and a Shodex DS-4 (pump) and

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TABLE I
Reactions of Fluoroalkanoyl Peroxides with APDAPS

No.	R _F in (R _F CO ₂) ₂	(R _F CO ₂) ₂ (mmol)	APDAPS (mmol)	R _F -(APDAPS) _n -R _F	
				Yield ^a (%)	M _n (M _w /M _n) ^b
1	C ₃ F ₇	4.4	13.1	64	19500 (1.93)
2		1.1	10.9	79	25100 (1.73)
3		0.7	13.1	78	22500 (1.80)
4	C ₃ F ₇ OCF(CF ₃)	3.3	10.0	95	27900 (1.64)
5		0.8	8.4	71	32000 (2.19)
6		0.5	10.1	96	15200 (2.17)
7	C ₃ F ₇ OCF(CF ₃)CF ₂ OCF(CF ₃)	1.4	4.1	36	18500 (1.95)
8		0.6	6.2	60	20500 (1.97)
9		0.4	8.2	73	10000 (1.96)
10	C ₃ F ₇ OCF(CF ₃)CF ₂ OCF(CF ₃)CF ₂ OCF(CF ₃)	1.0	3.0	40	19800 (1.87)
11		0.9	9.4	56	32200 (1.86)
12		0.4	8.8	86	14800 (2.73)
13	C ₃ F ₇ OCF(CF ₃)CF ₂ OCF(CF ₃)CF ₂ OCF(CF ₃)CF ₂ OCF(CF ₃)	0.4	1.1	25	26100 (1.84)

^a The yields are based on the starting materials: APDAPS and the decarboxylated peroxide unit (R_F-R_F).

^b The molecular weights were calculated based on GPC by using 0.1M NaNO₃ as the eluent at 30°C.

Shodex RI-71 (detector) gel permeation chromatography (GPC, Tokyo, Japan) calibrated with standard pullulan using 0.1M (or 0.5M) NaNO₃ solution as the eluent [or water (distilled water that was passed through ion-exchange resin) as the eluent], respectively. The surface tensions of aqueous solutions of the fluoroalkyl end-capped polymers were measured at 30°C using a Wilhelmy-type surface tensiometer (ST-1; Shimadzu, Kyoto, Japan) with a glass plate. Static light scattering of polymer solutions was measured using Wyatt DAWN DSP and NICOMP 380ZSL particle-sizing systems (California). Solution viscosities were measured by using a falling-sphere Haake viscometer D1-G (Haake, Bersdorff, Germany).

Materials

A series of fluoroalkanoyl peroxides [(R_FCOO)₂] were prepared by the method described in the literature.⁶ 3-[N-(3-Acrylamido)propyl-N,N-dimethylammonio]propanesulfonate (APDAPS) was prepared by the reaction of (3-acrylamidopropyl)dimethylamine (Kojin, Japan) with 1,3-propanesultone in tetrahydrofuran according to published procedures.^{1(b),(c)} 2-Vinylpyridinio propane sulfonate (VPPS) was purchased from Monomer-Polymer and Dajac Laboratories, Inc. (Pennsylvania).

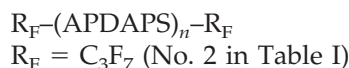
General procedure for the synthesis of fluoroalkyl end-capped APDAPS polymers

Perfluorobutyryl peroxide (4.4 mmol) in 1 : 1 mixed solvents (AK-225) of 1,1-dichloro-2,2,3,3,3-pentaflu-

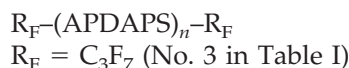
oropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane (100 g) was added to an aqueous solution (50%, w/w) of APDAPS (13.1 mmol). The heterogeneous solution was stirred vigorously at 45°C for 5 h under nitrogen. After evaporating the solvent, the crude product obtained was reprecipitated from water-acetone to give an α,ω -bis(perfluoropropylated) APDAPS polymer (No. 1 in Table I: 3.27 g).

This polymer exhibited the following spectra characteristics: IR (ν /cm⁻¹) 3430 (NH), 1650 [C(=O)], 1390 (CF₃), 1230 (CF₂), 1190 (SO₃⁻); ¹H-NMR (D₂O) δ 1.20–2.22 (CH₂, CH), 2.78–3.44 (CH₂, CH₃); ¹⁹F-NMR (D₂O, ext. CF₃CO₂H) δ -7.82 (6F), -45.54 (4F), -54.62 (4F).

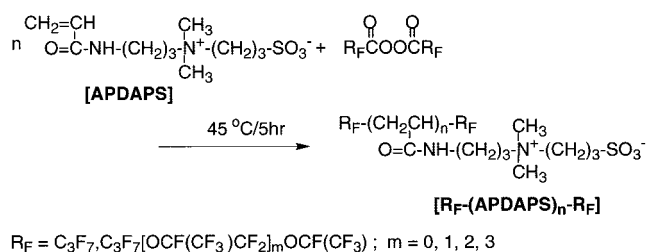
The other products obtained exhibited the following spectral characteristics:



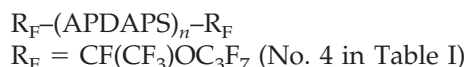
IR (ν /cm⁻¹) 3450 (NH), 1670 [C(=O)], 1320 (CF₃), 1230 (CF₂), 1190 (SO₃⁻); ¹H-NMR (D₂O) δ 1.11–2.19 (CH₂, CH), 2.59–3.51 (CH₂, CH₃); ¹⁹F-NMR (D₂O, ext. CF₃CO₂H) δ -5.58 (6F), -43.09 (4F), -52.00 (4F).



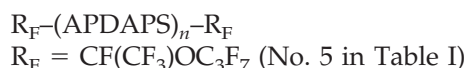
IR (ν /cm⁻¹) 3460 (NH), 1650 [C(=O)], 1380 (CF₃), 1200 (CF₂), 1190 (SO₃⁻); ¹H-NMR (D₂O) δ 1.08–2.10 (CH₂, CH), 2.61–3.46 (CH₂, CH₃); ¹⁹F-NMR (D₂O, ext. CF₃CO₂H) δ -5.58 (6F), -43.10 (4F), -52.18 (4F).



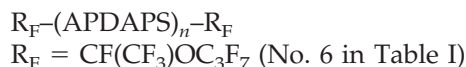
Scheme 1



IR (ν/cm^{-1}) 3460 (NH), 1650 [C(=O)], 1390 (CF₃), 1200 (CF₂), 1040 (SO₃⁻); ¹H-NMR (D₂O) δ 1.24–2.22 (CH₂, CH), 2.62–3.68 (CH₂, CH₃).



IR (ν/cm^{-1}) 3460 (NH), 1650 [C(=O)], 1310 (CF₃), 1205 (CF₂), 1039 (SO₃⁻); ¹H-NMR (D₂O) δ 0.98–2.18 (CH₂, CH), 2.51–3.48 (CH₂, CH₃).



IR (ν/cm^{-1}) 3460 (NH), 1650 [C(=O)], 1310 (CF₃), 1205 (CF₂), 1039 (SO₃⁻); ¹H-NMR (D₂O) δ 1.02–2.29 (CH₂, CH), 2.72–3.63 (CH₂, CH₃).



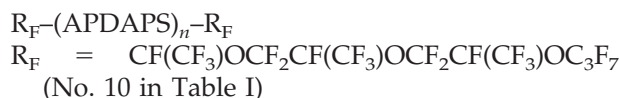
IR (ν/cm^{-1}) 3524 (NH), 1650 [C(=O)], 1315 (CF₃), 1210 (CF₂), 1040 (SO₃⁻); ¹H-NMR (D₂O) δ 1.20–2.30 (CH₂, CH), 2.62–3.51 (CH₂, CH₃); ¹⁹F-NMR (D₂O, ext. CF₃COOH) δ -5.82 to -8.62 (26F), -53.82 to -54.65 (6F), -78.72 (2F).



IR (ν/cm^{-1}) 3460 (NH), 1657 [C(=O)], 1310 (CF₃), 1200 (CF₂), 1038 (SO₃⁻); ¹H-NMR (D₂O) δ 0.96–2.21 (CH₂, CH), 2.51–3.52 (CH₂, CH₃).



IR (ν/cm^{-1}) 3468 (NH), 1653 [C(=O)], 1308 (CF₃), 1207 (CF₂), 1039 (SO₃⁻); ¹H-NMR (D₂O) δ 0.98–2.20 (CH₂, CH), 2.58–3.46 (CH₂, CH₃).



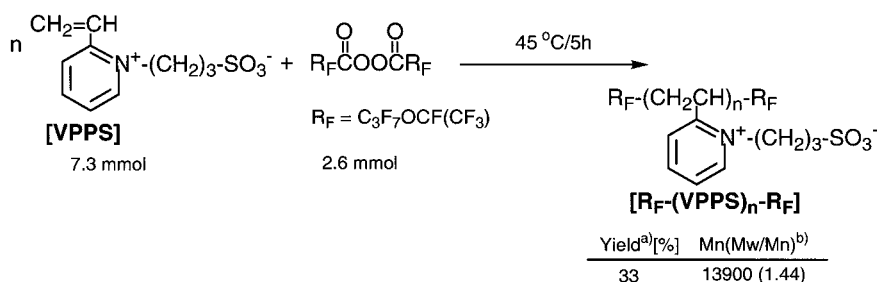
IR (ν/cm^{-1}) 3490 (NH), 1660 [C(=O)], 1310 (CF₃), 1240 (CF₂), 1040 (SO₃⁻); ¹H-NMR (D₂O) δ 1.00–2.22 (CH₂, CH), 2.59–3.54 (CH₂, CH₃); ¹⁹F-NMR (D₂O, ext. CF₃COOH) δ -4.65 to -8.57 (36F), -53.52 (6F), -67.16 to -72.54 (4F).



IR (ν/cm^{-1}) 3467 (NH), 1650 [C(=O)], 1308 (CF₃), 1235 (CF₂), 1050 (SO₃⁻); ¹H-NMR (D₂O) δ 0.98–2.12 (CH₂, CH), 2.52–3.52 (CH₂, CH₃); ¹⁹F-NMR (D₂O, ext. CF₃COOH) δ -4.60 to -9.06 (36F), -54.57 to -56.52 (6F), -67.19 to -78.92 (4F).



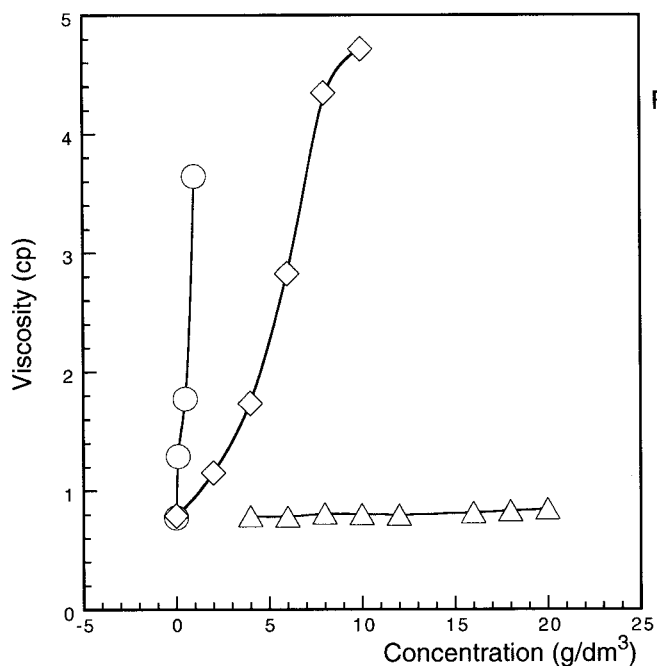
IR (ν/cm^{-1}) 3490 (NH), 1670 [C(=O)], 1305 (CF₃), 1220 (CF₂), 1090 (SO₃⁻); ¹H-NMR (D₂O) δ 0.91–2.29 (CH₂, CH), 2.53–3.59 (CH₂, CH₃); ¹⁹F-NMR (D₂O, ext. CF₃COOH) δ



a) The yield is based on the starting material (VPPS) and the decarboxylated peroxide unit (R_F-R_F).

b) The molecular weight was calculated based on GPC by using 0.1M NaNO₃ as the eluent at 30°C.

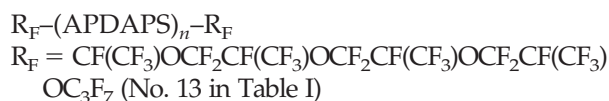
Scheme 2



- : R_F-(AMPS)_n-R_F (see Ref. 4b)
 ◇: R_F-(APDMAE)_n-R_F (see Ref. 5)
 △: R_F-(APDAPS)_n-R_F (No 10 in Table 1)
 R_F = C₃F₇OCF(CF₃)CF₂OCF(CF₃)CF₂OCF(CF₃)

Figure 1 Effect of concentration on viscosity of fluoroalkyl end-capped betaine-type polymers measured at 30°C by using a falling-sphere viscometer.

-5.32 to -7.71 (36F), -52.75 to -54.60 (6F), -73.00 to -83.00 (4F).



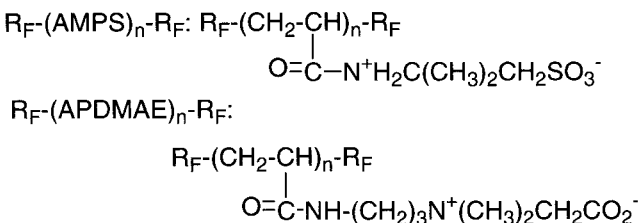
IR (ν/cm^{-1}) 3532 (NH), 1650 [C(=O)], 1310 (CF₃), 1210 (CF₂), 1049 (SO₃⁻); ¹H-NMR (D₂O) δ 1.21-2.22 (CH₂, CH), 2.71-3.51 (CH₂, CH₃); ¹⁹F-NMR (D₂O, ext. CF₃COOH) δ -5.32 to -7.71 (46F), -52.75 to -54.60 (6F), -73.00 to -83.00 (6F).



IR (ν/cm^{-1}) 1380 (CF₃), 1200 (CF₂), 1040 (SO₃⁻); ¹H-NMR (D₂O) δ 0.68-3.45 (CH₂, CH), 3.46-5.40 (CH₂), 7.01-9.20 (aromatic protons); ¹⁹F-NMR (D₂O, ext. CF₃COOH) δ -4.60 to -7.04 (16F), -48.29 (6F).

Viscosity measurements

The viscosities of aqueous solutions of fluoroalkyl end-capped APDAPS polymers and fluoroalkyl end-



capped AMPS polymers were measured at 30°C using a falling-sphere viscometer (Haake viscometer D1-G).

Antiviral assays

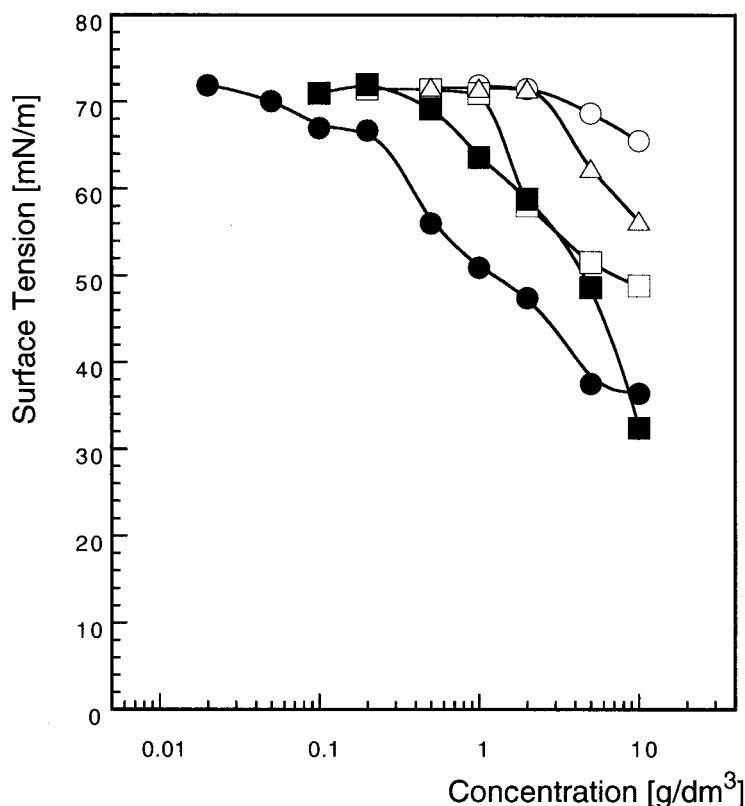
The antiviral activity of the compounds against HIV-1 (HTLB-IIIb starin) replication was based on the inhibition of the virus-induced cytopathic effect in MT-4 cells as previously described.⁷

Antibacterial assessment

The antibacterial activity of the polymers was evaluated against *Staphylococcus aureus* and *Escherichia coli* by a viable cell-counting method as described previously.⁸

RESULTS AND DISCUSSION

The reactions of sulfobetaine monomer [3-[N-(3-acrylamido)propyl-N,N-dimethylammonio]propanesulfonate (APDAPS)] with fluoroalkanoyl peroxides were carried out at 45°C for 5 h under nitrogen. The reaction is depicted in Scheme 1.



- : $R_F = C_3F_7$ (No 3 in Table 1)
 □: $R_F = C_3F_7OCF(CF_3)$ (No 6 in Table 1)
 △: $R_F = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$ (No 9 in Table 1)
 ●: $R_F = C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2OCF(CF_3)$ (No 12 in Table 1)
 ■: $R_F = C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2OCF(CF_3)CF_2OCF(CF_3)$ (No 13 in Table 1)

Figure 2 Surface tension of aqueous solutions of $R_F-(APDAPS)_n-R_F$ at 30°C.

As shown in Scheme 1 and Table I, fluoroalkanoyl peroxides were found to react with APDAPS under very mild conditions to afford fluoroalkyl end-capped APDAPS polymers in 25–96% isolated yields. The molecular weights of these fluoroalkyl end-capped APDAPS polymers were measured by GPC (gel permeation chromatography) by using 0.1 mol/dm³ NaNO₃ solution as the eluent, and the obtained values (M_n) were in the range 10,000–30,000. Considering the fact that water-soluble fluoroalkyl end-capped polymers can easily form the self-assembled molecular aggregates in aqueous solutions, the obtained molecular weights by GPC suggest the apparent molecular weights.

Fluoroalkyl end-capped APDAPS polymers were easily soluble in water; however, these polymers exhibited no solubility in other solvents such as ethanol, tetrahydrofuran, chloroform, carbon tetrachloride, benzene, ethyl acetate, dimethyl sulfoxide, and *N,N*-dimethylformamide. In particular interest, our present

fluoroalkyl end-capped APDAPS polymers in Table I could cause gelation in methanol, although the corresponding nonfluorinated APDAPS polymers ($M_n = 12,700$) exhibited a good solubility in both methanol and water. This interesting gelling behavior in methanol cannot be explained in detail at the present time; however, one thought is that the ionic interactions of sulfobetaine segments in fluorinated polymers could strongly participate in the gelator, which is constructed by the aggregations of end-capped fluoroalkyl segments in methanol attributed to the lower solvation to fluorinated APDAPS polymers by methanol compared with that by water.

Similarly, we tried to react the other sulfobetaine monomer [2-vinylpyridinio propane sulfonate (VPPS)] with fluoroalkanoyl peroxide, and the result is shown in Scheme 2.

As shown in Scheme 2, the reaction of VPPS with fluoroalkanoyl peroxide was found to afford fluoroalkyl end-capped VPPS polymer in 33% isolated yield.

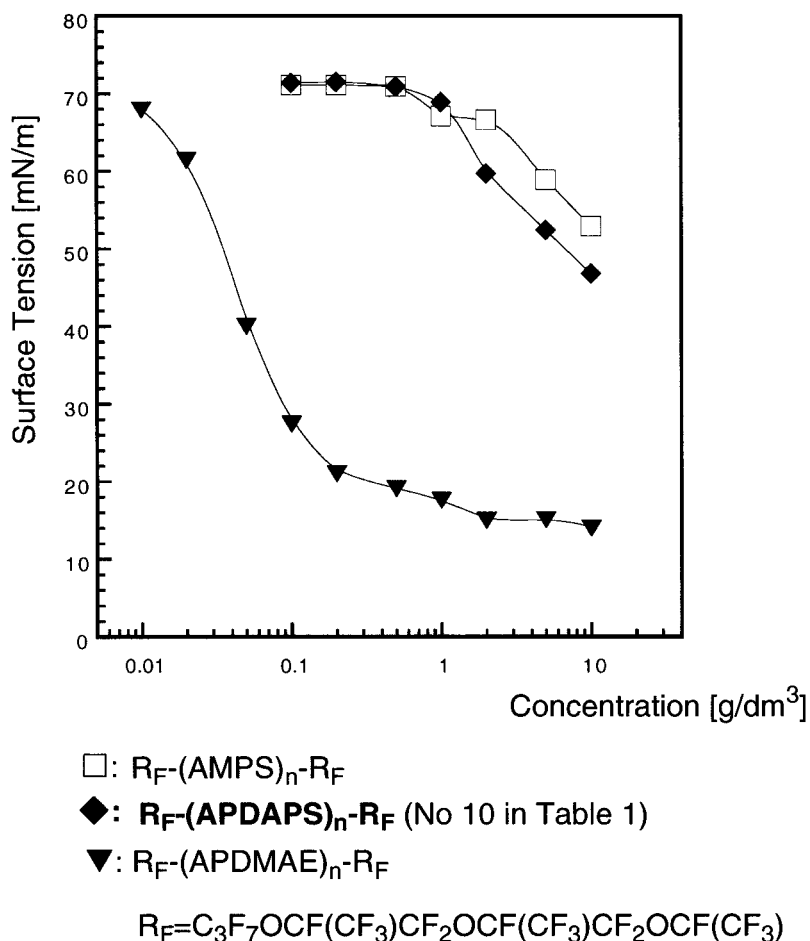


Figure 3 Surface tension of aqueous solutions of fluoroalkyl end-capped betaine-type polymers at 30°C.

R_F -(VPPA)_n- R_F polymer was easily soluble in water, but this polymer was not soluble in other solvents at all. The corresponding nonfluorinated VPPS polymer [-(VPPS)_n-] also exhibited a solubility similar to that of the fluorinated polymer.

In addition, the gelation of R_F -(VPPS)_n- R_F was not observed in methanol. This finding would depend on the ionic interactions between pyridinio propane sulfonate segments in fluorinated polymer, which become weaker because of the steric hindrance of pyridinio segments. In contrast, we previously reported that fluoroalkyl end-capped 2-acrylamido-2-methylpropanesulfonic acid polymers [R_F -[CH₂CHC(=O)N⁺H₂CMe₂CH₂SO₃⁻]_n- R_F : R_F -(AMPS)_n- R_F] can cause gelation in methanol. This would depend on the strong ionic interaction between the betaine-type (AMPS) segments that can participate in the gelator, which is constructed by the aggregations of end-capped fluoroalkyl segments compared with those of R_F -(APDAPS)_n- R_F and R_F -(VPPS)_n- R_F .

To clarify the solution properties of fluoroalkyl end-capped APDAPS polymers, we measured the

viscosity of an aqueous solution of R_F -(APDAP)_n- R_F , and the viscosities of aqueous solutions of R_F -(AMPS)_n- R_F and fluoroalkyl end-capped 2-(3-acrylamidopropyl)dimethylammonio)ethanoate polymer [R_F -(APDMAE)_n- R_F] were also measured under similar conditions for comparison. These results are shown in Figure 1.

As shown in Figure 1, the viscosity of R_F -(APDAPS)_n- R_F polymer increased only slightly with increasing concentrations, and the gel did not form. On the other hand, the viscosity of R_F -(AMPS)_n- R_F increased significantly with increasing concentration, and we were unable to measure their viscosity because of the gelation at concentrations > 1 g/dm³. Previously, we reported that R_F -(APDMAE)_n- R_F polymers, especially the longer perfluoroalkyl end-capped APDMAE polymer, can cause gelation in water derived from the synergistic interaction of the aggregations of the longer fluoroalkyl segments and the ionic interactions of the betaine segments.⁵ The viscosity of R_F -(APDMAE)_n- R_F increased with increasing concentration, and gelation was observed above 10 g/dm³. These phenomena suggest that in a

series of fluoroalkyl end-capped betaine-type polymers, fluoroalkyl end-capped APDAPS polymers could not afford the strong ionic interaction between the APDAPS betaine segments to cause gelation in aqueous solutions. The molecular weights of these fluorinated polymers [$R_F = \text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$] measured by GPC by using distilled water as the eluent, which was passed through ion-exchanged resin, are as follows:

	M_n (M_w/M_n)
$R_F\text{-(APDAPS)}_n\text{-}R_F$ (No. 10 in Table I)	16,100 (1.33) ^a
$R_F\text{-(APDMAE)}_n\text{-}R_F$	35,000,000 (26,000)
$R_F\text{-(AMPS)}_n\text{-}R_F$	3,300,000 (190,000)

^a Another peak was observed, and this peak area corresponds to $M_n = 5,250,000$ ($M_w/M_n = 433$).

With respect to the molecular weights of these fluorinated polymers, the apparent molecular weight,

especially the M_w/M_n values of $R_F\text{-(APDAPS)}_n\text{-}R_F$ polymer, were extremely low compared with those of $R_F\text{-(AMPS)}_n\text{-}R_F$ and $R_F\text{-(APDMAE)}_n\text{-}R_F$. The viscosity of these fluorinated polymers shown in Figure 1 substantially increased with increasing M_w/M_n values. These findings suggest that $R_F\text{-(AMPS)}_n\text{-}R_F$ and $R_F\text{-(APDMAE)}_n\text{-}R_F$ polymers could interact strongly with each other with the aggregations of the end-capped fluoroalkyl segments in polymers and the ionic interactions between the betaine segments to induce gel formation. On the other hand, in $R_F\text{-(APDAPS)}_n\text{-}R_F$ polymers, the aggregation of the end-capped fluoroalkyl segments would predominantly operate because of the electrostatic repulsion between the sulfonate units in betaine segments, and these polymers could not form gels.

Our present APDAPS polymers were shown to be soluble in water. Therefore, it was of interest to study the surfactant properties of these fluorinated APDAPS polymers. We measured the surface tension of their aqueous solutions by the Wilhelmy

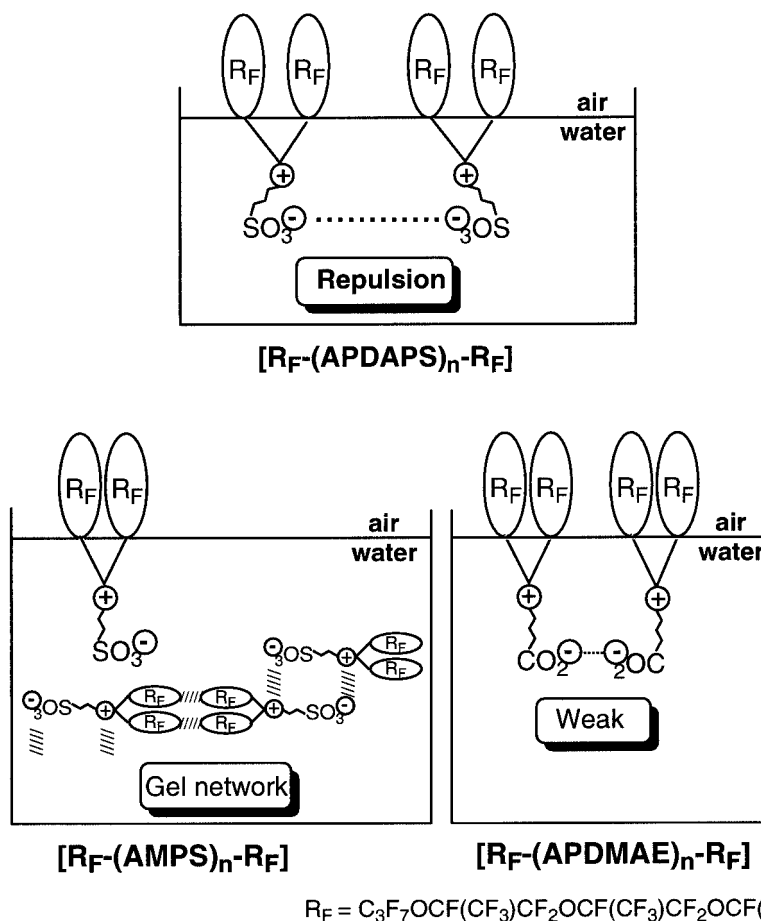


Figure 4 Schematic illustration of the surface arrangement of end-capped fluoroalkyl segments in aqueous solutions of $R_F\text{-(APDAPS)}_n\text{-}R_F$, $R_F\text{-(AMPS)}_n\text{-}R_F$, and $R_F\text{-(APDMAE)}_n\text{-}R_F$ polymers.

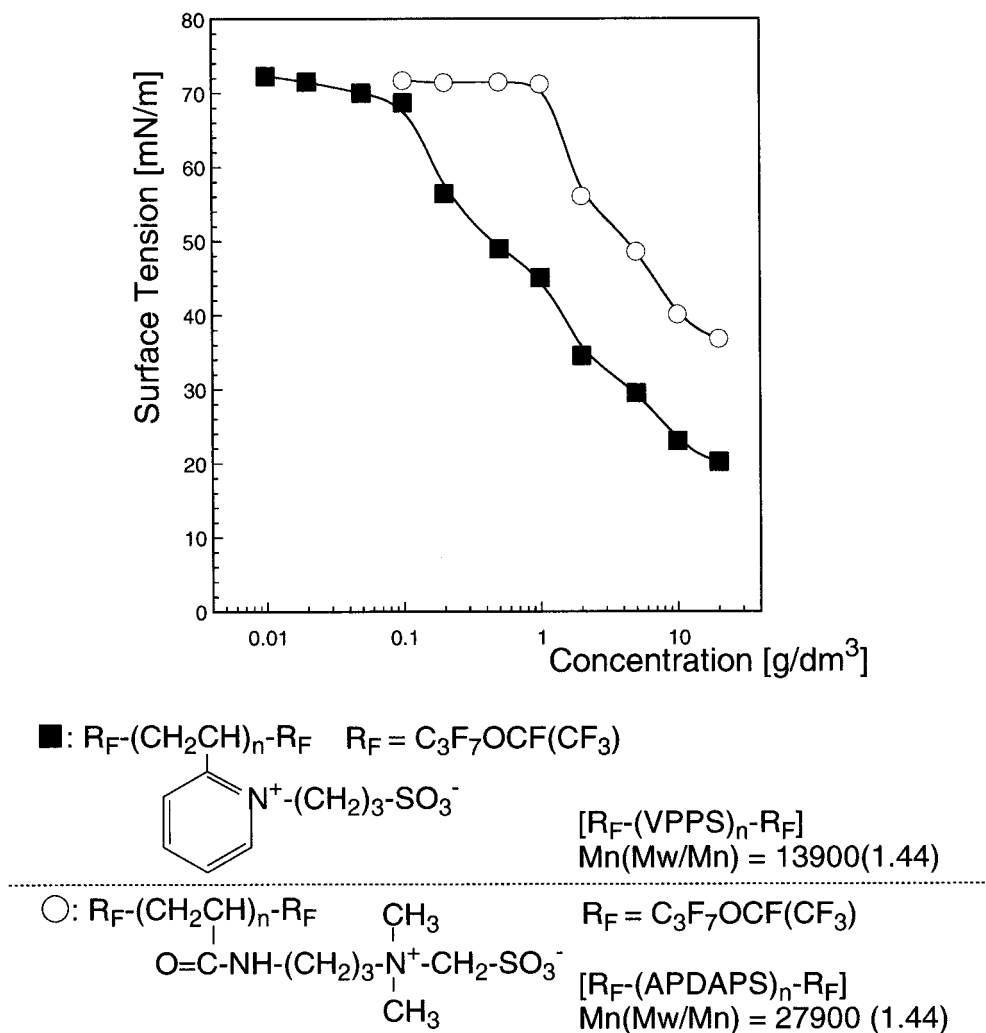


Figure 5 Surface tension of aqueous solutions of fluoroalkyl ebd-capped VPPS polymer at 30°C.

plate method at 30°C. These results are shown in Figure 2.

As shown in Figure 2, a significant decrease in the surface tension of water was observed in each APDAPS polymer. In particular, longer perfluoroalkyl end-capped APDAPS oligomers were more effective for reducing the surface tension of water. In Figure 3, we show the surface tension of aqueous solutions of R_F -(AMPS) $_n$ - R_F polymer and R_F -(APDMAE) $_n$ - R_F polymer⁵ for comparison.

R_F -(APDAPS) $_n$ - R_F polymer and R_F -(AMPS) $_n$ - R_F polymer could not have clear break points resembling a cmc (critical micelle concentration), although R_F -(APDMAE) $_n$ - R_F polymer was able to reduce the surface tension of water quite effectively to around 15 mN/m with a clear break point. Because of a relatively weak electrostatic repulsion between the betaine segments in R_F -(APDMAE) $_n$ - R_F polymers, fluoroalkyl segments are likely to be arranged regularly above the water surface to exhibit a clear

break point in the surface tension measurements. In contrast, in R_F -(APDAPS) $_n$ - R_F polymer or R_F -(AMPS) $_n$ - R_F polymer, fluoroalkyl segments are not likely to be arranged regularly above the water surface because of the strong electrostatic repulsion between the sulfonate units in APDAPS segments or the strong gel formation derived from the ionic interaction between the betaine-type AMPS segments, respectively, as illustrated in Figure 4.

Similarly, we measured the surface tension of aqueous solutions of R_F -(VPPS) $_n$ - R_F polymer, and the results are shown in Figure 5.

As shown in Figure 5, R_F -(VPPS) $_n$ - R_F polymer was found to be more effective than R_F -(APDAPS) $_n$ - R_F polymer for reducing the surface tension of water to around 20 mN/m. This would depend on the relatively weak electrostatic repulsion of betaine units attributed to the steric hindrance of pyridiniumpropylsulfonate segments in VPPS polymer.

TABLE II
Molecular Weights of Fluoroalkyl End-Capped APDAPS and VPPS Polymers Calculated Based on GPC by Using Water, 0.1M NaNO₃ and 0.5M NaNO₃ as the Eluents at 30°C

No ^a	Polymer	$M_n (M_w/M_n)$		
		Water	0.1 M NaNO ₃	0.5 M NaNO ₃
1	R _F -(APDAPS) _n -R _F C ₃ F ₇	10900 (1.59);9030000 (666)	19500 (1.93)	37100 (1.52)
		11300 (1.74);7230000 (53.6)	25100 (1.73)	17100 (1.97)
		12800 (1.40);2080000 (135)	22500 (1.80)	24000 (1.97)
4	C ₃ F ₇ OCF(CF ₃)	10900 (1.64);6910000 (77.7)	27900 (1.64)	36700 (1.44)
		8300 (1.69);5160000 (2055)	32000 (2.19)	25300 (1.77)
		8100 (1.70);2440000 (6.88)	15200 (2.17)	36600 (1.42)
7	C ₃ F ₇ OCF(CF ₃)CF ₂ OCF(CF ₃)	3400 (4.43);5840000 (740)	18500 (1.95)	23000 (1.83)
		10000 (1.41);4000000 (358)	20500 (1.97)	25100 (1.79)
		4800 (1.55);1750000 (168)	10000 (1.96)	11300 (2.74)
10	C ₃ F ₇ OCF(CF ₃)CF ₂ OCF(CF ₃)CF ₂ OCF(CF ₃)	16100 (1.33);5250000 (433)	19800 (1.87)	25000 (2.00)
		—	32200 (1.86)	40500 (1.34)
		—	14800 (2.73)	14600 (2.80)
13	C ₃ F ₇ OCF(CF ₃)CF ₂ OCF(CF ₃)CF ₂ OCF(CF ₃)CF ₂ OCF(CF ₃)	10200 (1.46);4150000 (8780)	26100 (1.84)	23800 (1.87)
		—	—	—
		—	—	—
	-(APDAPS) _n -	7300 (1.66)	12700 (1.95)	30200 (1.66)
	R _F -(VPPS) _n -R _F [R _F = CF(CF ₃)OC ₃ F ₇]	8000 (2.20)	—	13900 (1.44)
	-(VPPS) _n -	24200 (1.29)	—	19400 (1.50)

^a Each different from those in Table I.

In this way, fluoroalkyl end-capped APDAPS polymers were demonstrated to form the molecular aggregates in aqueous solutions. To clarify this behavior, we measured the molecular weights of these fluorinated APDAPS polymers by GPC measurements, and the results are shown in Table II. We also measured the molecular weight of R_F-(VPPS)_n-R_F polymer for comparison.

As shown in Table II, interestingly, the molecular weights of R_F-(APDAPS)_n-R_F polymer calculated based on GPC measurements increased significantly by the use of water as the eluent, compared to those by use of NaNO₃ solutions. In particular, in this case, we can obtain two molecular weight areas that consist of the 10,000 and several million levels, although the molecular weight of nonfluorinated APDAPS polymer exhibited almost the same values in each eluent. R_F-(APDAPS)_n-R_F polymers could form the self-assemblies with the aggregation of end-capped fluoroalkyl segments and the ionic interaction between the betaine segments in aqueous solution. In contrast, in the NaNO₃ solutions, the molecular weights of R_F-

(APDAPS)_n-R_F polymers are suggested to significantly decrease because of lowering the ionic interaction between the betaine segments in the presence of NaNO₃. The molecular weight of R_F-(VPPS)_n-R_F polymer by GPC did not change very much in each eluent. This finding would result from the weakness of the ionic interaction between the VPPS betaine segments.

The molecular weights of R_F-(APDAPS)_n-R_F polymer and R_F-(VPPS)_n-R_F polymer by static light-scattering measurements showed a tendency similar to that of GPC measurements. The molecular weight (MW = 6,610,000) of R_F-(APDAPS)_n-R_F polymer in 0.1M NaNO₃ was found to increase more extremely than that (MW = 17,300) of the corresponding nonfluorinated APDAPS polymer [-(APDAPS)_n-], although the molecular weight (MW = 6780) of R_F-(VPPS)_n-R_F in 0.1M NaNO₃ did not change compared with that (MW = 6060) of -(VPPS)_n- polymer.

We previously reported that fluoroalkyl end-capped AMPS polymers possess a potent and selective inhibitory effect against HIV-1 replication *in vitro*, and

some $R_F-(APDMAE)_n-R_F$ polymers exhibit antibacterial activity. Therefore, it is of particular interest to investigate the potential of our present polymers as biologically active materials. Thus, a series of fluoroalkyl end-capped APDAPS polymers were evaluated for activity against HIV-1 replication in MT4 cells. However, these fluorinated polymers were found to be inactive against HIV-1 replication. In addition, the polymers were also evaluated for their antibacterial activity against *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) by a viable cell-counting method. About 10^8 cells of *S. aureus* and *E. coli* were exposed to 1 mg/mL of the polymers in saline. These fluorinated polymers were generally inactive; however, of these fluorinated polymers, polymers 7 and 9 in Table I were found to exhibit antibacterial activity to some extent (from 1.7×10^8 to 2.9×10^6 and 5.6×10^6 colony-forming units levels, respectively) against *S. aureus*.

CONCLUSIONS

In conclusion, a variety of fluoroalkyl APDAPS polymers were prepared under very mild conditions by the use of a fluoroalkanoyl peroxide, a key intermediate. Fluoroalkyl end-capped VPPS polymer was also prepared under similar conditions. These fluorinated APDAPS and VPPS polymers thus obtained were easily soluble in water; however, these polymers were insoluble in other solvents. Of particular interest, fluorinated APDAPS polymers were able to cause gelation in methanol, although fluorinated VPPS polymer

exhibited no gelation in methanol. Fluorinated APDAPS polymers can easily form self-assembled molecular aggregates with the aggregations of end-capped fluoroalkyl segments and the ionic interaction between the sulfobetaine units in polymers in aqueous solutions. In contrast, it was suggested that fluorinated VPPS polymer is not likely to form molecular aggregates in aqueous solution because of the steric hindrance of pyridinio betaine units.

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