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Synthesis of novel fluoroalkylated 4-vinylpyridinium chloride oligomers as functional materials possessing surfactant and biological properties

Hideo Sawada [a,*], Atsuhito Wake [a], Tomomi Maekawa [b], Tokuzo Kawase [b], Yoshio Hayakawa [c], Toshio Tomita [d], Masanori Baba [e]

[a] *Department of Chemistry, Nara National College of Technology, Yata, Yamatokoriyama, Nara 639-11, Japan*

[b] *Faculty of Science of Living, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558, Japan*

[c] *National Industrial Research Institute of Nagoya, Kita-ku, Nagoya 462, Japan*

[d] *Faculty of Agriculture, Tohoku University, Tsutsumidori-Amamiya, Aoba-ku, Sendai 981, Japan*

[e] *Division of Human Retroviruses, Center for Chronic Viral Diseases, Faculty of Medicine, Kagoshima University, Kagoshima 890, Japan*

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Abstract

Perfluoropropylated and perfluoro-oxaalkylated 4-vinylpyridinium chloride oligomers were prepared by the reactions of fluoroalkanoyl peroxides with 4-vinylpyridinium chloride under very mild conditions. A series of fluoroalkylated 4-vinylpyridinium chloride co-oligomers containing carboxyl or trimethylsilyl segments were also obtained by the reactions of fluoroalkanoyl peroxides with 4-vinylpyridinium chloride and acrylic acid or trimethylvinylsilane under similar conditions. These fluoroalkylated homo- and co-oligomers containing carboxyl or trimethylsilyl segments were soluble in water and methanol. Furthermore, these oligomers were able to reduce the surface tension of water to 10–18 mN m^{-1} levels with a clear break point resembling a CMC (critical micelle concentration), and are applicable to new fluorinated cationic oligosurfactants. Fluoroalkylated co-oligomers were found to possess antibacterial activity against *Staphylococcus aureus*. In addition, fluoroalkylated co-oligomers containing carboxyl groups were potent and selective inhibitors of HIV-1 (human immunodeficiency virus type 1) in MT-4 cells. Interestingly, one of these fluoroalkylated co-oligomers containing carboxyl groups was clarified to show both antibacterial and anti-HIV-1 activities. Therefore, these oligomers are suggested to have high potential for new functional materials through their surfactant and biological properties. © 1997 Elsevier Science S.A.

Keywords: Fluoroalkylated pyridinium oligomers; Surface tension; Cationic surfactants; Anti-HIV-1 activity; Antibacterial activity; Fluoroalkanoyl peroxides

1. Introduction

Recently, there has been an increasing interest in the hydrophobically modified polyelectrolytes (polysoaps or micellar polymers) owing to their high potential in various industrial, biological, and environmental applications [1]. Especially, cationic polysoaps such as quaternized poly(4-vinylpyridinium) [2] and poly(alkylmethyldiallylammonium bromides) [3] have been studied in detail from a more fundamental point of view. In contrast, fluoroalkylated polysoaps are expected to show quite different properties that set them apart from the corresponding hydrocarbon polysoaps, in particular greater hydrophobicity, constrained conformational states of the fluoroalkyl chain, and chemical inertness. However, the exploration of fluoroalkylated polysoaps (polyelectrolytes modified by fluoroalkyl segments) constructed by carbon–carbon bond formation has hitherto been very limited owing to their synthetic difficulties. During our comprehensive study on the reactivities of fluoroalkanoyl peroxides [4], we found that they are useful tools for the preparation of a series of fluoroalkylated oligomers by carbon–carbon bond formation [5]. In these fluoroalkylated oligomers, homo- and co-oligomers of fluoroalkylated acrylic acid were shown to exhibit unique properties such as surface activity and anti-HIV-1 activity imparted by fluorine, although these compounds are oligomeric (high molecular mass) materials [6]. From such a point of view, it would be interesting to develop the fluoroalkylated cationic polysoaps. Very recently, we have succeeded in preparing some fluoroalkylated cationic polysoaps (oligomeric soaps or oligosoaps) such as fluoroalkylated allyl- and diallyl-ammonium chloride oligomers [7], and fluoroalkylated oligomers containing trimethylammonium units [8]. Generally, it is well known that polycations show an outstandingly high antibac-

* Corresponding author.

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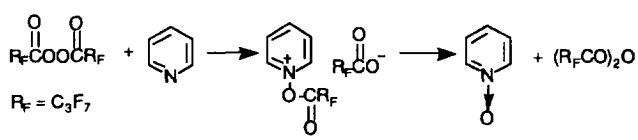
terial activity against gram-positive and gram-negative strains and exhibit a wide spectrum of antimicrobial activity [9]. In our continuing effort to design and develop new fluoroalkylated cationic oligosoaps, we reported the synthesis of novel fluoroalkylated 4-vinylpyridinium chloride (4-VPC) oligomers in a preliminary communication [10]. We now give a full account of the synthesis and properties of these fluoroalkylated oligomers, with particular emphasis on the anti-HIV-1 activity and antibacterial activity.

2. Results and discussion

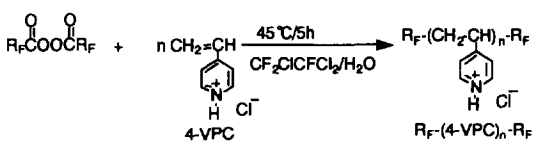
Previously, we have reported that styrene reacts with fluoroalkanoyl peroxides to afford 1:1 adducts [$PhCH(OCOR_F)$-CH_2R_F] via a single electron transfer from styrene to peroxide [11], although it is well known that styrene is a monomer readily polymerized by radicals. Furthermore, we have reported a similar nucleophilic attack of *N*-lone pair electrons of pyridine on the O–O bond of a fluoroalkanoyl peroxide to give pyridine-*N*-oxide as shown in Scheme 1 [12]. Based on these results, we were interested in reacting directly fluoroalkanoyl peroxides with 4-VPC which has no nucleophilic property. In addition, 4-VPC has been calculated using the MNDO-PM3 semiemprical MO method [13] to have a lower HOMO energy level (−14.017 eV) than that of 4-vinylpyridine (−9.688 eV) or styrene (−9.132 eV). This finding suggests that a weaker interaction of 4-VPC and LUMO (peroxide) in comparison with that of styrene could cause an interaction between HOMO (4-VPC) and SOMO of the fluoroalkyl radical ($R_F\cdot$) to promote not an electron transfer from 4-VPC to peroxide but an unusual radical oligomerization.

As shown in Scheme 2, the oligomerization of 4-VPC with various fluoroalkanoyl peroxides was found to proceed under very mild conditions to afford the expected fluoroalkylated 4-VPC oligomers in excellent to moderate yields. These results were listed in Table 1.

As Table 1 shows, both perfluoropropylated and perfluorooxaalkylated 4-VPC oligomers were produced from the corresponding fluoroalkanoyl peroxides under mild conditions. Hardly any 1:1 adducts formed via a single electron transfer



Scheme 1.



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

Scheme 2.

Table 1
Reactions of fluoroalkanoyl peroxides with 4-vinylpyridinium chloride (4-VPC)

R_F in peroxide (mmol)	4-VPC (mmol)	R_F–(4-VPC)$_n$–R_F	
		Yield (%) [a]	$\overline{M_n}$ ($\overline{M_w}/\overline{M_n}$)
C_3F_7			
4	12	43 (58)[b]	10400 (4.38)
$CF(CF_3)OC_3F_7$			
2	17	74 (14)	7010 (2.47)
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$			
5	8	7 (7)	5090 (1.27)
3	8	36 (23)	2850 (1.80)
2	12	38 (10)	6800 (2.33)
2	18	68 (10)	6250 (2.77)
$CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$			
4	12	40 (15)	4700 (1.93)

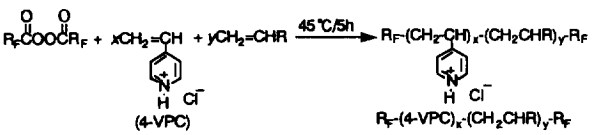
[a] The yields are based on the starting materials [4-vinylpyridinium chloride and the decarboxylated peroxide unit (R_F–F_F)].
[b] Each product also contains an ionene oligomer [-(CH2-CH2-  -)m Cl⁻], and the value in parenthesis indicates the ratio (%) of the ionene oligomer determined by ^{1}H NMR.

reaction as observed in the case of styrene were detected. These results suggest that the reactions of 4-VPC with fluoroalkanoyl peroxides proceed via a primary radical termination or a radical chain transfer to the peroxide under our oligomerization conditions, in which the concentration of the peroxide was almost the same as that of 4-VPC (molar ratio of 4-VPC/peroxide = 2–9), to afford mainly oligomers containing two fluoroalkylated end-groups [5–8]. However, in these reactions, it was found that spontaneous polymerization of 4-VPC also occurs to give the corresponding poly(1,4-pyridiniumdiylethylene chloride) as a by-product in each case. Furthermore, we tried to separate this ionene oligomer from the product, but various trials failed and gel permeation chromatography (G.P.C.) analyses of each oligomeric mixture obtained showed only one peak. Spontaneous polymerization of 4-vinylpyridinium salts initiated by an addition of nucleophile (counter anion in 4-vinylpyridinium salt) to the double bond to give an ionene polymer [poly(1,4-pyridiniumdiylethylene salt)] has been reported [14]. In the reaction with perfluorobutyryl peroxide, the molecular weight and polydispersity ($\overline{M_w}/\overline{M_n}$) of the obtained oligomer are relatively higher [$\overline{M_n}$ = 10 400 ($\overline{M_w}/\overline{M_n}$ = 4.38)] than those of the other oligomers. Previously, we reported that the decomposition of perfluorobutyryl peroxide [$(C_3F_7COO)_2$] is remarkably accelerated by the addition of water, whereas that of perfluorooctanoyl peroxide is only slightly accelerated [15]. Thus, a strong repulsion for water, owing to the high surface-active property of the long chain perfluoroalkyl group (perfluoroheptyl group), was suggested to affect hydrolysis of perfluorooctanoyl peroxide. These results indicate that under our aqueous oligomerization conditions, the hydrolysis of perfluorobutyryl peroxide should occur extensively prior to oligomerization. On the other hand, perfluoro-oxaalkanoyl

peroxides are suggested to have a strong repulsion for water owing to longer perfluoro-oxaalkyl groups. Thus, the radical oligomerizations with perfluoro-oxaalkanoyl peroxides should be predominant in comparison with the spontaneous oligomerization of 4-VPC.

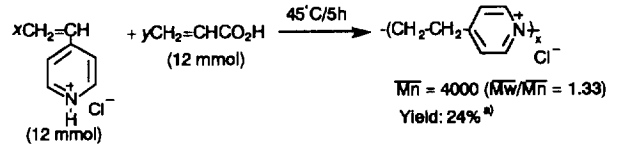
We also tried to prepare a series of fluoroalkylated 4-VPC co-oligomers containing carboxyl or trimethylsilyl groups as co-oligomer segments via the reactions of fluoroalkanoyl peroxides with 4-VPC in the presence of acrylic acid or trimethylvinylsilane as shown in Scheme 3.

Table 2 shows the results for the co-oligomerizations of 4-VPC and acrylic acid or trimethylvinylsilane with fluoroalkanoyl peroxides. Perfluoropropylated and perfluoro-oxaalkylated 4-VPC co-oligomers containing not only carboxyl but also trimethylsilyl segments were obtained under mild conditions similar to those of the homo-oligomerizations. Again, the ionene oligomer was obtained as a by-product in each case, as well as some of the homo-oligomer of 4-VPC with the fluoroalkanoyl peroxide. Therefore, we studied the spontaneous oligomerization of 4-VPC in the presence of acrylic acid, which is well known to be a highly polymerizable monomer compared with trimethylvinylsilane. The result is shown in Scheme 4.



R_F = C_3F_7, $CF(CF_3)O[CF_2CF(CF_3)O]_mC_3F_7$; m = 0, 1
R = CO_2H, $SiMe_3$

Scheme 3.



a) The yield is based on 4-VPC

Scheme 4.

As shown in Scheme 4, under similar conditions as those of the co-oligomerizations of 4-VPC with fluoroalkanoyl peroxides, we could detect no ionene oligomer containing carboxyl segments in the product, which was poly(1,4-pyridiniumdiylethylene chloride) (24% yield) arising by spontaneous oligomerization of 4-VPC. This finding suggests that the series of fluoroalkylated 4-VPC co-oligomers are formed not by spontaneous oligomerization but by radical co-oligomerization with fluoroalkanoyl peroxides.

Fluoroalkylated 4-vinylpyridinium homo- and co-oligomers thus obtained were easily soluble in water and methanol. Thus, the surface properties of these new cationic homo- and co-oligomers were evaluated by measuring the surface tension of aqueous solutions by the Wilhelmy plate method at 30 °C. These results are shown in Figs. 1 and 2.

Table 2
Reactions of fluoroalkanoyl peroxides with 4-VPC in the presence of acrylic acid (ACA) or trimethylvinylsilane (VM-Si)

R_F in peroxide (mmol)	4-VPC (mmol)	Co-monomer (mmol)	R_F–(4-VPC)$_x$–(CH_2CHR)$_y$–R_F		
			Yield (%) [a]	x:y [b]	$\overline{M_n}$ ($\overline{M_w}/\overline{M_n}$)
		ACA			
C_3F_7					
4	10	10	43 (59) [c]	73:27	7300 (1.35)
3	17	17	47 (77)	57:43	5200 (1.15)
3	10	17	40 (72)	93:7	9600 (1.38)
3	17	11	78 (52)	48:52	5500 (1.20)
$CF(CF_3)OC_3F_7$					
4	10	10	41 (14)	55:45	4800 (1.44)
3	10	17	30 (27)	52:48	7600 (1.76)
4	17	17	56 (17)	57:43	9200 (1.82)
4	17	10	63 (16)	58:42	11200 (2.57)
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$					
4	10	10	55 (12)	71:29	4200 (1.78)
4	18	17	59 (25)	36:64	5700 (1.21)
4	10	10	22 (14)	59:41	8000 (1.53)
4	17	10	50 (31)	31:69	6100 (1.20)
		VM-Si			
C_3F_7					
6	12	13	19 (83)	75:25	4600 (1.31)
$CF(CF_3)OC_3F_7$					
6	12	12	20 (23)	89:11	5800 (1.10)

[a] The yields are based on the starting materials [4-VPC, co-monomer and the decarboxylated peroxide unit (R_F–R_F)].
[b] Co-oligomerization ratio determined by ^1H NMR.
[c] Each product also contains an ionene oligomer [-(CH$_2$-CH$_2$- )$_m$], and the value in parentheses indicates the ratio (%) of the ionene oligomer determined by ^1H NMR.

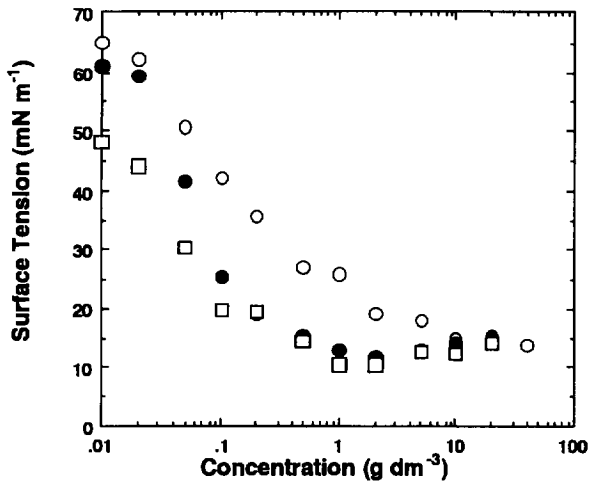


Fig. 1. Surface tension of aqueous solution of R_F–(VPC)$_n$–R_F: ○: $R_F = C_3F_7$; $\overline{M_n}$ = 10400, ●: R_F = CF(CF$_3$)OC$_3$F$_7$; $\overline{M_n}$ = 7010, □: R_F = CF(CF$_3$)OCF$_2$-CF(CF$_3$)OC$_3$F$_7$; $\overline{M_n}$ = 6800.

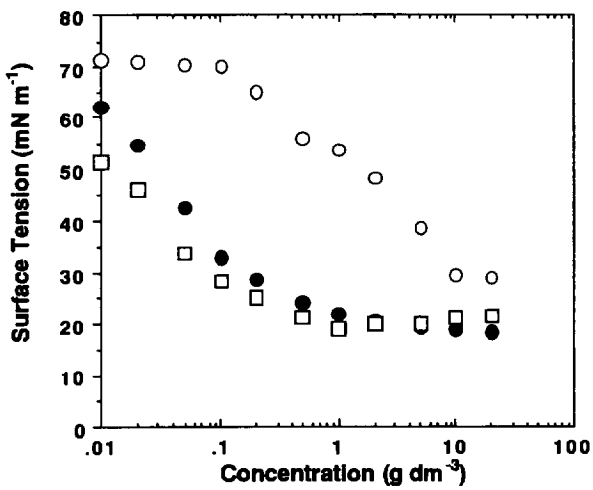


Fig. 2. Surface tension of aqueous solution of R_F–(VPC)$_x$–(ACA)$_y$–R_F: ○: $R_F = C_3F_7$; $\overline{M_n}$ = 5500, ●: R_F = CF(CF$_3$)OC$_3$F$_7$; $\overline{M_n}$ = 4800, □: R_F = CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$; $\overline{M_n}$ = 8000.

As shown in Fig. 1, the degree of reduction in surface tension of water depends on the length of fluoroalkyl groups in the oligomers as in the cases of the usual fluorinated surfactants [16]. Perfluoro-oxaalkylated oligomers were more effective for reducing the surface tension of water to around 10 mN m^{-1} than the perfluoropropylated one. Similarly, a significant decrease in the surface tension of water, to ca. 18 mN m^{-1}, was also found for fluoroalkylated 4-VPC-acrylic acid co-oligomers, and the co-oligomers containing perfluoro-oxaalkyl chains were more effective in reducing the surface tension of water than the perfluoropropylated one as shown in Fig. 2.

Thus, these fluoroalkylated cationic oligomers are novel high-molecular-mass surfactants which can reduce the surface tension of water effectively. In particular, fluoroalkylated 4-VPC–acrylic acid co-oligomers possessing both pyridinium and carboxylate segments are possible new zwitterionic-type fluorinated oligo-surfactants. Interestingly, these oligomers were shown to possess a break point resembling a CMC (critical micelle concentration) and to be useful as new fluorinated oligosoaps, although hydrocarbon polysoap solutions are well known to exhibit no CMC or break point resembling a CMC [17]. In fact, the surface tension study of aqueous solutions of non-fluorinated 4-VPC oligomer [-(4-VPC)$_n$-; $\overline{M_n}$ = 9780, ($\overline{M_w}/\overline{M_n}$) = 1.93] containing poly(1,4-pyridiniumdiylethylene chloride), which was prepared by the oligomerization of 4-VPC with azo-initiator [2,2′-azobis(2-methylpropionamidine) dihydrochloride], showed that this oligomer has no a break point resembling a CMC. Furthermore, Laschewsky et al. recently reported that cationic polysoaps with fluorocarbon hydrophobic chains, which were prepared by random copolymerization of choline methacrylate with 1,1,2,2-tetrahydroperfluorooctyl methacrylate, can not reduce the surface tension of water effectively (ca. 50 mN m^{-1} levels), and no CMC or break point resembling a CMC is observed in such fluorinated polymers [18]. Therefore, our present results are considered to be unique for fluorinated cationic polysoaps. The characteristic features of our fluorinated oligomers in aqueous solutions may arise because are likely to have a mode of arrangement with the fluoroalkyl chains above the water surface, and form intra- or inter-molecular aggregates in aqueous solutions owing to their unique structure (fluoroalkylated end-capped).

Very recently, we reported that fluoroalkylated oligomers containing trimethylammonium segments can reduce the surface tension of water effectively, and possess antibacterial activity against *Staphylococcus aureus* [8]. Furthermore, we have already reported that fluroalkylated oligomers containing carboxyl groups are potent and selective inhibitors of HIV-1 in vitro [6]. Therefore, our present fluoroalkylated 4-VPC homo-oligomers or the co-oligomers containing carboxyl groups are expected to show antibacterial activity or anti-HIV-1 activity. They have been evaluated for their antibacterial activity against *Staphylococcus aureus* by viable cell counting method as already reported [8]. The result obtained are listed in Table 3.

As shown in Table 3, fluoroalkylated 4-VPC homo-oligomers were inactive. However, fluoroalkylated 4-VPC co-oligomers were found to show bacterial activity to some extent ($\approx 10^5$ colony forming units levels). Of these, the perfluoropropylated 4-VPC-trimethylvinylsilane co-oligomer [R_F–(4-VPC)$_x$–(VM-Si)$_y$–R_F; $R_F = C_3F_7$] was the most active, with 3.1×10^5 c.f.u. These results suggest that the antibacterial activity of fluoroalkylated 4-VPC oligomers would increase with increasing hydrophobicity or hydrophilicity of the oligomers compared with the corresponding homo-oligomers.

Fluoroalkylated 4-VPC co-oligomers containing carboxyl segments were found to be potent inhibitors of HIV-1 replication in MT-4 cells as shown in Table 4. These compounds showed a 50% effective concentration (EC_{50}) of 6.8–20 μg ml^{-1} whereas the 50% cytotoxic concentration (CC_{50}) was > 100 μg ml^{-1} in each case. Among them, perfluoro-1-methyl-2-oxapentylated co-oligomer [R_F–(4-VPC)$_x$–(ACA)$_y$–R_F; R_F = CF(CF$_3$)OC$_3$F$_7$; $\overline{M_n}$] = 9200 was

Table 3
Antibacterial activity of fluoroalkylated 4-vinylpyridinium chloride oligomers against *Staphylococcus aureus* [a]

R_F in oligmer	$\overline{M_n}$	*Staphlococcus aureus* (c.f.u. ml^{-1}) [b]
none		3.4×10^8
R_F–(4VPC)$_n$–R_F		
C_3F_7	10400	1.6×10^8
$CF(CF_3)OC_3F_7$	7010	1.7×10^8
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	2850	1.9×10^8
$CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	4700	2.5×10^8
R_F–(4-VPC)$_x$–(VM-Si)$_y$–R_F		
C_3F_7	4600	3.1×10^5 [c]
$CF(CF_3)OC_3F_7$	5800	1.1×10^7 [c]
R_F–(4-VPC)$_x$–(ACA)$_y$–R_F		
C_3F_7	7300	1.3×10^6 [c]
$CF(CF_3)OC_3F_7$	7600	5.6×10^6 [c]

[a] Concentration of each oligomer was 100 μg ml^{-1}.
[b] c.f.u. indicates colony forming units.
[c] c.f.u. in the absence of oligomer is 2.0×10^8.

Table 4
Inhibitory effect of R_F–(4-VPC)$_x$–(ACA)$_y$–R_F on the replication of HIV-1 in MT-4 cells

R_F in oligmer	$\overline{M_n}$	EC_{50} (μg ml^{-1}) [a]	CC_{50} (μg ml^{-1}) [b]
$CF(CF_3)OC_3F_7$	4800	7.8	>100
	7600	8.2	>100
	9200	6.8	>100
	11200	7.0	>100
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$	8000	20	>100
Dextran sulfate	5000	3.5	>100

[a] 50% effective concentration, based on the inhibition of HIV-1 induced cytopathic effecets in MT-4 cells.
[b] 50% cytotoxic concentration, based on the impairment of viability of mock-infected MT-4 cells.

the most active with a 50% effective concentration (EC_{50}) of 6.8 μg ml^{-1}. This EC_{50} value is similar to that of dextran sulfate, which is considered to be a potent and selective inhibitor at present. On the other hand, the corresponding perfluoropropylated co-oligomers in Table 2 were inactive against HIV-1 replication. This finding and the results of Tables 3 and 4 suggest that anti-bacterial and anti-HIV-1 properties are not arising from the ionene oligomer present.

Perfluoro-1-methyl-2-oxapentylated co-oligomer [R_F–(4-VPC)$_x$–(ACA)$_y$–R_F; $R_F=CF(CF_3)OC_3F_7$; $\overline{M_n}$] = 7600 shows not only antiabcterial activity but also anti-HIV-1 activity (Tables 3 and 4). To our knowledge, this is the first example which shows that polymeric compounds can exhibit both antibacterial activity and anti-HIV-1 activity. Therefore, our present fluoroalkylated 4-VPC oligomers may be developed into novel functional polymeric materials possessing even better biological activities and surfactant properties.

3. Experimental details

3.1. Measurements

NMR spectra were measured with a JEOL-EX-270 FT-NMR (270 MHz) and Varian Unity-plus 500 (500 MHz) spectrometer while IR spectra were recorded on a HORIBA FT-IR spectrophotometer. Molecular weights were calculated by using a JASCO 830-RI G.P.C. calibrated with standard poly(ethylene glycol) by using 30% acetonitrile solution containing 0.2 M acetic acid and 0.2 M sodium acetate as the eluent.

3.2. Materials

A series of fluoroalkanoyl peroxides [$(R_FCOO)_2$] were prepared from the corresponding acyl halides and hydrogen peroxides in the presence of aqueous sodium hydroxide according to our previously reported method [19]. 4-VPC was prepared by the reaction of 4-vinylpyridine with excess hydrochloric acid in methanol according to Salamone's reported method [14].

3.3. General procedure for the synthesis of fluoroalkylated 4-VPC oligomers

Perfluoro-2,5-dimethyl-3,6-dioxanonanoyl peroxide (3 mmol) in 1,1,2-trichloro-1,2,2-trifluoroethane (39 g) was added to an aqueous solution (50%, w/w) of 4-VPC (8 mmol). The heterogeneous mixture was stirred vigorously at 45 °C for 5 h under nitrogen. After evaporating the solvent, the crude product obtained was reprecipitated from water–tetrahydrofuran to give the product (1.38 g) containing bis(perfluoro-1,4-dimethyl-2,5-dioxaoctylated) 4-VPC oligomer [R_F–(4-VPC)$_n$–R_F; $R_F=CF(CF_3)OCF_2CF(CF_3)OC_3F_7$] and poly(1,4-pyridiniumdiylethylene chloride). This product showed the following spectral data: I.R. ν(cm^{-1}) 3051, 1639, 1508(NH), 1350(CF_3), 1242(CF_2); ^1H NMR(D_2O) δ 1.44–2.25(CH_2), 2.55–2.85(CH), 7.26–7.78 (aromatic protons, 2H), 8.25–8.65 (aromatic protons, 2H), 3.61–3.80(CH_2), 4.80–5.18(CH_2), 7.84–8.16 (aromatic protons, 2H), 8.70–8.91 (aromatic protons, 2H) [Underlined peaks were assigned as poly(1,4-pyridiniumdiylethylene chloride)]; ^{19}F NMR (D_2O, ext. CF_3CO_2H) δ −1.0 to −6.4(26F), −44.8(6F), −70.0(2F); average molar mass ($\overline{M_n}$) = 2850, $\overline{M_w}/\overline{M_n}$ = 1.80 (determined by gel permeation chromatography).

Other fluoroalkylated 4-VPC homo- and co-oligomers were obtained under similarly mild conditions. The following spectral data were obtained for the other products studied:

3.3.1. C_3F_7–(4-VPC)$_n$–C_3F_7

I.R. ν(cm^{-1}) 3080, 1510(NH), 1350(CF_3), 1238(CF_2); ^1H NMR(D_2O) δ 1.56–2.44(CH_2), 2.57–3.03(CH), 7.34–7.89 (aromatic protons, 2H), 8.28–8.61 (aromatic protons, 2H), 3.60–3.83(CH_2), 4.85–5.17(CH_2), 7.90–8.21 (aro-

matic protons, 2H), 8.69–8.98 (aromatic protons, 2H) [Underlined peaks were assigned as poly(1,4-pyridiniumdiylethylene chloride)]; ^{19}F NMR(D_2O, ext. CF_3CO_2H) δ −1.7(6F), −38.7(4F), −47.9(4F).

3.3.2. $C_3F_7O(CF_3)CF$–(4-VPC)$_n$–$CF(CF_3)OC_3F_7$

I.R. ν(cm^{-1}) 3070, 1639, 1508(NH), 1350(CF_3), 1240(CF_2); ^{1}H NMR(D_2O) δ 1.52–2.28(CH_2), 2.53–2.87(CH), 7.28–7.82 (aromatic protons, 2H), 8.25–8.62 (aromatic protons, 2H), 3.62–3.82(CH_2), 4.83–5.12(CH_2), 7.93–8.21 (aromatic protons, 2H), 8.70–8.97 (aromatic protons, 2H) [Underlined peaks were assigned as poly(1,4-pyridiniumdiylethylene chloride)]; ^{19}F NMR(D_2O, ext. CF_3CO_2H) δ −0.9 to −6.8(16F), −48.9(6F).

3.3.3. $C_3F_7O(CF_3)CFCF_2O(CF_3)CFCF_2O(CF_3)CF$–(4-VPC)$_n$–$CF(CF_3)OCF_2CFC(F_3)OCF_2CF(CF_3)OC_3F_7$

I.R. ν(cm^{-1}) 1639, 1508(NH), 1306(CF_3), 1242(CF_2); ^{1}H NMR(D_2O) δ 1.94–2.80(CH_2), 2.85–3.33(CH), 7.78–8.20 (aromatic protons, 2H), 8.65–8.99 (aromatic protons, 2H), 3.81–4.09(CH_2), 5.01–5.38(CH_2), 8.22–8.41 (aromatic protons, 2H), 8.99–9.13 (aromatic protons, 2H) [Underlined peaks were assigned as poly(1,4-pyridiniumdiylethylene chloride)]; ^{19}F NMR(D_2O, ext. CF_3CO_2H) δ −0.8 to −5.9(36F), −51.2(6F), −66.2(4F).

3.3.4. C_3F_7–(4-VPC)$_x$–(CH_2CHCO_2H)$_y$–C_3F_7

I.R. ν(cm^{-1}) 3448(OH), 1724(C=O), 1512(NH), 1330(CF_3), 1228(CF_2); ^{1}H NMR(D_2O) δ 1.45–2.41(CH_2), 2.86–3.23(CH), 7.38–7.82 (aromatic protons, 2H), 8.29–8.65 (aromatic protons, 2H), 3.57–3.79(CH_2), 4.98–5.11(CH_2), 7.97–8.20 (aromatic protons, 2H), 8.65–8.97 (aromatic protons, 2H) [Underlined peaks were assigned as poly(1,4-pyridiniumdiylethylene chloride)]; ^{19}F NMR(D_2O, ext. CF_3CO_2H) δ −5.5(6F), −42.9(4F), −52.1(4F).

3.3.5. $C_3F_7O(CF_3)CF$–(4-VPC)$_x$–(CH_2CHCO_2H)$_y$–$CF(CF_3)OC_3F_7$

I.R. ν(cm^{-1}) 3447(OH), 1724(C=O), 1641, 1508(NH), 1333(CF_3), 1240(CF_2); ^{1}H NMR(D_2O) δ 1.23–2.59(CH_2), 2.77–3.22(CH), 7.58–8.10 (aromatic protons, 2H), 8.54–8.99 (aromatic protons, 2H), 3.61–3.91(CH_2), 4.98–5.10(CH_2), 8.12–8.23 (aromatic protons, 2H), 9.01–9.20 (aromatic protons, 2H) [Underlined peaks were assigned as poly(1,4-pyridiniumdiylethylene chloride)]; ^{19}F NMR(D_2O, ext. CF_3CO_2H) δ −4.2 to −9.1(16F), −55.2(6F).

3.3.6. $C_3F_7O(CF_3)CFCF_2O(CF_3)CF$–(4-VPC)$_x$–($CH_2CHCO_2H$)$_y$–$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$

I.R. ν(cm^{-1}) 3440(OH), 1728(C=O), 1641, 1510(NH), 1304(CF_3), 1244(CF_2); ^{1}H NMR(D_2O) δ 1.20–2.52(CH_2), 2.59–2.84(CH), 7.37–7.81 (aromatic protons, 2H), 8.21–8.62 (aromatic protons, 2H), 3.50–3.78(CH_2), 4.90–5.09(CH_2), 7.83–8.19 (aromatic protons, 2H), 8.63–9.02 (aromatic protons, 2H) [Underlined peaks were assigned as poly(1,4-pyridiniumdiylethylene chloride)]; ^{19}F NMR(D_2O, ext. CF_3CO_2H) δ −4.3 to −10.3(26F), −56.0(6F), −70.7(2F).

3.3.7. C_3F_7–(4-VPC)$_x$–($CH_2CHSiMe_3$)$_y$–C_3F_7

I.R. ν(cm^{-1}) 3427(OH), 1641, 1516(NH), 1500(CF_3), 1234(CF_2); ^{1}H NMR(D_2O) δ0.24(CH_3), 1.39–2.43(CH_2), 2.90–3.24(CH), 7.11–7.80 (aromatic protons, 2H), 8.20–8.59 (aromatic protons, 2H), 3.45–3.83(CH_2), 4.96–5.12(CH_2), 7.88–8.20 (aromatic protons, 2H), 8.64–8.99 (aromatic protons, 2H) [Underlined peaks were assigned as poly(1,4-pyridiniumdiylethylene chloride)]; ^{19}F NMR-(D_2O, ext. CF_3CO_2H) δ −5.4(6F), −42.9(4F), −52.9(4F).

3.3.8. $C_3F_7O(CF_3)CF$–(4-VPC)$_x$–($CH_2CHSiMe_3$)$_y$–$CF(CF_3)OC_3F_7$

I.R. ν(cm^{-1}) 3384(OH), 1637, 1508(NH), 1331(CF_3), 1244(CF_2); ^{1}H NMR(D_2O) δ −0.78–0.21(CH_3), 1.39–2.38(CH_2), 2.49–3.01(CH), 7.23–7.74 (aromatic protons, 2H), 8.20–8.61 (aromatic protons, 2H), 3.51–3.80(CH_2), 4.96–5.14(CH_2), 7.90–8.19 (aromatic protons, 2H), 8.70–8.93 (aromatic protons, 2H) [Underlined peaks were assigned as poly(1,4-pyridiniumdiylethylene chloride)]; ^{19}F NMR(D_2O, ext. CF_3CO_2H) δ −5.5 to −7.6(16F), −53.2(6F).

3.4. Reaction of 4-VPC with acrylic acid

Acrylic acid (12 mmol) in 1,1,2-trichloro-1,2,2-trifluoroethane (39 g) was added to an aqueous solution (50%, w/w) of 4-VPC (12 mmol). The heterogeneous mixture was stirred vigorously at 45 °C for 5 h under nitrogen. After evaporating the solvent, the crude product obtained was reprecipitated from water–tetrahydrofuran to give the product (0.41 g) This product showed the following spectral data: I.R. ν(cm^{-1}) 1641, 1521; ^{1}H NMR(D_2O) δ 3.62–3.79(CH_2), 4.93–5.10(CH_2), 7.85–8.17 (aromatic protons, 2H), 8.79–8.92 (aromatic protons, 2H).

3.5. Antibacterial assessment

The antibacterial activity of the oligomers was evaluated against *Staphylococcus aureus* by viable cell counting method as described previously [8].

3.6. Antiviral assays

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 described previously [6].

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