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Synthesis and surfactant properties of novel fluoroalkylated allyl- and diallylammonium chloride oligomers

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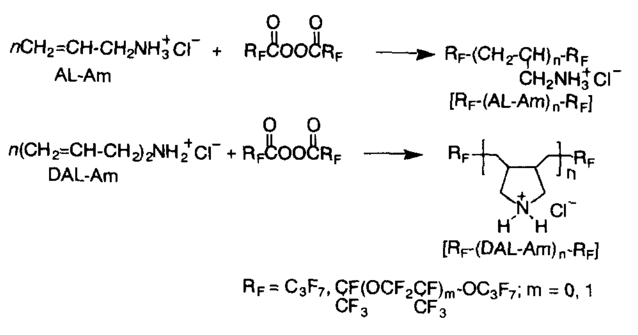
New fluoroalkylated allyl- and diallylammonium chloride oligomers with carbon–carbon bond formation have been prepared by the oligomerization of allylammonium chloride and the cyclo-oligomerization of diallylammonium chloride by the use of fluoroalkanoyl peroxides, respectively. These obtained fluoroalkylated cationic oligomers were able to reduce the surface tension of water to around 10 mN m^{-1}, and are applicable to new cationic oligosurfactants containing fluoroalkyl groups.

(Keywords: fluoroalkylated oligomers; surface tension; cationic surfactants)

Recently, there has been great interest in single-chain and double-chain ammonium salt amphiphiles which possess long alkyl chains, in particular long perfluoroalkyl chains in the hydrophobic portion, owing to their ability to form stable bilayer membranes in water[1]. Perfluoroalkyl amphiphiles are known to have unique properties, such as greater hydrophobicity, constrained conformational states and chemical inertness, that set them apart from more common hydrocarbon surfactants[1]. In general, the introduction of perfluoroalkyl groups into hydrocarbon moieties is not easy, since the usual alkylations cannot be applied to perfluoroalkylation due to the high electronegativity of fluorine. Thus, the perfluoroalkyl groups are introduced into such amphiphiles through the amide or ester bond, and these materials are in general unstable under acid or alkaline conditions. Hence, the synthesis of single- or double-chain fluoroalkylated cationic amphiphiles with carbon–carbon bond formation has been the subject of considerable research of both a fundamental and applied nature.

In the course of our comprehensive studies on the fluorinated organic peroxides[2,3], we have succeeded in preparing a series of vinylsilane[4], acrylic acid[5], allyl alcohol[6] and vinyl alcohol[7] oligomers containing two fluoroalkylated end-groups by using fluoroalkanoyl peroxides as the key materials. These oligomers were shown to exhibit unique properties imparted by fluorine, although these compounds are oligomeric (high molecular mass) materials. In addition, these fluoroalkylated oligomers have interesting structures: they are considered as new double-chain oligomeric materials possessing fluoroalkyl groups. From the viewpoint of investigating new cationic surfactants containing fluoroalkyl groups, it is of much interest to synthesize novel cationic oligomers containing fluoroalkylated end-groups using fluoroalkanoyl peroxides. We have found that fluoroalkanoyl peroxides react with allyl- and diallylammonium chlorides (AL-Am and DAL-Am) to afford the corresponding cationic oligomers containing two fluoroalkylated end-groups [R_F–(AL-Am)$_n$–R_F, R_F–(DAL-Am)$_n$–R_F] (*Scheme 1*), and these oligomers were shown to be



Scheme 1

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Table 1 Reactions of fluoroalkanoyl peroxides with allyl- and diallylammonium clorides

R_F in peroxide (mmol)	AL-Am or DAL-Am (mmol)	Product	
		Yield (%)[a]	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)
	AL-Am		R_F-(AL-Am)$_n$-R_F
C_3F_7 (9)	43	1	2050 (1.43)
C_3F_7 (6)	59	1	3210 (1.63)
$CF(CF_3)OC_3F_7$ (9)	43	6	1900 (1.82)
$CF(CF_3)OC_3F_7$ (8)	76	10	2640 (1.72)
$CF(CF_3)OC_3F_7$ (8)	114	12	3200 (1.71)
$CF(CF_3)OC_3F_7$ (8)	152	14	3200 (1.72)
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (9)	43	10	1300 (2.13)
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (9)	64	12	1630 (2.34)
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (4)	61	17	2220 (1.71)
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (4)	81	10	2530 (1.84)
	DAL-Am		R_F-(DAL-Am)$_n$-R_F
C_3F_7 (3)	44	trace	–
$CF(CF_3)OC_3F_7$ (9)	43	29	1320 (1.69)
$CF(CF_3)OC_3F_7$ (4)	43	21	1500 (2.15)
$CF(CF_3)OC_3F_7$ (4)	58	21	1550 (2.25)
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (2)	10	44	1420 (2.22)
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (2)	20	11	1430 (2.07)
$CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (2)	41	22	2330 (2.99)

[a] The yields were based on the starting materials (allyl- or diallylammonium chloride and the decarboxylated peroxide unit, R_F–R_F)

applicable as new double-chain surfactants possessing fluoroalkyl groups. The results are described herein.

A typical experiment for the synthesis of fluoroalkylated allylammonium chloride oligomers is as follows. Perfluoro-2,5-dimethyl-3,6-dioxanonanoyl peroxide (9 mmol) in freon 113 ($CF_2ClCFCl_2$) solution (100 g) was added to the aqueous solution (50%, w/w) of allylammonium chloride (43 mmol). The heterogeneous solution was stirred vigorously at 45°C for 5 h under nitrogen. After evaporating the solvent, the obtained crude product was reprecipitated from the water–methanol system to give bis(perfluoro-1,4-dimethyl-2,5-dioxaoctylated) allylammonium chloride oligomers (1.20 g). This oligomer showed the following spectral data: i.r. ν (cm^{-1}) 3440, 3043, 1604 (NH_3^+), 1306 (CF_3), 1242 (CF_2); ^{19}F n.m.r. (D_2O, ext. CF_3CO_2H) δ -3.60 to -8.20 (26F), -57.1 (6F), -68.52 (2F); ^1H n.m.r. (D_2O) δ 1.22–1.78 (-CH_2-), 1.81–2.13 (=CH-), 2.80–3.22 (-CH_2); average molar mass ($\bar{M}_n$) = 1300, $\bar{M}_w/\bar{M}_n = 2.13$ (determined by gel permeation chromatography calibrated with standard poly(ethylene glycol) by using 30% acetonitrile solution containing 0.5 M acetic acid and 0.5 M sodium acetate as the eluent). Other fluoroalkylated allylammonium chloride oligomers were obtained under similarly mild conditions.

We also succeeded in preparing a series of fluoroalkylated diallylammonium chloride oligomers possessing five-membered ring structures by the reactions of diallylammonium chloride with fluoroalkanoyl peroxides under conditions similar to those used with allylammonium chloride. (For instance, bis(perfluoro-1,4-dimethyl-2,5-dioxaoctylated) diallylammonium chloride oligomers ($\bar{M}_n = 2330$), which were obtained by the reaction of diallylammonium chloride with perfluoro-2,5-dimethyl-3,6-dioxanonanoyl peroxide, showed the following spectral data: i.r. ν (cm^{-1}) 3440, 2940, 1625 (NH_3^+), 1308 (CF_3), 1246 (CF_2); ^{19}F n.m.r. (D_2O, ext. CF_3CO_2H) δ -2.94 to -7.35 (26F), -52.68 (6F), -68.20 (2F); ^1H n.m.r. (D_2O) δ 0.92–1.80 (-CH_2-), 1.92 (br s, =CH- (ring, *trans*)), 2.33 (br s, =CH- (ring, *cis*)), 2.81–3.18 (-CH_2- (ring, *cis/trans*)), 3.30–3.61 (-CH_2- (ring, *cis/trans*)). These data support the five-membered ring formation. In addition, it was shown by using electron spin resonance that cyclopolymers possessing five-membered ring structures are formed by the free-radical head–head cyclopolymerization of diallylamine derivatives[8,9]. Recently, Yang and Engberts[10] also reported that poly(alkylmethyldiallylammonium bromides) possessing five-membered ring structures are obtained by free-radical head–head cyclopolymerization of alkylmethyldiallylammonium bromides in aqueous solution by using t-butyl hydroperoxide or ammonium persulfate as the radical initiator. These results indicate that the presence of six-membered ring structures, which would be obtained by free-radical head–tail cyclopolymerization of diallylamine derivatives, in the macromolecule should be ruled out.) The ^1H n.m.r. spectra of these fluoroalkylated oligomers showed no allyl resonances. The results for the reactions of fluoroalkanoyl peroxides with AL-Am and DAL-Am are listed in *Table 1*.

As shown in *Table 1*, perfluoro-oxaalkylated allyl- and diallylammonium chloride oligomers were obtained in 6–44% isolated yields; however, perfluoropropylated allyl- and diallylammonium chloride oligomers were obtained in very low isolated yields (~1%). Previously, we reported that the decomposition of perfluorobutyryl peroxide [$(C_3F_7COO)_2$] is remarkably accelerated by the addition of water[11,12]. This indicates that under our aqueous oligomeric conditions, the hydrolysis of perfluorobutyryl peroxide should occur preferentially to

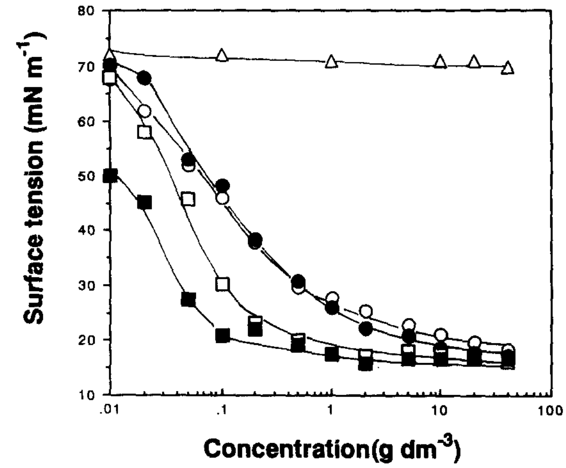

Figure 1 Surface tension of aqueous solutions of [R_F–(AL-Am)$_n$–R_F] and [R_F–(DAL-Am)$_n$–R_F]: △, poly(allylammonium chlorides) ($\bar{M}_n = 11\,000$); ○, R_F–(AL-Am)$_n$–R_F, $R_F = CF(CF_3)OC_3F_7$ ($\bar{M}_n = 1900$); ●, R_F–(AL-Am)$_n$–R_F, $R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ ($\bar{M}_n = 1300$); □, R_F–(DAL-Am)$_n$–R_F, $R_F = CF(CF_3)OC_3F_7$ ($\bar{M}_n = 1320$); ■, R_F–(DAL-Am)$_n$–R_F, $R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ ($\bar{M}_n = 1420$)

oligomerization with peroxide. On the other hand, perfluoro-oxaalkanoyl peroxides are suggested to have strong repulsion for water owing to longer perfluoro-oxaalkyl groups {$CF(CF_3)O[CF_2CF(CF_3)O]_mC_3F_7$, $m = 0, 1$}. Thus, the oligomerization with these peroxides should be the predominant process in comparison with the hydrolysis of peroxides. The molecular masses of the oligomers depended upon the molar ratio of AL-Am or DAL-Am to peroxide, increasing slightly with higher ratios as is usual for radical oligomerization. In addition, it is suggested that under our oligomeric conditions, in which the concentration of the peroxide was almost the same as that of AL-Am or DAL-Am (molar ratio of AL-Am (DAL-Am)/peroxide = 5–21), mainly oligomers with two fluoroalkyl groups would be obtained via primary radical termination or radical chain transfer to the peroxide, as in the cases of our previously reported fluoroalkylated acrylic acid[5,13], vinylsilane[4], allyl alcohol[6] and vinyl alcohol[7] oligomers.

Fluoroalkylated allylammonium chloride oligomers [R_F–(AL-Am)$_n$–R_F] thus obtained were shown to be easily soluble in water. On the other hand, fluoroalkylated diallylammonium chloride oligomers [R_F–(DAL-Am)$_n$–R_F] were easily soluble not only in water but also in water-soluble organic solvents such as methanol, ethanol and dimethylsulfoxide. Thus, these fluoroalkylated oligomers are expected to be useful as new cationic oligosurfactants containing fluoroalkyl groups. In fact, the surface properties of these fluoroalkylated cationic oligomers were evaluated by measuring the reduction of surface tension of aqueous solutions by the fluorinated oligomers using the Wilhelmy plate method at 25°C. These results are listed in *Figure 1*.

As *Figure 1* shows, a significant decrease in the surface tension of water, to around 10 mN m^{-1}, was found for perfluoro-oxaalkylated oligomers compared with non-fluorinated poly(allylammonium chlorides). Thus, these fluoroalkylated oligomers are novel high-molecular-mass cationic surfactants which can reduce the surface tension of water effectively. In general, hydrophobically modified polyelectrolytes have been characterized as 'polysoaps'[14]. Polysoap solutions are known to exhibit a continuous decrease of surface tension with increasing concentration, as do the low-molecular-weight surfactants; however, no critical micelle concentration (*CMC*) or a break point resembling a *CMC* is observed in these polymers[14]. On the other hand, in our fluoroalkylated cationic oligomers, a break point was observed, as shown in *Figure 1*. This finding is an interesting feature in the oligomeric surfactants containing fluoroalkyl groups. It has been proposed that the structure of 'polymeric micelles' formed by polysoaps is classified into three major models: 'local micelle', 'regional micelle' and 'molecular micelle'[14]. A particular feature of our fluorinated allyl- or diallylammonium chloride oligomers in water cannot be explained in detail at the present time. However, our new fluorinated cationic oligomers are expected to be able to develop into the field of new oligomeric surfactants since these oligomers can significantly reduce the surface tension of water to around 10 mN m^{-1}. Further investigations of the synthesis and properties of fluorinated cationic oligomers with fluoroalkanoyl peroxides are now in progress.

References

1 Kunitake, T. *Angew. Chem. Int. Edn Engl.* 1992, **31**, 709
2 Sawada, H. and Kobayashi, M. *Yuki Gosei Kagaku Kyokaishi* 1986, **44**, 600
3 Sawada, H. 'Reviews on Heteroatom Chemistry' (Ed. S. Oae), Myu, Tokyo, 1993, Vol. 8, p. 205
4 Sawada, H. and Nakayama, M. *J. Chem. Soc., Chem. Commun.* 1991, 677
5 Sawada, H., Gong, Y.-F., Minoshima, Y., Matsumoto, T., Nakayama, M., Kosugi, M. and Migita, T. *J. Chem. Soc., Chem. Commun.* 1992, 537
6 Sawada, H., Tanba, K., Oue, M., Kawase, T., Mitani, M., Minoshima, Y., Nakajima, H., Nishida, M. and Moriya, Y. *Polymer* 1994, **35**, 4028
7 Sawada, H., Yamaguchi, K., Mitani, M., Nakajima, H., Nishida, M. and Moriya, Y. *Polymer* 1994, **35**, 444
8 Solomon, D. H. *J. Macromol. Sci. – Chem.* 1975, **A9**, 97
9 Beckwith, A. L. J., Ong, A. K. and Solomon, D. H. *J. Macromol. Sci. – Chem.* 1975, **A9**, 115
10 Yang, Y.-J. and Engberts, B. F. N. *J. Org. Chem.* 1991, **56**, 4300
11 Sawada, H., Nakayama, M., Yoshida, M. and Kamigata, N. *J. Jpn Oil Chem. Soc.* 1989, **38**, 577
12 Yoshida, M., Kobayashi, M., Sawada, H., Hagii, H. and Aoshima, K. *Nippon Kagaku Kaishi* 1985, 1958
13 Sawada, H., Minoshima, Y. and Nakajima, H. *J. Fluorine Chem.* 1993, **65**, 169
14 Anton, P., Koberle, P. and Laschewsky, A. *Makromol. Chem.* 1993, **194**, 1