Synthesis and surfactant properties of novel fluoroalkylated amphiphilic oligomers

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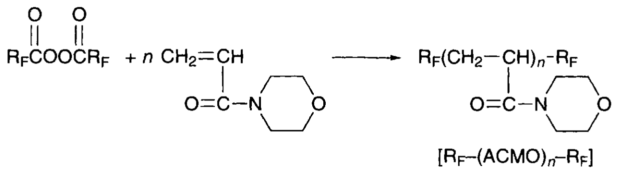
New fluoroalkylated oligomers containing morpholino groups are prepared by the reactions of fluoroalkanoyl peroxides with acryloyl morpholine; these oligomers show a good solubility in not only water but also common organic solvents, including non-polar solvents, and are applicable to non-ionic fluorinated amphiphilic oligosurfactants owing to reducing the surface tension of both water and in particular *m*-xylene quite effectively.

Fluorinated polymeric materials are well known to exhibit various unique properties imparted by fluorine which cannot be achieved by the corresponding non-fluorinated materials. However, these fluorinated materials in general exhibit an extremely poor solubility in organic solvents.[1] On the other hand, it has been recently demonstrated that partially protonated ring-containing fluoropolymers become soluble in polar aprotic solvents such as acetone, acetonitrile, dimethylformamide and tetrahydrofuran although these polymers are insoluble in benzene, chloroform, and methanol.[2] Therefore, the preparation of fluoroalkylated polymeric materials which have relatively high solubility in both water and common organic solvents (including non-polar organic solvents) will open a new route to the development of the field of new functional fluorinated materials. We have been actively studying the development of fluoroalkylated oligomers by using fluoroalkanoyl peroxides as key materials.[3] Very recently, we have found that a series of fluoroalkylated acrylic acids, and allyl- or diallyl-ammonium chloride oligomers are soluble in both water and water-soluble polar solvents such as methanol, despite being oligomeric (high molecular mass) materials.[4] From the viewpoint of the development of novel fluoroalkylated amphiphiles which show good solubility in both water and common organic solvents, including non-polar solvents, we were interested in preparing fluoroalkylated oligomers containing morpholino groups which should give good solubility.

A typical experiment for the synthesis of fluoroalkylated oligomers was as follows (Scheme 1); perfluoro-2-methyl-3-oxahexanoyl peroxide (5 mmol) in 1,1-dichloro-2,2,3,3,3-pentafluoropropane–1,3-dichloro-1,2,2,3,3-pentafluoropropane (1 : 1, 35 g, AK-225[5]) was added to a mixture of acryloyl morpholine (24 mmol) and AK-225 (50 g). The solutions was stirred at 45 °C for 5 h under nitrogen. After evaporating the solvent, the crude products were reprecipitated from AK-225–hexane to give bis(perfluoro-1-methyl-2-oxapentyl) acryloyl morpholine oligomers (4.55 g). This oligomer showed the following spectral data: IR ν/cm^{-1} 1633(C=O), 1320(CF$_3$), 1238(CF$_2$), 1115(–O–); ^{1}H NMR (CDCl$_3$) δ 1.46–1.92 (CH$_2$), 2.34–2.76 (CH), 3.18–3.93 (CH$_2$); ^{19}F NMR (CDCl$_3$, ext. CF$_3$CO$_2$H) δ −7.24 to −9.89 (16 F), −54.65 (6 F); average molar mass ($\bar{M}_\mathrm{n}$) = 1860, $\bar{M}_\mathrm{w}/\bar{M}_n$ = 1.41 [determined by gel permeation chromatography (GPC) calibrated with standard polystyrenes by using tetrahydrofuran as the eluent].

As listed in Table 1, a series of fluoroalkylated oligomers containing morpholino groups were obtained in moderate to excellent isolated yields. Especially, the molecular masses of the longer perfluorooxaalkylated oligomers were shown to become higher. Under the oligomerization conditions employed in which the concentration of the peroxide is almost the same as that of acryloyl morpholine, acryloyl morpholine oligomers with two fluoroalkyl groups would be mainly obtained *via* a primary radical termination or a radical chain transfer to the peroxide as observed in our previously reported oligomerizations of vinylsilane[6] and acrylic acid oligomers[4a] containing two terminal fluoroalkyl groups [R$_\mathrm{F}$(CH$_2$CHR)$_n$R$_\mathrm{F}$; R = Si(R′)$_3$, CO$_2$H] by the use of fluoroalkanoyl peroxides. The obtained products are polydispersant mixtures of oligomers as indicated in Table 1 ($\bar{M}_\mathrm{w}/\bar{M}_n$ > 1), and the relative molecular masses of the fluoroalkylated acryloyl morpholine oligomers obtained by GPC using polystyrene calibration are only approximate.

Interestingly, the fluoroalkylated acryloyl morpholine oligomers showed good solubility in water. The oligomers also show solubility in not only polar organic solvents such as methanol, ethanol, tetrahydrofuran, dimethyl sulfoxide, *N,N*-dimethylformamide, chloroform, ethyl acetate and dichloro-



R$_\mathrm{F}$ = C$_3$F$_7$, CF(CF$_3$)O[CF$_2$CF(CF$_3$)O]$_m$C$_3$F$_7$; *m* = 0, 1, 2

Scheme 1 Preparation of fluoroalkylated oligomers

Table 1 Reactions of fluoroalkanoyl peroxides with acryloyl moropholine (ACMO)

R$_\mathrm{F}$ in peroxide (mmol)	ACMO (mmol)	Product: R$_\mathrm{F}$–(ACMO)$_n$–R$_\mathrm{F}$	
		Yield (%)[a]	$\bar{M}_n(\bar{M}_\mathrm{w}/\bar{M}_n)$
C$_3$F$_7$ (5)	24	83	1700 (1.59)
CF(CF$_3$)OC$_3$F$_7$ (5)	24	73	1860 (1.41)
CF(CF$_3$)OCF$_2$CF(CF$_3$)OC$_3$F$_7$ (7)	37	57	4730 (1.50)
CF(CF$_3$)O[CF$_2$CF(CF$_3$)O]$_2$C$_3$F$_7$ (5)	24	60	7290 (2.42)

[a] The yields are based on the starting materials (acryloyl moropholine and the decarboxylated peroxide unit (R$_\mathrm{F}$–R$_\mathrm{F}$).

methane, but also in non-polar aromatic solvents such as benzene, toluene and xylene as well as in tetrachloromethane. However, these fluoroalkylated oligomers showed poor solubility in aliphatic solvents such as hexane. Furthermore, these oligomers show general characteristics of non-ionic surfactants, for instance, bis(perfluoro-1-methyl-2-oxapentyl) acryloyl morpholine oligomers was shown to have a cloud point around 45 °C. Usually, fluorinated materials possess only limited solubility in various solvents, and this remarkable improvement in their solubility is of clear importance.[1,2,7] For example, fluoroalkylated vinylsilane oligomers $\{R_F\text{–}[CH_2CHSi(R)_3]_n\text{–}R_F;\ R_F = \text{Me, OMe}\}$ prepared by using fluoroalkanoyl peroxides, are in general only soluble in fluorinated solvents,[6] while fluoroalkylated acrylic acid oligomers $[R_F\text{–}(CH_2CHCO_2H)_n\text{–}R_F]$ have been shown to be soluble in water and water-soluble polar solvents such as methanol and tetrahydrofuran but not in non-polar aromatic solvents.[4a]

In order to clarify the surfactant properties of our new fluoroalkylated oligomers, we measured the surface tension of aqueous and *m*-xylene solutions using the Wilhelmy plate method at 30 °C. These results are shown in Fig. 1 and 2.

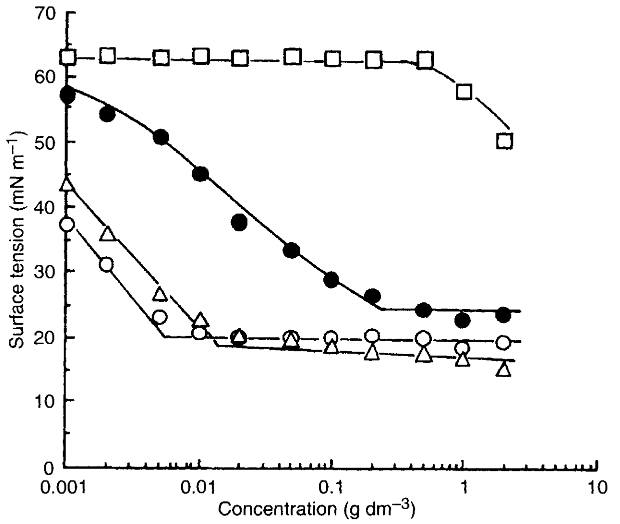


Fig. 1 Surface tensions of aqueous solutions of $R_F\text{–}(ACMO)_n\text{–}R_F$: (●), $R_F = C_3F_7$ ($\bar{M}_n$ = 1700); (○), $R_F = CF(CF_3)OC_3F_7$ ($\bar{M}_n$ = 1860); (△) $R_F = CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ ($\bar{M}_n$ = 7290) and (□) $\text{–}(ACMO)_n\text{–}$ ($\bar{M}_n$ = 3750, ($\bar{M}_w/\bar{M}_n$ = 1.99)

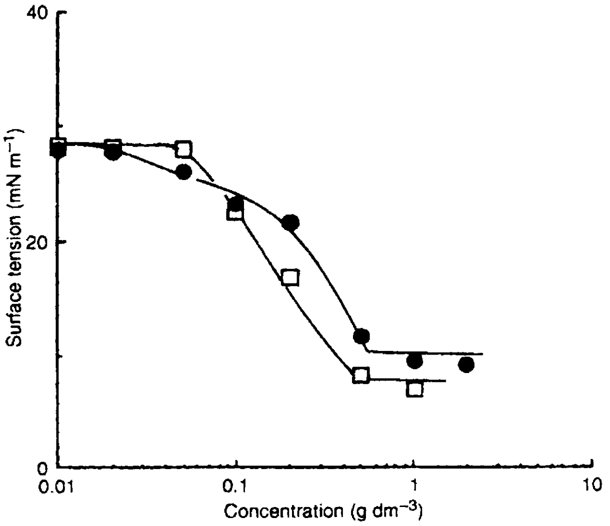


Fig. 2 Surface tension of *m*-xylene solutions of $R_F\text{–}(ACMO)_n\text{–}R_F$: (□) $R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ ($\bar{M}_n$ = 4730); (●) $R_F = CF(CF_3)OCF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ ($\bar{M}_n$ = 7290)

As shown in Fig. 1, a significant decrease in the surface tension of water, to around 20 mN m^{-1}, was observed for each fluoroalkylated acryloyl morpholine oligomer in contrast to the corresponding non-fluorinated oligomer. Especially, perfluorooxaalkylated oligomers are more effective in reducing the surface tension of water than the perfluoropropyl oligomer. In addition, each fluoroalkylated acryloyl morpholine oligomer exhibited a clear break point resembling a CMC (critical micelle concentration). This finding is unique and is an interesting feature in our fluoroalkylated non-ionic oligosurfactants and also suggests the formation of intra- or inter-molecular aggregates in aqueous solutions, although it has been recently reported that hydrocarbon polysoap solutions have no CMC or a break point resembling a CMC.[8]

Of additional interest, it was found that these oligomers were able to reduce the surface tension of *m*-xylene quite effectively to *ca.* 7–9 mN m^{-1} as shown in Fig. 2.

Previously, we found that fluoroalkylated, and especially, perfluorooxaalkylated benzenes (R_F–Ph; R_F = perfluoroalkyl, perfluorooxaalkyl groups) are able to reduce the surface tension of *m*-xylene to *ca.* 10 mN m^{-1}.[9] Thus, our partially fluoroalkylated oligomers were demonstrated to behave almost the same effectiveness as low molecular-weight perfluorooxaalkylated benzene surfactants. Surfactants possessing longer perfluorooxaalkyl groups showed a break at a specific surfactant concentration (0.5 g dm^{-3}), above which the surface tension remains nearly constant (Fig. 2). This finding suggests that our new fluoroalkylated oligomers could form intra- or inter-molecular aggregates in *m*-xylene solution resembling a reverse micelle of low molecular-mass amphiphiles.

To our knowledge, this is the first example in which polymeric compounds effectively reduce the surface tension of both water and *m*-xylene to levels of 15 and 7–9 mN m^{-1}, and respectively, and to aggregates resembling normal and reverse micelles in water and organic solvents, respectively. Further investigations of the synthesis and properties of fluoroalkylated acryloyl morpholine oligomers possessing unique surfactant behaviour are actively in progress.

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References

1 L. A. Wall, *Fluoropolymers*, Wiley, New York, 1972, vol. XXV.
2 Z.-Y. Yang, A. E. Feiring and B. E. Smart, *J. Am. Chem. Soc.*, 1994, **116**, 4135.
3 H. Sawada, *J. Fluorine Chem.*, 1993, **61**, 253 and references therein.
4 (*a*) H. Sawada, Y.-F. Gong, Y. Minoshima, T. Matsumoto, M. Nakayama, M. Kosugi and T. Migita, *J. Chem. Soc., Chem. Commun.*, 1992, 537; (*b*) H. Sawada, K.-i. Tanba, M. Oue, T. Kawase, Y. Hayakawa, M. Mitani, Y. Minoshima, M. Nishida and Y. Moriya, *Polymer*, 1995, **43**, 2103.
5 Very recently, we have demonstrated that AK-225 is a suitable alternative solvent to 1,1,2-trichloro-1,2,2-trifluoroethane for the preparation and reactions of a series of fluoroalkanoyl peroxides; H. Sawada, M. Mitani and Y. Moriya, *J.Jpn. Res. Institute Mater. Technol.*, 1995, **13**, 47; H. Sawada, M. Mitani, Y. Minoshima, H. Nakajima, M. Nishida and Y. Moriya, *J. Jpn. Res. Institute Mater. Technol.*, 1995, **13**, 212.
6 H. Sawada and M. Nakayama, *J. Chem. Soc., Chem. Commun.*, 1991, 677.
7 D. P. Carlson and W. Schmiegel, *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, New York, 1988, vol. A11, p. 393.
8 P. Anton, P. Koberle and A. Laschewsky, *Makromol. Chem.*, 1993, **194**, 1.
9 M. Abe, K. Morikawa, K. Ogino, H. Sawada, T. Matsumoto and M. Nakayama, *Langmuir*, 1992, **8**, 763.

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