Synthesis and Surfactant Properties of Fluoroalkylated Oligomers Containing Carboxy Groups

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The reactions of acrylic acid with various of difluoroalkanoyl peroxides {$(R_fCO_2)_2$, R_f = C_3F_7, C_6F_{13}, $CF(CF_3)[OCF_2CF(CF_3)]_mOC_3F_7$, m = 0, 1, 2} have been found to give new fluoroalkylated oligomers containing carboxy groups {$R_f[CH_2CH(CO_2H)]_nR_f$} under mild conditions, and these compounds are able to reduce the surface tension of water to 10 mN m^{-1} levels.

Recently, there has been great interest in organofluorine compounds due to the unique physical properties such as water- and oil-repellency, low surface energy, high chemical and light resistance, high affinity for oxygen and bioinactivity imparted by fluorine.[1] Much effort has been especially focused on the synthesis and surfactant properties of long-chain fluorinated amphiphiles such as perfluoroalkyl-polyoxyethylenes, in which the hydrophobic tail is a chemically relatively non-reactive perfluoroalkyl chain and the hydrophilic head is a polyoxyethylene unit.[2,3] It has been shown that a Williamson-type condensation between a fluoroalcohol ($C_mF_{2m+1}CH_2OH$) and ethylene oxide is a convenient strategy for the synthesis of these compounds. However, preparative methods for these fluorinated amphiphiles have hitherto been limited but these compounds have been the subject of considerable research of both a fundamental and applied nature. We have been studying the reaction behaviour of a series of difluoroalkanoyl peroxides; {$R_fCO_2O_2CR_f$, R_f = CF_3, C_2F_5, C_3F_7, C_6F_{13}, C_7F_{15}, $CF(CF_3)[OCF_2CF(CF_3)]_n$-$OC_3F_7$, n = 0, 1, 2}, which are useful reagents for the introduction of fluoroalkyl groups into arenes,[4] vinylsilanes,[5] or allylsilanes.[6] It is of interest to synthesize new fluorinated amphiphiles using difluoroalkanoyl peroxides. In this communication, we report the synthesis and surfactant properties of new fluoroalkylated oligomers containing carboxy groups by the reactions of acrylic acid with difluoroalkanoyl peroxides.

A typical experiment for the synthesis of fluoroalkylated oligomers containing carboxy groups is as follows. Diperfluoro-2-methyl-3-oxa-hexanoyl peroxide (236 mmol) in Freon 113 ($CF_2ClCFCl_2$) solution (1000 g) was added to a mixture of acrylic acid (566 mmol) and Freon 113 (500 g). The solution was stirred at 35 °C for 5 h under nitrogen, and the resulting white powder was reprecipitated from methanol–ethyl acetate to give bis(perfluoro-1-methyl-2-oxa-pentylated) oligomers containing carboxy groups (78.6 g). This oligomer mixture showed the following spectral data: IR ν/cm^{-1} 3200 (OH), 1720 (C=O), 1330 (CF_3), 1235 (CF_2); ^{19}F NMR (CD_3OD, ext. CF_3CO_2H) δ −2.12–−8.91 (16F), −54.30 (6F); ^{1}H NMR (CD_3OD) δ 1.35–2.19 (–CH_2–), 2.21–2.72 (–CH–); average molar mass ($\bar{M}_n$) = 12000, $\bar{M}_w/\bar{M}_n$ = 1.96 [determined by gel permeation chromatography (GPC) calibrated with standard polystyrenes]. Similarly, the reactions of acrylic acid with some other difluoroalkanoyl peroxides were carried out, and the results are summarized in Table 1.

As shown in Table 1, it was clarified that bis(perfluoro-1,4-dimethyl-2,5-dioxa-octylated), bis(perfluoro-1,4,7-trimethyl-2,5,8-trioxa-undecylated), bis(perfluorohexylated) and bis-(perfluoropropylated) acrylic acid oligomers were obtained in similar isolated yields under mild conditions. The products obtained are polydispersant mixtures of oligomers as indicated by Table 1 ($\bar{M}_w/\bar{M}_n$ >1), and the relative molecular masses of acrylic acid oligomers obtained by GPC using a polystyrene calibration will only be approximate averages. The reactions of acrylic acid with difluoroalkanoyl peroxides

$$n\,CH_2{=}CHCO_2H + R_fCOOCR_f \xrightarrow[CF_2ClCFCl_2]{35\,^\circ C,\ 5\ h} R_f{-}(CH_2{-}\underset{CO_2H}{CH})_n{-}R_f + CO_2$$

R_f = C_3F_7, C_6F_{13}, $CF(CF_3)[OCF_2CF(CF_3)]_mOC_3F_7$, m = 0, 1, 2

Table 1 Reactions of acrylic acid with difluoroalkanoyl peroxides

Run	Acrylic acid/mmol	R_f in $(R_fCO_2)_2$/ mmol	Isolated yield (%)[a]	$\bar{M}_n(\bar{M}_w/\bar{M}_n)$
1	17	$CF(OCF_2CF)_2OC_3F_7$ CF_3 CF_3 (6.8)	29	12800 (1.72)
2	120	$CFOCF_2CFOC_3F_7$ CF_3 CF_3 (50)	34	11200 (1.54)
3	566	$CFOC_3F_7$ CF_3 (236)	45	12000 (1.54)
4	204	C_3F_7 (95)	39	5100 (1.47)
5	69	C_6F_{13} (29)	26	4600 (1.43)

[a] The yields are based on the starting materials [acrylic acid and the decarboxylated peroxide unit (R_f–R_f)].

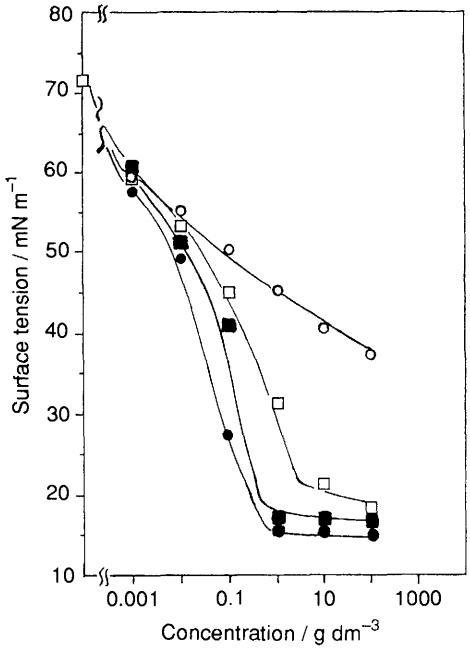

Fig. 1 Surface tensions of aqueous solutions of bis(fluoroalkylated) acrylic acid oligomers {R_f–$[CH_2$–$CH(CO_2H)]_n$–R_f}: ○ polyacrylic acid†; □ R_f = C_3F_7 ($\bar{M}_n$ = 5100); ■ R_f = C_6F_{13} ($\bar{M}_n$ = 4600); ● R_f = $CF(CF_3)OC_3F_7$ ($\bar{M}_n$ = 12000).

† Commercially available polyacrylic acid was used.

were considered to proceed by the usual radical addition to acrylic acid of fluoroalkyl radicals produced by the thermal decomposition of peroxides. Some of the oligomeric products could contain only one fluorinated end-group per molecule (assuming free radical additions) with $\bar{M}_w/\bar{M}_n > 1.5$. The bis(fluoroalkylated) acrylic acid oligomers have been shown to be soluble in the solvents such as water, methanol, ethanol and tetrahydrofuran. The surfactant properties of the fluorinated oligomers were evaluated by surface tension measurements of their aqueous solutions at 25 °C. The effect of varying the concentration of these compounds on surface tension is shown in Fig. 1.

The decrease in the surface tension of water was found for both bis(perfluoroalkylated) and bis(perfluoro-oxa-alkylated) acrylic acid oligomers. Notably, it is observed that the oligomer bearing perfluoro-oxa-alkyl groups is a novel high molecular mass surfactant which can reduce the surface tension of water. This property could be dependent upon the flexibility of perfluoro-oxa-alkyl group owing to the ether linkage. To our knowledge, this is the first example which shows that the oligomeric (high molecular mass) compounds can reduce the surface tension of water to 10 mN m^{-1} levels.

Further investigations of the synthesis and properties of a series of fluoroalkylated oligomers containing functional groups are now in progress.

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References

1 R. E. Banks, *Organofluorine Chemicals and their Industrial Application*, Ellis Horwood, London, 1979.
2 G. Mathis, P. Leempoel, J.-C. Ravey, C. Selve and J.-J. Delpuech, *J. Am. Chem. Soc.*, 1984, **106**, 6162; C. Selve and S. Achiiefu, *J. Chem. Soc., Chem. Commun.*, 1990, 911.
3 I. Rico, A. Lattes, K. P. Das and B. Lindman, *J. Am. Chem. Soc.*, 1989, **111**, 7266; M. Gautier, I. Rico and A. Lattes, *J. Org. Chem.*, 1990, **55**, 1500.
4 H. Sawada, M. Nakayama, M. Yoshida, T. Yoshida and N. Kamigata, *J. Fluorine Chem.*, 1990, **46**, 423; H. Sawada and M. Nakayama, *J. Fluorine Chem.*, 1991, **51**, 117.
5 H. Sawada and M. Nakayama, *J. Chem. Soc., Chem. Commun.*, 1991, 677.
6 H. Sawada, Y.-F. Gong, T. Matsumoto, M. Nakayama, M. Kosugi and T. Migita, *J. Jpn. Oil. Chem. Soc.*, 1991, **40**, 730.