Synthesis of fluoroalkylated *N*-vinyl-2-pyrrolidone–acrylic acid cooligomers from fluoroalkanoyl peroxides; a receptor for binding free calcium ions

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New fluoroalkylated *N*-vinyl-2-pyrrolidone–acrylic acid cooligomers are prepared by treating fluoroalkanoyl peroxides with *N*-vinyl-2-pyrrolidone (NVP) and acrylic acid (ACA); these fluoroalkylated cooligomers reduce the surface tension of water and have a high calcium ion binding power compared to traditional organic chelating agents.

It is well-known that organic chelating agents such as EDTA (ethylenediaminetetraacetic acid), phosphates and polyelectrolytes such as poly(acrylic acid) and poly(maleic acid) are effective in removing free multivalent ions from solution.[1] Recently much attention has focused on chelactants (chelating surfactants such as lauroyl ethylenediaminetriacetate) which combine the properties of strong surfactancy and an ability to chelate multivalent ions.[2] Organofluorine compounds often show various unique properties such as water- and oil-repellency, low surface energy and high chemical and light resistance; the corresponding non-fluorinated compounds do not exhibit these properties.[3] We were thus particularly interested in developing fluoroalkylated chelating surfactants.

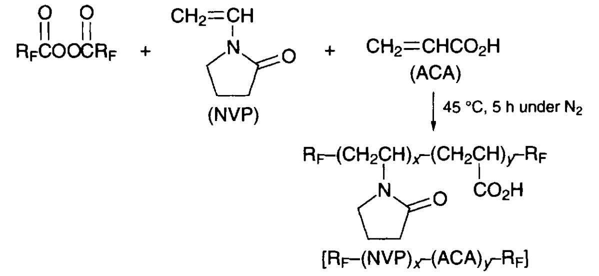
We have recently prepared a series of vinylsilane,[4] acrylic acid,[5] allyl alcohol[6] and allylamine[7] oligomers containing two fluoroalkylated end-groups using fluoroalkanoyl peroxides. These compounds were shown to possess unique properties imparted by fluorine, although they are oligomeric (high molecular mass). Here we report the synthesis and properties of new fluoroalkylated chelating oligosurfactants containing moieties that enable them to be used as chelating agents with fluoroalkanoyl peroxides.

Firstly we were interested in preparing fluoroalkylated pyrrolidone oligomers possessing the amino and carbonyl moieties. Compounds bearing such moieties are able to chelate. We attempted the preparation of the fluoroalkylated pyrrolidone oligomers by treating fluoroalkanoyl peroxides with *N*-vinyl-2-pyrrolidone, an excellent, well-known radical polymerizable monomer. We were not able to isolate the expected oligomers; however, the substituted compounds of the R_F group to the β-carbon of *N*-vinyl-2-pyrrolidone were mainly obtained *via* the single electron transfer from *N*-vinyl-2-pyrrolidone to the peroxide. We have already reported a similar electron transfer in the reactions of styrene with fluoroalkanoyl peroxides.[8] In the reactions of *N*-vinyl-2-pyrrolidone, the higher HOMO energy level (−9.004 eV; calculated by MNDO-PM3 semiempirical MO methods with the MOPAC 5.0 program) would cause an electron transfer as in styrene (−9.132 eV). It was therefore suggested that the oligomerization with fluoroalkanoyl peroxide could proceed by lowering the HOMO energy level of *N*-vinyl-2-pyrrolidone. Thus, we tried to use acrylic acid as an acidic comonomer in the above reaction system. As shown in Scheme 1, the cooligomerization with fluoroalkanoyl peroxides proceeded under very mild conditions to afford the expected fluoroalkylated *N*-vinyl-2-pyrrolidone-acrylic acid cooligomers.

The cooligomers obtained were identified by IR, ^1H and ^{19}F NMR spectroscopy.†

As shown in Table 1, both the perfluoropropylated and perfluorooxaalkylated *N*-vinyl-2-pyrrolidone–acrylic acid cooligomers were obtained in similar isolated yields. The products obtained are polydisperse mixtures of cooligomers ($\overline{M}w/\overline{M}n$ > 1). The molecular weights of the obtained cooligomers are in general lower than those of the fluoroalkylated acrylic acid homooligomers [R_F–$(CH_2CHCO_2H)_n$–R_F; $\overline{M}n$ = *ca.* ~ 12 800].[5] This suggests that addition to acrylic acid or *N*-vinyl-2-pyrrolidone by the propagation radical would be suppressed by the interaction of the acid (acrylic acid) and basic moiety (> N–) of *N*-vinyl-2-pyrrolidone.

The new fluoroalkylated *N*-vinyl-2-pyrrolidone-acrylic acid cooligomers were shown to be readily soluble not only in water but also in polar solvents such as methanol, ethanol, *N*,*N*-dimethylformamide and dimethyl sulfoxide. Therefore, our cooligomers can act as new fluorinated oligosurfactants containing both pyrrolidonyl and carboxyl segments. The surface



Scheme 1

Table 1 Reactions of fluoroalkanoyl peroxides with *N*-vinyl-2-pyrrolidone (NVP) and acrylic acid (ACA)

			R_F–$(NVP)_x$–$(ACA)_y$–R_F	
R_F in peroxide mmol	NVP/ mmol	ACA/ mmol	Yield (%)[a]	$\overline{M}n$ ($\overline{M}w/\overline{M}n$) [$x:y$][b]
C_3F_7 (7)	37	37	24	1130 (1.05) [37 : 63]
C_3F_7 (7)	22	27	36	2000 (1.84) [74 : 26]
$CF(CF_3)OC_3F_7$ (5)	24	24	46	1080 (1.05) [65 : 35]
$CF(CF_3)OC_3F_7$ (5)	14	24	52	1070 (1.09) [47 : 53]
$CF(CF_3)OCF_2$-$CF(CF_3)OC_3F_7$ (3)	13	13	24	2190 (2.16) [65 : 35]
$CF(CF_3)OCF_2$-$CF(CF_3)OC_3F_7$ (3)	8	13	44	2230 (2.27) [53 : 47]

[a] The yields are based on the starting materials [NVP, ACA and the decarboxylated peroxide unit (R_F–R_F)]. [b] Cooligomerization ratio was determined by ^1H NMR.

properties of these cooligomers were evaluated by measuring the reduction of the surface tension of aqueous solutions using the Wilhelmy plate method at 30 °C. These fluoroalkylated cooligomers were found to effectively decrease the surface tension of water and to exhibit a clear break point resembling a CMC (critical micelle concentration). For example, R_F–$(NVP)_x$–$(ACA)_y$–R_F [R_F = $CF(CF_3)OCF_2CF(CF_3)OC_3F_7$; $\overline{Mn}$ = 2230] reduced the surface tension from 72 to *ca.* 16 mN m^{-1} and exhibited a break point at *ca.* 0.09 mmol dm^{-3}. The surface tension of water by the corresponding non-fluorinated cooligomer [–$(NVP)_x$–$(ACA)_y$–] was decreased, reaching a minimum of *ca.* 50 mN m^{-1}. This cooligomer didn't have a break point. Recently, we reported that fluoroalkylated oligomers containing morpholino groups effectively reduce the surface tension of both water and xylene and similarly exhibit a clear break point resembling a CMC.[9] Furthermore, we measured the equilibrium calcium ion concentrations in the presence of R_F–$(NVP)_x$–$(ACA)_y$–R_F [concentration of each oligomer is 0.5 g dm^{-3}; R_F = C_3F_7 (0.25 mmol dm^{-3}), $CF(CF_3)OC_3F_7$ (0.46 mmol dm^{-3}), $CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (0.22 mmol dm^{-3})] by using a calcium ion electrode and a digital pH/ion meter (HORIBA F-23). The results are shown in Fig. 1.

As shown in Fig. 1, the fluoroalkylated cooligomers above the concentrations of the break points have an extraordinarily high calcium ion binding power compared to the corresponding non-fluorinated cooligomer: –$(NVP)_x$–$(ACA)_y$–, non-fluorinated acrylic acid oligomer: –$(CH_2CHCO_2H)_n$– and fluoroalkylated acrylic acid homo-oligomers: R_F–$(CH_2CHCO_2H)_n$–R_F. Poly(*N*-vinylpyrrolidone) [–$(NVP)_n$–; $\overline{Mn}$ = 10 000], did not show any calcium ion binding power. For example, the calcium binding ratio (Ca/A: the average number of bound calcium ions per carboxylate group in the cooligomers) of R_F–$(NVP)_x$–$(ACA)_y$–R_F [R_F = $CF(CF_3)OC_3F_7$: $\overline{Mn}$ = 1030; concentration: 0.5 g dm^{-3}] was at maximum 20. The higher calcium binding ratios were obtained in the longer fluoroalkylated cooligomers. Usually poly(acrylic acid) is effective in removing free calcium ions from solution and the binding ratio at lower concentrations is slightly higher than the theoretical binding ratio (0.5) of poly(acrylic acid) due to the electrostatic effect.[1] Furthermore, the chelating ability of chelating surfactants is in general not so high (*e.g.* the maximum calcium chelating ratio of sodium lauroyl ethylenediaminotriacetate is 190 mg $CaCO_3$ g^{-1}).[2] The ratios of our fluoroalkylated cooligomers are extraordinarily higher. Although the unique calcium binding power of the present cooligomers cannot yet be explained in detail one thought is that the cooligomers form bilayer vesicles (stable bilayer membrane), or intra- or inter-molecular aggregates resembling micelles in water as they exhibit a clear break point in aqueous solutions like low molecular weight surfactants. Also the calcium ions can act as a guest molecule for the bilayer vesicles or the inter-aggregates resembling micelles.[10] To our knowledge, this is the first example which shows that these oligomeric compounds have an extraordinarily high calcium ion binding power.

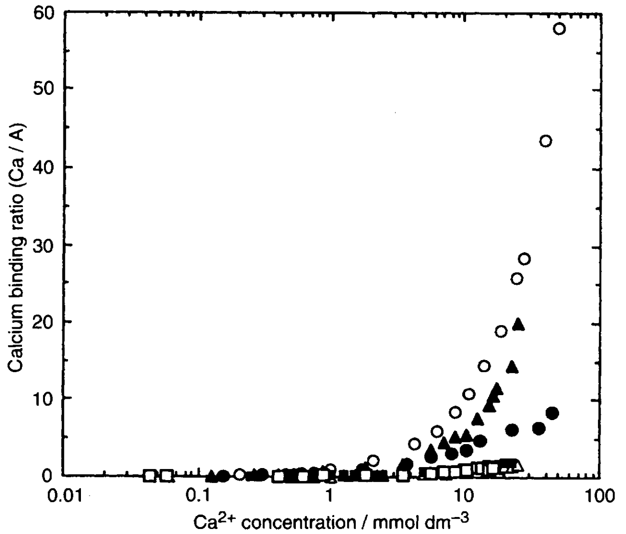


Fig. 1 Ca^{2+} binding isotherms of R_F–$(NVP)_x$–$(ACA)_y$–R_F (0.5 g dm^{-3}). ● R_F = C_3F_7 ($\overline{Mn}$ = 2000); ▲ R_F = $CF(CF_3)OC_3F_7$ ($\overline{Mn}$ = 1080); ○ R_F = $CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ ($\overline{Mn}$ = 2230); △ –$(CH_2CHCO_2H)_n$– ($\overline{Mn}$ = 2000); ■ R_F–$(CH_2CHCO_2H)_n$–R_F; R_F = $CF(CF_3)OC_3F_7$ ($\overline{Mn}$ = 6700); □ –$(NVP)_x$–$(ACA)_y$– (x:y = 62:38; $\overline{Mn}$ = 12 700).

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Footnote

† *Selected spectroscopic data* for the cooligomers [R_F = $CF(CF_3)OC_3F_7$]: IR (cm^{-1}) 3453(OH), 1722(C=O), 1647(C=O), 1296(CF_3) and 1238(CF_2); ^1H NMR (D_2O) δ 1.58–2.58 (CH_2, CH) and 3.28–3.69 (CH_2); ^{19}F NMR (D_2O, ext. CF_3CO_2H) δ −5.89–7.13 (16 F) and −57.54 (6 F); average molar mass ($\overline{Mn}$) = 1080 ($\overline{Mw}/\overline{Mn}$ = 1.05) [determined by gel permeation chromatography (GPC) calibrated with standard pullulan using 0.2 mol dm^{-3} sodium phosphate dibasic.

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