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ORIGINAL ARTICLE

Synthesis and the Structure to Property Relationship of Monoperfluoroalkyl Polyethylene Glycol

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Abstract Monoprotected polyethylene glycols (PEG) react with epichlorohydrin to furnish PEGylated epoxides. The latter were converted into the corresponding α-(2-*F*-alkylethyl)thiomethyl polyethylene glycols by treatment with 2-*F*-alkylethanethiol. Surface activity of the obtained surfactants was investigated by evaluation of PEG and perfluoroalkyl chains length on the critical micelle concentration (CMC), surface and interfacial tensions.

Keywords Surfactant · Fluorine · Thiol · Surface tension

Introduction

Highly fluorinated amphiphiles are highly stable against acidic, alkaline, oxidative and reductive reagents as well as elevated temperature. They are very potent in their ability to form aqueous solutions with lower surface tensions when compared to their non fluorinated analogues [1, 2].

Nonionic fluorinated surfactants are important compounds for a wide variety of industrial applications. They can be applied as monolayers on glass, metal or plastic surfaces to form an effective antifogging film [3, 4]. They are useful antistatic and leveling agents for coatings, and wetting agents in hard surface cleaner formulations [5]. On the other hand, the growing importance of nonionic and nontoxic (biocompatible) surfactants has encouraged the search for improved synthesis routes to such compounds [6–8].

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This paper reports on the synthesis and characterization of some fluorinated nonionic surfactants, in which the hydrophilic and lipophilic characters are respectively assumed to be due to the PEG and perfluoroalkyl chains.

Experimental Section

Materials

Melting points were determined by a SMAP 11 apparatus. The IR spectra were recorded on a Bruker IFS 66v/s spectrometer. ^{1}H-, ^{19}F- and ^{13}C-NMR spectra were recorded on a Bruker AC 300 spectrometer (300 MHz proton, 282 MHz fluorine, 75 MHz carbon). All spectra were obtained using $CDCl_3$ as the solvent and referenced to TMS for ^{1}H, ^{13}C NMR and $CFCl_3$ for ^{19}F NMR. The following abbreviations are used to denote multiplicity of the signals in the NMR spectra; s, singlet; t, triplet; m, multiplet. Surface tension measurements (γ_s and γ_i) were performed using a Krüss tensiometer, the solution contained 0.1 % (w/w) of amphiphile in water and was measured at 25 °C. Analytical TLC was conducted using percolated aluminium TLC plates: silica gel/UV 254. Column chromatography was carried out with silica gel (Silica gel, 0.060–0.200 mm, 40 Ä). The microanalysis was performed with a CHNS instrument by the Analysis Central Service, CNRS, Vernaison, France.

Preparation of Polyethylene Glycol Monotrityl Ethers **2**: General Procedure

To a mixture of 35.5 mmol of polyethylene glycol and 36 mmol (5 mL) of triethylamine in 60 mL of CH_2Cl_2 was added 9.2 g (33 mmol) of trityl chloride. After stirring for

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4 h at room temperature, the mixture was washed once with 50 mL of ice cold water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified as indicated below. The main IR signals encountered were: $\nu_{C-O-C} = 1{,}100–1{,}150$, $\nu_{C=C(arom.)} = 1{,}456–1{,}459$, $\nu_{OH} = 3{,}400–3{,}490\ cm^{-1}$.

2a: recrystallization (EtOAc/hexane), 60 % yield.
2b: recrystallization (EtOAc/hexane), 62 % yield.
2c: column chromatography (silica gel, dichloromethane/methanol: 95/5, v/v), 65 % yield.
2d: column chromatography (silica gel, dichloromethane/methanol: 95/5, v/v), 67 % yield.
2e: column chromatography (silica gel, dichloromethane/methanol: 95/5, v/v), 70 % yield.

Preparation of Polyethylene Glycol Glycidyl Trityl Ethers **3**: General Procedure

Polyethylene glycol monotrityl ether (50 mmol) was added dropwise under rapid stirring to a mixture of epichlorohydrin (27 g, 300 mmol), sodium hydroxide pellets (12 g, 300 mmol) water (12 mL) and tetrabutylammonium hydrogen sulfate (0.33 g, 2 %). The temperature was kept below 45 °C. After the addition was completed, stirring was continued for 40 min at 40 °C. The solid material was filtered off and washed with dichloromethane (2 × 30 mL). The organic solution was dried (Na_2SO_4). Solvent and epichlorohydrin excess were evaporated under vacuum. The residue obtained was purified as indicated below. Main IR signals encountered: $\nu_{C-O-C} = 1{,}100–1{,}130$, $\nu_{C=C(arom.)} = 1{,}456–1{,}459\ cm^{-1}$.

3a: recrystallization (hexane/chloroform), mp = 72 °C, 83 % yield.
3b: recrystallization (hexane/chloroform), mp = 69 °C, 82 % yield.
3c: recrystallization (hexane/chloroform), mp = 67 °C, 90 % yield.
3d: recrystallization (hexane/chloroform), mp = 57 °C, 87 % yield.
3e: column chromatography (silica gel, dichloromethane/methanol: 95/5, v/v), 80 % yield.

Preparation of Thioether Monotritylated Polyethylene Glycols **4**: General Procedure

A 100-mL round-bottomed flask, equipped with a magnetic stirrer was charged with 5 mmol of polyethylene glycol glycidyl trityl ether in 20 mL of CH_2Cl_2, 5 mmol of thiol and 10 drops of triton B. The mixture was stirred at room temperature until completion (TLC: silica gel, dichloromethane/methanol 95/5) (24 h). The mixture was poured into water and extracted with ether. The organic solution was dried (Na_2SO_4) and then the solvent was evaporated under vacuum. The obtained crude thioether **4** was purified by column chromatography (dichloromethane/methanol 95/5). Main IR signals encountered: $\nu_{C-S} = 645–649$, $\nu_{C-O-C} = 1{,}100–1{,}150$, $\nu_{C-F} = 1{,}000–1{,}100$, $\nu_{C=C(arom.)} = 1{,}456–1{,}459\ cm^{-1}$.

Deprotection of Thioether Monotritylated Polyethylene Glycols **5**: General Procedure

A 100-ml round-bottomed flask, equipped with a magnetic stirrer was charged with 5 mmol of monotritylated thioether **4**, CH_2Cl_2 (10 mL) and 2 mL of concentrated HCl. The mixture was stirred for 1 h at room temperature until completion (TLC: silica gel, dichloromethane/methanol 95/5). The mixture was poured into water and extracted with dichloromethane. The organic solution was dried (Na_2SO_4) and then the solvent was evaporated under vacuum. The residue was dissolved in methanol (15 mL). On cooling the solution to 0 °C, the crystallized byproduct (trityl chloride) was filtered off. After having concentrated the filtrate, the crude thioether obtained **5** was purified by column chromatography (dichloromethane/methanol: 95/5, v/v) or by recrystallization from hexane/chloroform (Table 1). Main IR signals encountered: $\nu_{C-S} = 645–649$, $\nu_{C-F} = 1{,}000–1{,}100$, $\nu_{C-O-C} = 1{,}100–1{,}150$, $\nu_{O-H} = 3{,}400–3{,}490\ cm^{-1}$.

α-(2-*F*-hexylethyl)thiomethyl Diethylene Glycol (**5a**)

^{1}H NMR ($CDCl_3$/TMS): δ = 2.30–2.50 (m, 2H, $SCH_2C\underline{H}_2C_6F_{13}$), 2.65 (m, 2H, $C\underline{H}_2SC_2H_4C_6F_{13}$), 2.83 (m, 2H, $SC\underline{H}_2CH_2C_6F_{13}$), 3.52 (m, 4H, $OC\underline{H}_2C\underline{H}_2O$ + 2 × OH), 3.73 (m, 2H, $OCH_2C\underline{H}_2OH$), 3.52–3.64 (m, 2H, $CH_2CHOH\underline{CH}_2O$), 4.05 (m, H, $SCH_2C\underline{H}OH$) ppm. ^{13}C-{^{1}H} NMR ($CDCl_3$/TMS): δ = 23.52 (s, $\underline{C}H_2CH_2C_6F_{13}$), 29.81 (t, $CH_2\underline{C}H_2C_6F_{13}$, $^3J_{C-F} = 22.01$ Hz), 35.98 (s, $\underline{C}H_2SC_2H_4C_6F_{13}$), 65.43 (m, $OCH_2\underline{C}H_2OH$), 70.57 (s, $SCH_2\underline{C}HOHCH_2$), 72.68 (s, $O\underline{C}H_2CH_2OH$), 74.99 (s, $OCH_2CHOH\underline{C}H_2$), 108.94–120.12 (m, $\underline{C}_6F_{13}$) ppm. ^{19}F NMR ($CDCl_3$/$CFCl_3$): δ = −82.52 (t, 3F, CF_3, $^3J_{FF} = 9.76$ Hz), −115.69 (m, 2F, $CF_{2\alpha}$), −123.34 (m, 2F, $CF_{2\beta}$), −124.36 (m, 2F, $CF_{2\gamma}$), −124.82 (m, 2F, $CF_{2\delta}$), −127.71 (m, 2F, $CF_{2\omega}$) ppm. Anal. Calc. for $C_{13}H_{15}F_{13}O_3S$: C, 31.33; H, 3.03. Found: C, 31.48; H, 3.18.

α-(2-*F*-hexylethyl)thiomethyl Triethylene Glycol (**5b**)

^{1}H NMR ($CDCl_3$/TMS): δ = 2.31–2.54 (m, 2H, $SCH_2C\underline{H}_2C_6F_{13}$), 2.78 (m, 2H, $C\underline{H}_2SC_2H_4C_6F_{13}$), 2.97 (m, 2H, $SC\underline{H}_2CH_2C_6F_{13}$), 3.45 (m, 2H, 2 × OH), 3.67 (m, 10H, $(C\underline{H}_2OC\underline{H}_2)_2C\underline{H}_2$), 4.00 (m, H, $SCH_2C\underline{H}OH$) ppm. ^{13}C-{^{1}H} NMR ($CDCl_3$/TMS): δ = 23.52 (s, $\underline{C}H_2CH_2$

C_6F_{13}), 31.96 (t, $CH_2\underline{C}H_2C_6F_{13}$, $^3J_{C-F} = 22.13$ Hz), 35.43 (s, $\underline{C}H_2SC_2H_4C_6F_{13}$), 61.60 (s, $OCH_2\underline{C}H_2OH$), 70.57 (s, $SCH_2\underline{C}HOHCH_2$), 72.79 (m, 2 × ($\underline{C}H_2O\underline{C}H_2$)), 74.53 (s, $CH_2CHOH\underline{C}H_2O$), 110.72–117.72 (m, $\underline{C}_6F_{13}$) ppm. ^{19}F NMR ($CDCl_3$/$CFCl_3$): δ = −82.33 (t, 3F, CF_3, $^3J_{FF}$ = 9.72 Hz), −115.60 (m, 2F, $CF_{2\alpha}$), −123.22 (m, 2F, $CF_{2\beta}$), −124.56 (m, 2F, $CF_{2\delta}$), −124.71 (m, 2F, $CF_{2\gamma}$), −127.82 (m, 2F, $CF_{2\omega}$) ppm. Anal. Calc. for $C_{15}H_{19}F_{13}O_4S$: C, 33.22; H, 3.53. Found: C, 33.36; H, 3.49.

α-(2-*F*-hexylethyl)thiomethyl Tetraethylene Glycol (**5c**)

^{1}H NMR ($CDCl_3$/TMS): δ = 2.35 (m, 2H, $SCH_2C\underline{H}_2C_6F_{13}$), 2.69 (m, 2H, $C\underline{H}_2SC_2H_4C_6F_{13}$), 2.70–2.86 (m, 2H, $SC\underline{H}_2CH_2C_6F_{13}$), 3.41 (m, 2H, 2 × OH), 3.69–3.73 (m, 14H, $(C\underline{H}_2O\underline{CH}_2)_3C\underline{H}_2$), 4.05 (m, H, $SCH_2C\underline{H}OH$) ppm. ^{13}C-{^{1}H} NMR ($CDCl_3$/TMS): δ = 23.52 (s, $\underline{C}H_2CH_2C_6F_{13}$), 31.96 (t, $CH_2\underline{C}H_2C_6F_{13}$, $^3J_{C-F}$ = 22.16 Hz), 35.43 (s, $\underline{C}H_2SC_2H_4C_6F_{13}$), 61.60 (s, $CH_2\underline{C}H_2OH$), 70.57 (s, $SCH_2\underline{C}HOH$), 72.05 (s, $(O\underline{C}H_2\underline{C}H_2)_2O\underline{C}H_2$), 74.53 (m, $CHOH\underline{C}H_2O$), 110.72–117.72 (m, $\underline{C}_6F_{13}$) ppm. ^{19}F RMN ($CDCl_3$/$CFCl_3$): δ = −82.33 (m, 3F, CF_3), −115.60 (m, 2F, $CF_{2\alpha}$), −123.22 (m, 2F, $CF_{2\beta}$), −124.56 (m, 2F, $CF_{2\delta}$), −124.71 (m, 2F, $CF_{2\gamma}$), −127.82 (m, 2F, $CF_{2\omega}$) ppm. Anal. Calc. for $C_{17}H_{23}F_{13}O_5S$: C, 34.82; H, 3.95. Found: C, 34.79; H, 4.02.

α-(2-*F*-hexylethyl)thiomethyl Pentaethylene Glycol (**5d**)

^{1}H NMR ($CDCl_3$/TMS): δ = 2.30–2.50 (m, 2H, $SCH_2C\underline{H}_2C_6F_{13}$), 2.75 (m, 2H, $C\underline{H}_2SC_2H_4C_6F_{13}$), 2.83 (m, 2H, $SC\underline{H}_2CH_2C_6F_{13}$), 3.52 (m, 2H, $OCH_2CHOHC\underline{H}_2O$), 3.69 (m, 18H, $C\underline{H}_2(C\underline{H}_2O\underline{CH}_2)_3C\underline{H}_2$ + 2 × OH), 4.05 (m, H, $SCH_2C\underline{H}OH$) ppm. ^{13}C-{^{1}H} NMR ($CDCl_3$/TMS): δ = 23.51 (s, $\underline{C}H_2CH_2C_6F_{13}$), 29.52 (t, $CH_2\underline{C}H_2C_6F_{13}$, $^3J_{C-F}$ = 21.21 Hz), 35.98 (s, $\underline{C}H_2SC_2H_4C_6F_{13}$), 65.43 (s, $OCH_2\underline{C}H_2OH$), 70.57 (s, $SCH_2\underline{C}HOH$), 72.68 (m, $O\underline{C}H_2(\underline{C}H_2\ O\underline{C}H_2)_3$), 74.99 (s, $CH_2CHOH\underline{C}H_2O$), 108.94–120.12 (m, $\underline{C}_6F_{13}$) ppm. ^{19}F RMN ($CDCl_3$/$CFCl_3$): δ = −82.52 (t, 3F, CF_3, $^3J_{FF}$ = 9.76 Hz), −115.69 (m, 2F, $CF_{2\alpha}$), −123.34 (m, 2F, $CF_{2\beta}$), −124.36 (m, 2F, $CF_{2\gamma}$), −124.82 (m, 2F, $CF_{2\delta}$), −127.70 (m, 2F, $CF_{2\omega}$) ppm. Anal. Calc. for $C_{19}H_{27}F_{13}O_6S$: C, 34.82; H, 3.95. Found: C, 34.79; H, 3.98.

α-(2-*F*-hexylethyl)thiomethyl Hexaethylene Glycol (**5e**)

^{1}H NMR ($CDCl_3$/TMS): δ = 2.30–2.46 (m, 2H, $SCH_2C\underline{H}_2C_6F_{13}$), 2.78 (m, 2H, $C\underline{H}_2SC_2H_4C_6F_{13}$), 2.85 (m, 2H, $SC\underline{H}_2CH_2C_6F_{13}$), 3.40 (m, 2H, 2 × OH), 3.56 (m, 2H, $CHOHC\underline{H}_2O$), 3.67 (m, 20H, $OC\underline{H}_2(C\underline{H}_2O\underline{CH}_2)_4C\underline{H}_2$), 4.01 (m, H, $SCH_2C\underline{H}OH$) ppm. ^{13}C-{^{1}H} NMR ($CDCl_3$/TMS): δ = 23.63 (s, $\underline{C}H_2CH_2C_6F_{13}$), 29.83 (t, $CH_2\underline{C}H_2C_6F_{13}$, $^3J_{C-F}$ = 21.73 Hz), 35.13 (s, $\underline{C}H_2SC_2H_4C_6F_{13}$), 61.54 (s, $CH_2\underline{C}H_2OH$), 70.09 (s, $SCH_2\underline{C}HOHCH_2$), 72.23 (m, $\underline{C}H_2(\underline{C}H_2O\underline{CH}_2)_4$), 74.02 (s, $CHOH\underline{C}H_2O$), 109.13–117.47 (m, $\underline{C}_6F_{13}$) ppm. ^{19}F RMN ($CDCl_3$/$CFCl_3$): δ = −82.76 (t, 3F, CF_3, $^3J_{FF}$ = 8.56 Hz), −115.58 (m, 2F, $CF_{2\alpha}$), −123.46 (m, 2F, $CF_{2\beta}$), −124.54 (m, 2F, $CF_{2\delta}$), −124.69 (m, 2F, $CF_{2\gamma}$), −127.95 (m, 2F, $CF_{2\omega}$) ppm. Anal. Calc. for $C_{21}H_{31}F_{13}O_7S$: C, 37.39; H, 4.63. Found: C, 37.44; H, 4.13.

α-(2-*F*-octylethyl)thiomethyl Diethylene Glycol (**5a′**)

^{1}H NMR ($CDCl_3$/TMS): δ = 2.31–2.54 (m, 2H, $SCH_2C\underline{H}_2C_8F_{17}$), 2.77 (m, 2H, $C\underline{H}_2SC_2H_4C_8F_{17}$), 2.97 (m, 2H, $SC\underline{H}_2CH_2C_8F_{17}$), 3.50–3.65 (m, 2H, $CHOHC\underline{H}_2O$), 3.67 (m, 4H, $OC\underline{H}_2CH_2OH$ + 2 × OH), 3.73 (m, 2H, $OCH_2C\underline{H}_2OH$), 4.00 (m, H, $SCH_2C\underline{H}OH$) ppm. ^{13}C-{^{1}H} NMR ($CDCl_3$/TMS): δ = 23.49 (s, $\underline{C}H_2CH_2C_8F_{17}$), 32.25 (t, $CH_2\underline{C}H_2C_8F_{17}$, $^3J_{C-F}$ = 21.96 Hz), 35.42 (s, $\underline{C}H_2SC_2H_4C_8F_{17}$), 61.24 (m, $OCH_2\underline{C}H_2OH$), 70.59 (s, $SCH_2\underline{C}HOHCH_2$), 72.68 (s, $O\underline{C}H_2CH_2OH$), 74.23 (s, $CH_2CHOH\underline{C}H_2O$), 128.86 (m, $\underline{C}_8F_{17}$) ppm. ^{19}F NMR ($CDCl_3$/$CFCl_3$): δ = −82.82 (t, 3F, CF_3, $^3J_{FF}$ = 9.76 Hz), −115.28 (m, 2F, $CF_{2\alpha}$), −122.20 (m, 2F, $CF_{2\beta\rightarrow\delta}$), −123.75 (m, 2F, $CF_{2\varepsilon}$), −124.36 (m, 2F, $CF_{2\xi}$), −127.71 (m, 2F, $CF_{2\omega}$) ppm. Anal. Calc. for $C_{15}H_{15}F_{17}O_3S$: C, 30.11; H, 2.53. Found: C, 30.19; H, 2.88.

α-(2-*F*-octylethyl)thiomethyl Triethylene Glycol (**5b′**)

^{1}H NMR ($CDCl_3$/TMS): δ = 2.35 (m, 2H, $SCH_2C\underline{H}_2C_8F_{17}$), 2.69 (m, 2H, $C\underline{H}_2SC_2H_4C_8F_{17}$), 2.73–2.86 (m, 2H, $SC\underline{H}_2CH_2C_8F_{17}$), 3.51 (m, 2H, 2 × OH), 3.67 (m, 10H, $C\underline{H}_2(OC\underline{H}_2C\underline{H}_2)_2$), 4.00 (m, H, $SCH_2C\underline{H}OH$) ppm. ^{13}C-{^{1}H} NMR ($CDCl_3$/TMS): δ = 23.17 (s, $\underline{C}H_2CH_2C_8F_{17}$), 32.13 (t, $CH_2\underline{C}H_2C_8F_{17}$, $^3J_{C-F}$ = 21.96 Hz), 35.54 (s, $\underline{C}H_2SC_2H_4C_8F_{17}$), 61.71 (s, $OCH_2\underline{C}H_2OH$), 70.57 (s, $SCH_2\underline{C}HOH$), 72.68 (m, $O\underline{C}H_2\underline{C}H_2O\underline{C}H_2$), 74.25 (s, $CHOH\underline{C}H_2O$), 112.14–122.23 (m, $\underline{C}_8F_{17}$) ppm. ^{19}F RMN ($CDCl_3$/$CFCl_3$): δ = −82.14 (t, 3F, CF_3, $^3J_{FF}$ = 9.23 Hz), −113.89 (m, 2F, $CF_{2\alpha}$), −121.96 (m, 6F, $CF_{2\beta\rightarrow\delta}$), −123.01 (m, 2F, $CF_{2\varepsilon}$), −123.48 (m, 2F, $CF_{2\xi}$), −126.98 (m, 2F, $CF_{2\omega}$) ppm. Anal. Calc. for $C_{17}H_{19}F_{17}O_4S$: C, 31.79; H, 2.98. Found: C, 31.53; H, 3.01.

α-(2-*F*-octylethyl)thiomethyl Tetraethylene Glycol (**5c′**)

^{1}H NMR ($CDCl_3$/TMS): δ = 2.28–2.56 (m, 2H, $CH_2C\underline{H}_2C_8F_{17}$), 2.87 (m, 2H, $C\underline{H}_2SC_2H_4C_8F_{17}$), 3.04 (m,

2H, $C\underline{H}_2CH_2C_8F_{17}$), 3.50–3.59 (m, 2H, $CH_2OC\underline{H}_2CHOH$), 3.69 (m, 14H, $OC\underline{H}_2(C\underline{H}_2OC\underline{H}_2)_2C\underline{H}_2 + 2 \times OH$), 4.03 (m, H, $SCH_2C\underline{H}OH$) ppm. ^{13}C-{^1H} NMR ($CDCl_3$/TMS): $\delta = 23.39$ (s, $\underline{C}H_2CH_2C_8F_{17}$), 32.04 (t, $CH_2\underline{C}H_2C_8F_{17}$, $^3J_{C-F} = 21.95$ Hz), 35.47 (s, $\underline{C}H_2SC_2H_4C_8F_{17}$), 63.29 (s, $OCH_2\underline{C}H_2OH$), 70.07 (s, $SCH_2\underline{C}HOH$), 72.05 (m, ($O\underline{C}H_2\underline{C}H_2)_2O\underline{C}H_2$), 74.74 (s, $CH_2CHOH\underline{C}H_2O$), 120.98 (m, $\underline{C}_8F_{17}$) ppm. ^{19}F RMN ($CDCl_3$/$CFCl_3$): $\delta = -82.14$ (t, 3F, CF_3, $^3J_{FF} = 9.23$ Hz), −113.89 (m, 2F, $CF_{2\alpha}$), −121.96 (m, 6F, $CF_{2\beta\rightarrow\delta}$), −123.01 (m, 2F, $CF_{2\varepsilon}$), −123.48 (m, 2F, $CF_{2\xi}$), −126.98 (m, 2F, $CF_{2\omega}$) ppm. Anal. Calc. for $C_{19}H_{23}F_{17}O_5S$: C, 33.25; H, 3.38. Found: C, 33.12; H, 3.42.

α-(2-*F*-octylethyl)thiomethyl Pentaethylene Glycol (**5d′**)

^1H NMR ($CDCl_3$/TMS): $\delta = 2.45$ (m, 2H, $SCH_2C\underline{H}_2C_8F_{17}$), 2.68 (m, 2H, $C\underline{H}_2SC_2H_4C_6F_{13}$), 2.80 (m, 2H, $SC\underline{H}_2CH_2C_8F_{17}$), 3.43 (m, 2H, $2 \times OH$), 3.68 (m, 16H, $(OC\underline{H}_2C\underline{H}_2)_4$), 3.91 (m, H, $SCH_2C\underline{H}OH$), 3.54 (m, 2H, $CHOHC\underline{H}_2O$) ppm. ^{13}C-{^1H} NMR ($CDCl_3$/TMS): $\delta = 23.49$ (s, $\underline{C}H_2CH_2C_8F_{17}$), 31.94 (t, $CH_2\underline{C}H_2C_8F_{17}$, $^3J_{C-F} = 20.96$ Hz), 35.32 (s, $\underline{C}H_2SC_2H_4C_8F_{17}$), 61.61 (s, $CH_2\underline{C}H_2OH$), 70.68 (s, $SCH_2\underline{C}HOH$), 72.70 (m, $\underline{C}H_2(\underline{C}H_2O\underline{C}H_2)_3$), 74.20 (s, $CHOH\underline{C}H_2O$), 109.20–119.93 (m, $\underline{C}_8F_{17}$) ppm. ^{19}F RMN ($CDCl_3$/$CFCl_3$): $\delta = -81.05$ (t, 3F, CF_3, $^3J_{FF} = 9.56$ Hz), −115.34 (m, 2F, $CF_{2\alpha}$), −122.77 (m, 6F, $CF_{2\beta\rightarrow\delta}$), −123.80 (m, 2F, $CF_{2\varepsilon}$), −124.42 (m, 2F, $CF_{2\xi}$), −127.20 (m, 2F, $CF_{2\omega}$) ppm. Anal. Calc. for $C_{21}H_{27}F_{17}O_6S$: C, 34.53; H, 3.73. Found: C, 34.33; H, 3.65.

α-(2-*F*-octylethyl)thiomethyl Hexaethylene Glycol (**5e′**)

^1H NMR ($CDCl_3$/TMS): $\delta = 2.49$ (m, 2H, $SCH_2C\underline{H}_2C_8F_{17}$), 2.61 (m, 2H, $C\underline{H}_2SC_2H_4C_8F_{17}$), 2.71 (m, 2H, $SC\underline{H}_2CH_2C_8F_{17}$), 3.66 (m, 22H, $(C\underline{H}_2OC\underline{H}_2)_5C\underline{H}_2$), 4.95 (m, H, $SCH_2C\underline{H}OH$) ppm. ^{13}C-{^1H} NMR ($CDCl_3$/TMS): $\delta = 23.41$ (s, $\underline{C}H_2CH_2C_8F_{17}$), 31.96 (t, $CH_2\underline{C}H_2C_8F_{17}$, $^3J_{C-F} = 20.16$ Hz), 35.27 (s, $\underline{C}H_2SC_2H_4C_8F_{17}$), 61.61 (s, $OCH_2\underline{C}H_2OH$), 70.70 (s, $SCH_2\underline{C}HOH$), 72.68 (m, $O\underline{C}H_2(\underline{C}H_2O\underline{C}H_2)_4$), 74.24 (s, $CHOH\underline{C}H_2O$), 116.17 (m, $\underline{C}_8F_{17}$) ppm. RMN ^{19}F ($CDCl_3$/$CFCl_3$): $\delta = -81.83$ (t, 3F, CF_3, $^3J_{F-F} = 8.56$ Hz), −115.43 (m, 2F, $CF_{2\alpha}$), −122.68 (m, 6F, $CF_{2\beta\rightarrow\delta}$), −123.75 (m, 2F, $CF_{2\varepsilon}$), −124.51 (m, 2F, $CF_{2\xi}$), −127.31 (m, 2F, $CF_{2\omega}$) ppm. Anal. Calc. for $C_{23}H_{31}F_{17}O_7S$: C, 35.67; H, 4.03. Found: C, 35.34; H, 3.99.

Results and Discussion

Protection of PEG by the reaction with trityl chloride [9, 10] furnished a mixture of mono- and diprotected derivatives. The monotritylated PEG, main product of the reaction, was purified by conventional techniques.

Monoprotected polyethylene glycol was epoxidized by the reaction of its monoprotected derivative **2** with epichlorohydrin [11, 12]. The coupling reaction of the epoxide **3** and 2-*F*-alkylethanethiol [13–20] furnished the adduct **4,** which was easily deprotected [9] into surfactant **5** (Scheme 1).

Compounds **5** are obtained in good yields as indicated in Table 1. Their surface tension γ_s and interfacial tension γ_i were measured by the Du Noüy ring method and grouped in Table 1.

As indicated in Table 1, γ_s values are remarkably low in comparison with those of conventional hydrocarbon surfactants. The values of γ_i are, however, slightly higher than those observed for hydrocarbon analogues [21].

The data provided in Table 1 show that γ_s as well as γ_i decrease when the perfluoroalkyl chain and/or polyoxyethylene (POE) chain length increases. The lowest values of γ_s and γ_i correspond to the surfactant which has the longest perfluoroalkyl and POE chains.

The presence of two hydroxyl groups in surfactant **5** probably contributes to lowering the surface tension since, for similar structures devoid of a hydroxyl group; the aqueous surface tensions are slightly higher [22–24].

Surfactant **5** may exhibit some crown ether properties. They should be able to complex small metallic cations due to their POE chain length.

We plotted in Figs. 1 and 2 the variation of surface tension against the logarithm of the molar concentration of compounds **5b–e** and **5c**, **5c′**, **5d**, **5d′**.

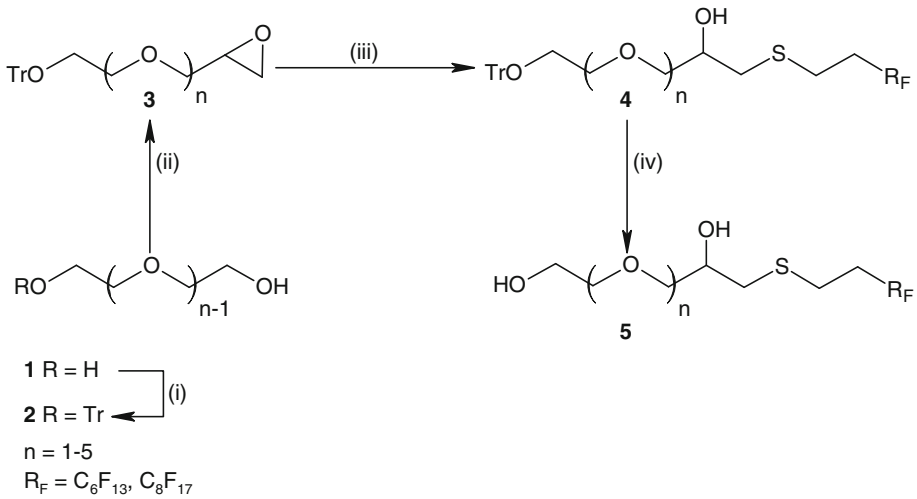
The values of the break points (CMC and corresponding surface tension γ_{CMC}) depicted from Figs. 1 and 2 are grouped in Table 2.

Values reported in Table 2 show that the CMC increases progressively with *n* (the number of ethylene oxide units). Thus, an increase of *n* from 2 to 5 induces an increase in the CMC from 0.50 to 3.98 μM. Since hydrophilicity of the surfactant headgroup hinders micellization, smaller PEG chains seem to favor micelle formation (Table 2).

In Fig. 2 are plotted the surface tensions against their concentration for compounds **5c**, **c′** and **5d**, **d′**. As indicated in Table 2, the γ_{CMC} decreases when the perfluoroalkyl chain becomes longer. For instance, γ_{CMC} values fall from 2.36 to 1.46 μM when the R_F goes from C_6F_{13} to C_8F_{17}. We have already signaled such behavior in previous works [25].

Nevertheless, amphiphiles **5** seem to be more sensitive to *n* variation, since when *n* and the R_F length increase, the overall effect is an increase in γ_{CMC}. Furthermore, this increase becomes more significant for higher values of *n*. For instance, when going from surfactant **5b** ($n = 2$,

Scheme 1 Synthesis of amphiphiles **5**



(i) TrCl, Et_3N/CH_2Cl_2, rt, 4h, (60-70%); (ii) Epichlorohydrin, $NaOH/H_2O$, TBAHS/40°C, 4h, (80-90%); (iii) $R_FC_2H_4SH/CH_2Cl_2$, Triton B, rt; (iv) HCl/CH_2Cl_2, rt.

Table 1 Amphiphiles **5** prepared

Surfactant	*n*	R_F	Yield (%)	mp[a] (°C)	γ_s^b (mN m^{-1})	γ_i^c (mN m^{-1})
5a	1	C_6F_{13}	93	–	17.90	26.30
5b	2		88	–	19.10	27.60
5c	3		86	–	20.45	28.15
5d	4		87	–	20.22	29.60
5e	5		91	–	21.90	33.30
5a′	1	C_8F_{17}	95	77	16.80	23.30
5b′	2		92	72	17.96	24.10
5c′	3		89	69	18.46	24.45
5d′	4		88	63	19.10	25.90
5e′	5		86	59	19.92	26.20

[a] Otherwise viscous oil, [b]Cyclohexane/water and [c]Aqueous 0.1 % (w/w) solution at 25 °C

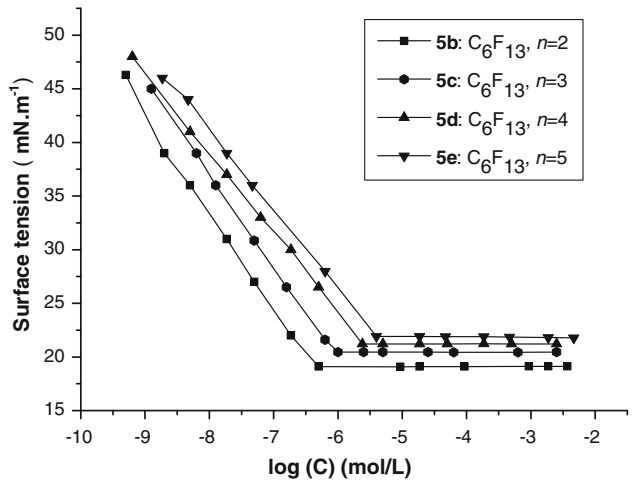


Fig. 1 Surface tension against log(c) for aqueous solutions of **5b–e** in water at 25 °C

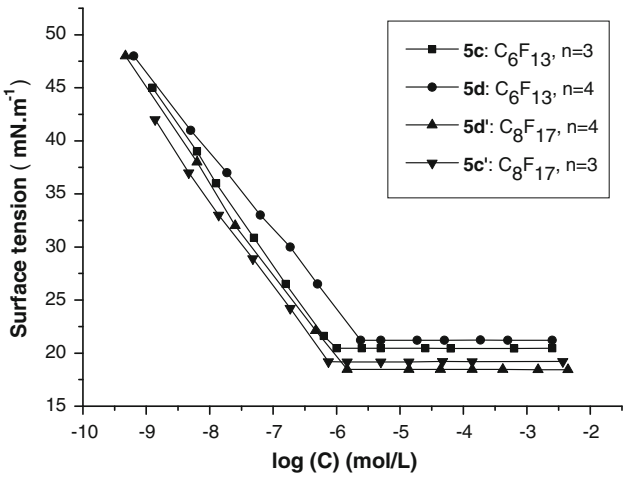


Fig. 2 Surface tension versus log(c) of compounds **5c**, **5c′**, **5d** and **5d′** in water at 25 °C

Table 2 CMC and γ_{CMC} values of compounds **5b–e**, **c′**, **d′**

Surfactant			Break points	
5	*n*	R_F	CMC (μM)	γ_{CMC} (mN/m)[a]
5b	2	C_6F_{13}	0.50	19.10
5c	3		0.98	20.45
5d	4		2.36	21.22
5e	5	C_8F_{17}	3.98	22.20
5c'	3		0.73	19.20
5d'	4		1.46	18.46

[a] Typical uncertainties on γ_{CMC} are ±0.04 mN/m

$R_F = C_6F_{13}$) to **5c′** ($n = 3$, $R_F = C_8F_{17}$), the augmentation of CMC is 0.23 μM, whereas an augmentation of 0.48 μM was observed for the transition from surfactant **5c** ($n = 3$, $R_F = C_6F_{13}$) to **5d′** ($n = 4$, $R_F = C_8F_{17}$).

Conclusion

In this paper we have presented an efficient pathway for the synthesis of new amphiphilic compounds. Acceptable yields were obtained by the use of simple experimental procedures which can be applied to large-scale production. The surface activity of these new compounds is closely dependent on the PEG chain length.

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