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New fluorinated surfactants based on vinylidene fluoride telomers

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ABSTRACT

The synthesis of $C_nF_{2n+1}(VDF)_x$–$(CH_2)_p$– where n = 2, 4; x = 2, 3, 4; p = 0, 1, 2 and VDF and stand for vinylidene fluoride (VDF) and I, OH, or CO_2H, respectively, are presented. First, the radical telomerization of VDF with C_nF_{2n+1}–I to direct low molecular weight-telomers was investigated in various experimental conditions: initiators, temperatures and solvents to favour the formation of $C_nF_{2n+1}(VDF)_xI$. Whatever the experimental conditions, it was observed the regioselective radical addition of $\bullet C_nF_{2n+1}$ radical onto the methylene site of VDF. Then, ethylenation of these VDF telomers was achieved in the presence of peroxy initiator with a quantitative conversion of the VDF-containing iodide reactants. Chemical change of $R_F(VDF)_xC_2H_4I$ into $R_F(VDF)C_2H_4OH$ occurred in two steps: (i) from a mixture of DMF/water (for which a 6/1 content led to the best conditions); (ii) followed by a basic medium to saponify $R_F(VDF)_xCH_2CH_2OCOH$ formiate into the corresponding VDF-containing alcohols. Suitable conditions were found to avoid any dehydrofluorination of the VDF telomeric chain. Oxidation of these fluorinated alcohols in the presence of H_2SO_4/CrO_3 mixture led to the corresponding $C_nF_{2n+1}(VDF)_xCH_2CO_2H$ carboxylic acids. Surface tensions of these VDF-containing carboxylic acids were achieved reaching a value of 19.8 mN m^{-1} for a surfactant concentration of 5 g L^{-1}, showing similar values as that of commercially available perfluorooctanoic acid (PFOA) while critical micellar concentration value of $C_2F_5CH_2CF_2CH_2CF_2CH_2CO_2H$ was 1.4 g L^{-1} at room temperature.

Research topics of the laboratory

Ingenierie & Architerctures Macromoleculaires (IAM) team belongs to Gerhardt of Montpellier (ICGM) and has many activities that many focus on the synthesis and characterization and original macromolecules in four topics: "Controlled Radical (Co)polymerization", "Heterochemistry" (P, Si, F chemistries), "Clean Process", "Green Chemistry and Sustainable Development" (see http://www.iam.icgm.fr). In the field of Fluorine Chemistry, main interests focus on the radical reactions and macromolecular engineering ranging from the synthesis of organofluorinated synthons or monomers to the design of macromolecular fluorinated architectures such as block, alternated, and graft copolymers, and this wide range of topics is rather unique. Main methodologies are: (i) the *telomerization* of commercially available fluorinated alkenes (such as vinylidene fluoride, 3,3,3-trifluoropropene, chlorotrifluoroethylene, trifluoroethylene) and synthesized fluoromonomers have been extensively investigated in the presence of numerous chain transfer agents and reviewed in a book (Ref. [37]); (ii) *radical copolymerization* of these above fluorinated alkenes with functional commercially or synthesized comonomers (see Chem. Rev. 109 (2009), 6632–6686), with efforts made in the design of specific comonomers to favour the copolymerization also involving concept of acceptor-donor copolymerization; (iii) the *controlled radical (co)polymerization* of these fluoroalkenes (see Ref. [38]). Further interests are the characterizations (spectroscopic, thermal, surface, or rheological) and applications dealing with surfactants (Ref. [22]), high performance elastomers, coatings, optics, nanofillers/fluoropolymers composites, or energy-relative activities such as fuel cell membranes (protonic, alkaline, or *quasi*-anhydrous), polymer electrolytes for lithium batteries, piezoelectrical and photovoltaic (co)polymers.

1. Introduction

Surfactants are valuable compounds, being either cationic, anionic, amphoteric or non-ionic [1,2]. Among them, fluorinated surfactants have found much interest since very low critical micellar concentration values have been assessed. Various commercially available compound have been marketed by Asahi Glass, Atofina, Clariant, Daikin, and DuPont Companies, under the Surlyn®, Forafac®, Fluowet®, Unidyne®, and Zonyl®, respectively.

Fluorinated surfactants, namely perfluorooctanoic acid ($C_7F_{15}CO_2H$, PFOA), ammonium perfluorooctanoate (APFO), and perfluorooctane sulfonate ($C_8F_{17}SO_3X$, with X = K, Na, H, PFOS), are found in more than 200 applications [1,3] including soil and stain-

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repellents, plane hydraulic fluids, fire fighting foams, paints, coatings for clothing fabrics, leather, carpets, paper coatings, electroplating, photographic emulsifiers, pressure sensitive additives, waxes, polishes, pharmaceuticals, insecticides, etc. In addition, PFOA is also frequently used as surfactant in aqueous media of polymerization of hydrophobic monomers, especially fluorinated monomers such as tetrafluoroethylene and other C_2–C_3 alkenes.

However, these fluorinated surfactants are *persistent*, *toxic*, *bioaccumulable* [4,5] and are possibly mutagenic because of the too stable perfluorinated chain which cannot degrade under enzymatic or metabolic decomposition [6]. For example, half life of PFOS is ca. 3.26 years in human blood [7,8]. Indeed, because of their ubiquitous occurrence, these products are found all over our planet (surface waters of Atlantic and Pacific Oceans [9], coastal waters, rivers, drinking and rain waters, fresh water ecosystems [10] air, urban centers, soils, sediments [11], high Arctic ice caps, and dust in Canadian homes [12], in the blood of many animal species (fish, rodents [3], birds, dolphin, mammals and even livers of polar bears [13]) and the general human population worldwide, as well-reported in an extensive review from Kovàrovà and Svobodovà [3]). In fact, perfluoroalkyl substances have been detected worldwide in human blood/serum, with PFOS being the most prevalent compound in humans, followed by PFOA [14].

For these above reasons, in 2002, the major manufacturers of PFOS, phased out the production of this surfactant (while its production and use at the end of the 1980s was estimated at 3,500 tons annually). Indeed, in 2005, PFOS underwent risk management evaluation by U.S. Environmental Protection Agency (U.S. EPA) [15] and from 2006, EPA launched the PFOA Stewardship Program [16] (involving eight major chemical industrial actors in organofluorine and macromolecular fluorine chemistries) to decrease the production of PFOA and PFOS to 95% by 2010 and to eliminate emissions and product contents of these chemicals by 2015. This program has gathered the most important manufacturers of PFOA, PFOS and fluorinated polymers.

Various attempts to degrade PFOA and PFOS were suggested by Parsons et al. [17] but these authors demonstrated that the lack of mineralization is probably caused by the stability of the C–F bond although there are examples of microbially catalyzed defluorination reactions. Though various strategies to synthesize PFOA, PFOS and other fluorinated surfactants were suggested [18], there has been an urgent interest to find out alternatives of PFOA and PFOS surfactants to overcome the issues of their bioaccumulation, persistence and toxicity.

In addition, many academic surveys have been reported [19–22] just like industrial approaches achieved by the 3M Company [23] that claimed the synthesis of original surfactants containing C_4F_9 end group.

Oligo(hexafluoropropylene oxide) oligomers have shown to be degraded but their synthesis occurs via the anionic ring opening polymerization of hexafluoropropylene oxide [24,25].

Moreover, the radical copolymerization of VDF and 3,3,3-trifluoropropene (TFP) controlled by fluorinated xanthate led to poly(VDF-*co*-TFP)-*b*-oligo(vinyl alcohol) block copolymers with valuable surface properties [26]. A couple of years ago, Kappler and Lina [27] claimed the synthesis of $C_2F_5(VDF)_n$–CH_2CO_2H prepared in four steps from C_2F_5I in a peculiar way. Unfortunately, that patent lacks of suitable characterizations of all the intermediates. That is why we have found it interesting to revisit that strategy to improve several steps and to fully describe all the different steps and to add complementary details: deeper NMR characterization, yields, and influence of the experimental conditions and to compare their surface tension to that of PFOA. These are the objectives of this present article.

2. Results and discussion

The synthesis of fluorinated surfactants $C_nF_{2n+1}(CH_2CF_2)_xCH_2COOH$ (FSurf *n*,*x*) was carried out into four steps: (i) first, the radical telomerization of vinylidene fluoride (VDF) with 1-iodoperfluoroalkane, followed by (ii) ethylenation, (iii) hydrolysis, and (iv) oxidation, as follows:

$$C_nF_{2n+1}I + x\,H_2C{=}CF_2 \longrightarrow C_nF_{2n+1}(VDF)_xI$$

$$C_nF_{2n+1}(VDF)_xI \xrightarrow[\text{ii) DMF/H}_2\text{O}]{\text{i) H}_2\text{C=CH}_2} C_nF_{2n+1}(CH_2CF_2)_x{-}CH_2{-}CO_2H$$

iii) H_2SO_4/CrO_3 — FSurf. n, x

Two surfactants were synthesized: $C_2F_5(CH_2CF_2)_2CH_2COOH$ and $C_4F_9(CH_2CF_2)_2CH_2COOH$. In the former case ($n = x = 2$), the reaction led to a PFOA alternative of similar C_8-chain length. Each step is described hereafter.

2.1. Radical telomerization of VDF with $C_nF_{n+1}I$

Telomerization reaction of vinylidene fluoride with 1-iodoperfluoroalkane was extensively reported under redox [28,29], thermal [28,30,31], photochemical [32] conditions, or in the presence of radical initiators [33–36] and reviewed in a book [37]. However, though CF_3I [33], C_4F_9I [34] and $C_6F_{13}I$ [35] were involved in radical telomerization of VDF, to the best of our knowledge, the description of $C_2F_5(VDF)_2I$ has not been reported in the literature. This telomer was synthesized from a two to five folder molar excess of VDF *versus* C_2F_5I and a 1.3 folder excess of C_2F_5I to the initiator. Two initiators were used: *tert*-butyl peroxypivalate and *tert*-butyl cyclohexyl peroxydicarbonate, the half lives of which were 74 and 60 °C, respectively. Both reactions were carried out for 6–8 h. After reaction, the total product mixture was a telomeric distribution that depended on the $[VDF]_o/[C_2F_5I]_o$ initial molar ratio. The higher that ratio, the higher the degree of telomerization. For a ratio of 3, a degree of telomerization of ca. 3 (Fig. 1) was obtained and the distillation of the monoadduct, $C_2F_5(VDF)_2I$ was characterized by ^{19}F NMR spectroscopy. That spectrum exhibits the characteristic signal centered at −39 ppm assigned to CH_2CF_2I end-group [27,30,32–35], while those ranging between −92 and −93.5 are attributed to CH_2–C**F$_2$**CH_2–C**F$_2$**CH_2-normal VDF addition. As noted in previous studies [33–36], the absence of reversed VDF addition at ca. 2.4 ppm evidences the *pseudo*-control of that radical reaction [38]. Interestingly, the signal centered at −83 ppm, assigned to C**F$_3$**- end-group, is a suitable label to assess the average number of VDF units according to the following equation:

$$\text{Number of VDF} = \frac{[(I_{-39} + I_{-92\,\text{to}\,-93.5})/2]}{[I_{-83}/3]}$$

where I_{-x} represents the integral of the signal in the ^{19}F NMR spectrum centered at $-x$ ppm.

In the case of the radical telomerization of VDF with C_4F_9I, the purification was also carried out by distillation. The same calculation was achieved from $C_4F_9(VDF)_2I$ telomer, the ^{19}F NMR spectrum of which also exhibits two additional signals in the −122 to −126 ppm range assigned to the C_2F_4 group adjacent to CF_3 end-group.

2.2. Ethylenation of $R_F(VDF)_xI$

Various ethylenation conditions can be used, as reviewed in a book [37]: redox, thermal, photochemical or in the presence of radical initiators. We have chosen to carry out such a reaction

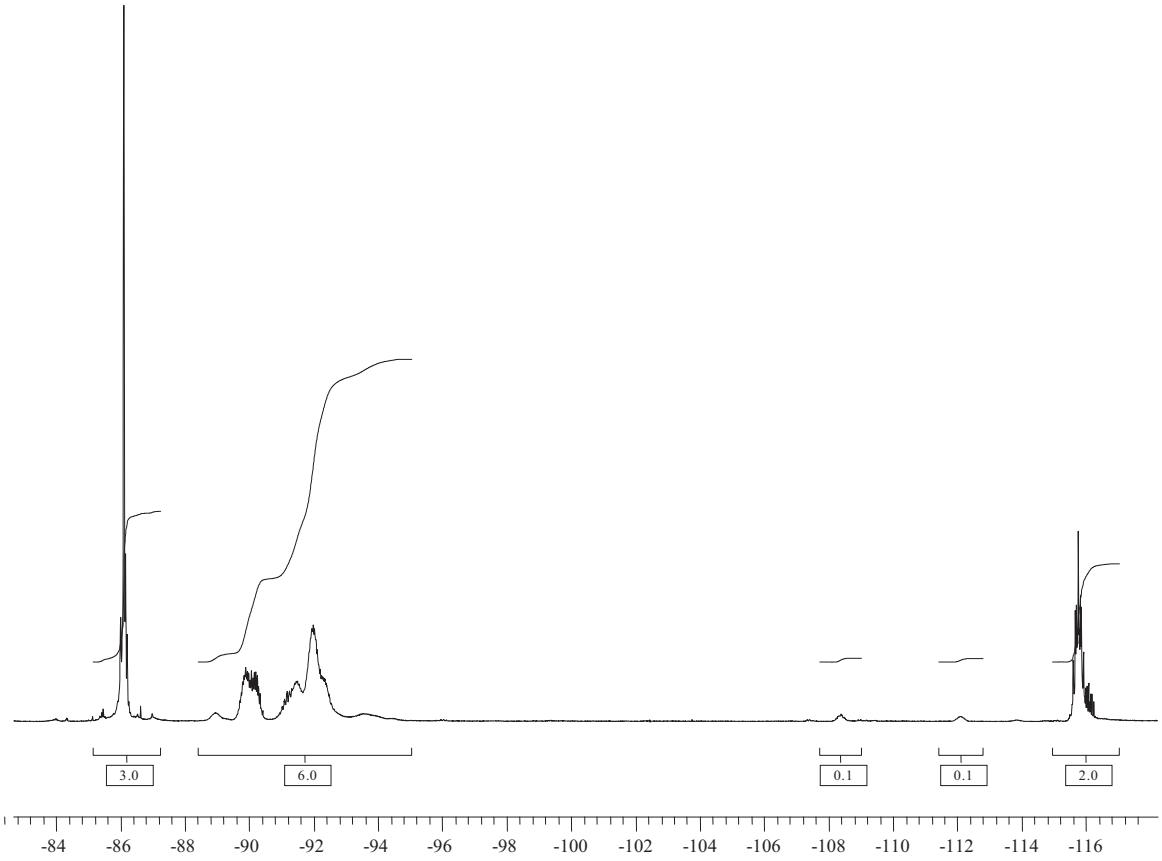

Fig. 1. Expansion of the −82 to −118 ppm zone of the ^{19}F NMR spectrum of the total product mixture of the radical telomerization of VDF with C_2F_5I initiated by *tert*-butyl peroxypivalate for a three folder excess of VDF about C_2F_5I (recorded in d_6-acetone).

under radical conditions, and have used *tert*-butyl peroxypivalate as the initiator that showed a high efficiency for that reaction. Its half life is 1 h at 74 °C and the ethylenation was achieved for 6 h with a 2.4-fold excess of ethylene with respect to $R_F(VDF)_xI$. The excess of ethylene does not induce the formation of diethylenated adducts, as previously reported [39]. After purification, the resulting $R_F(VDF)_xCH_2CH_2I$ was obtained in 78% yield with a quantitative conversion of $R_F(VDF)_xI$. These ethylene end-capping VDF telomers were evidenced by the ^{19}F NMR spectrum that exhibits the absence of the signal at −39 ppm that undergoes a high field shift toward −93 ppm. In addition, ^1H NMR spectrum of that original VDF telomer displays the presence of low field shifted new complex signal in the 3.2–3.4 ppm range.

2.3. Synthesis of $R_F(VDF)_xCH_2CH_2OH$

The hydrolysis of $R_FCH_2CH_2I$ into corresponding alcohols can be carried out either in the presence of $NaNO_2$/betaine [40] as a surfactant, $CuSO_4{\cdot}5H_2O$ or AgOAc [41], oleum H_2SO_4/SO_3 [42–44], or in the presence of formamide (e.g. DMF) [45]. We have chosen that last reactant, and especially a DMF/water mixture in 6/1 mol ratio. The reaction was monitored by IR spectroscopy, by the presence of the OH frequency centered at ca. 3500 cm^{-1}. After 6 h, the reaction was stopped. Actually, the formation of hydroxyl groups was also accompanied by the presence of a formiate function, as confirmed by NMR and gas chromatography analyses that identified the presence of two products: the produced alcohol with a characteristic signal (**CH_2**OH centered at 3.8 ppm) and the formiate (**CH_2**OCHO centered at 4.4 and 8.1 ppm, respectively).

The saponification of the formiate by-product was carried out with a twofold excess of sulfuric acid in methanol, and the reaction was monitored by IR spectroscopy. After 4 h, the reaction did not evidence any presence of the frequency attributed to formiate band. ^1H NMR spectrum enabled to check the total consumption of the formiate by the absence of signals centered at 4.4 and 8.1 ppm.

2.4. Oxidation of F-alcohol into F-carboxylic acid based on VDF telomers

To enable the acid extremity, various methods have already been reported, either from (i) the electrochemical fluorination of $CH_3(CH_2CH_2)_x$–COOH into $CF_3(CF_2CF_2)_x$–COF followed by the hydrolysis [46]; (ii) the oxidation of ethylenated tetrafluoroethylene (TFE) telomers, $CF_3(TFE)_x$–CH_2CH_2I, in the presence of dichromate [47]; (iii) the oxidation with $K_2Cr_2O_7$ [48], or with $KMnO_4$ in the presence of phase transfer catalysts [49] or under ozonolysis [50] of $R_F(TFE)_nCH{=}CH_2$, or by bleach in the presence of RuO_2 catalyst [51] of $R_F(TFE)_yCH{=}CH_2$; (iv) the oxidation of perfluoroalkyl iodides with oxygen under photochemical activation by UV radiation [52] or in the presence of nitric acid [53].

However, these above processes are highly polluting and difficult to control (especially the oxidation) or require specific equipment (in the case of ozonolysis or photochemical reactions).

More recently, Kappler and Lina [54] synthesized $R_F(TFE)_x$-SO_2Na (n = 2, 3) and $R_F(VDF)_4SO_2Na$ which could be oxidized into $R_F(TFE)_nCF_2COOH$ and $R_F(VDF)_3CH_2COOH$, respectively.

However, the oxidation of $CF_3(C_2F_4)_nCH_2CH_2OH$ into $CF_3(C_2F_4)_n$ CH_2CO_2H in the presence of the Jones reagent [55] was disclosed in a patent [56] and we have adapted such a strategy onto the VDF telomers.

$C_2F_5(VDF)_2CH_2CH_2OH$ was refluxed in the presence of a four folder molar excess of chromium oxide with respect to the alcohol.

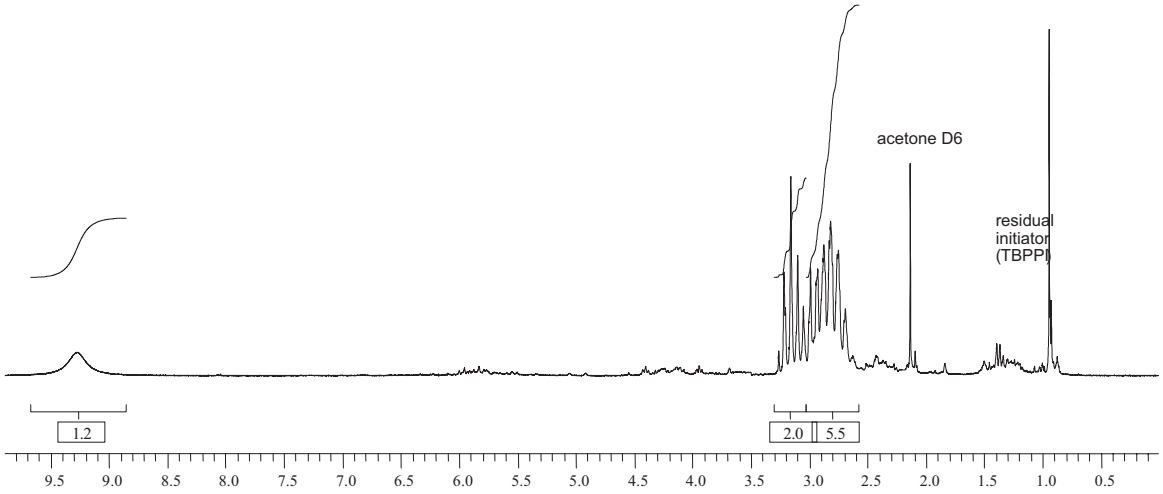

Fig. 2. ^{1}H NMR spectrum of 3,3,5,5,7,7,8,8,8-nonafluorooctanoic acid (recorded in d_6-acetone).

After work up, the fluorinated acid was purified by distillation, the ^{19}F NMR spectrum of which shows the characteristic signals (see Section 4). Additional signals in −122 to −126 ppm were noted in the ^{19}F NMR spectrum of $C_4F_9(VDF)_2CH_2CO_2H$, assigned to C_2F_4 unit adjacent to CF_3 end-group. The ^{1}H NMR spectrum (Fig. 2) exhibits the absence of the signal centered at 3.8 ppm assigned to methylene $C\underline{H}_2OH$ of the fluorinated alcohol and the presence of a quintet and a complex multiplet centered at 3.2 and 2.6–3.0 ppm assigned to the methylene group adjacent to C_2F_5 and to the carboxylic acid of $C_2F_5(VDF)_2CH_2CO_2H$ (**F-surf 2,2**), respectively. A similar ^{1}H NMR spectrum was obtained for **F-surf 4.2**. In addition, the ^{13}C NMR spectrum of **F-surf 4,2** (Fig. 3) also completes that NMR characterization by the presence of the carboxylic acid clearly identified at 173 ppm, and the three methylene and difluoromethylene groups centered at ca. 30–40 and 110–125 ppm ranges, respectively. **F-surf 2,2** surfactant was obtained in 20% overall yield from C_2F_5I while that of **F-surf 4,2** was 24% from C_4F_9I.

2.5. Surface tension assessment

$C_2F_5(VDF)_2CH_2CO_2H$ appears as an attractive amphiphilic molecule, the surfactant behavior of which has never been reported in the literature. This is a water-soluble compound for concentration at least up to 12 g L^{-1}. Hence, surface properties of 3,3,5,5,7,7,8,8,8-nonafluorooctanoic acid were assessed by means of tensiometry and compared to the surface tension of the perfluorooctanoic acid (PFOA), a commonly used surfactant, regarded as a reference. Actually, the surface tensions of both surfactants were plotted *versus* their concentrations (Fig. 4). Interestingly, it can be seen that the surface properties of such a VDF-containing surfactant are similar to those of PFOA. Its low surface tension (about 19.8 mN m^{-1} for a surfactant concentration of 5 g L^{-1}) and low critical micellar concentration (cmc) of 1.4 g L^{-1} at room temperature make such a molecule a potential surfactant, as a competitor of PFOA.

3. Conclusion

Vinylidene fluoride (VDF)-containing surfactants were synthesized and all intermediates were characterized with appropriate spectroscopic tools. The radical telomerization of VDF with C_nF_{2n+1}–I first enabled to obtain low molecular weight-telomers. Whatever the experimental conditions, it was observed the regioselective radical addition of $\bullet C_nF_{2n+1}$ radical onto the

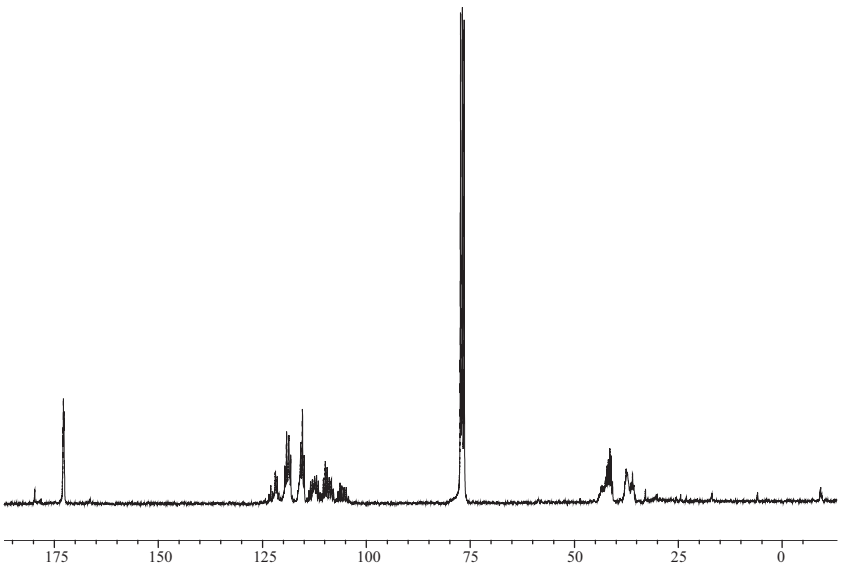

Fig. 3. ^{13}C NMR spectrum of 3,3,5,5,7,7,8,8,9,9,10, 10,10-tridecafluorodecanoic acid (recorded in $CDCl_3$).

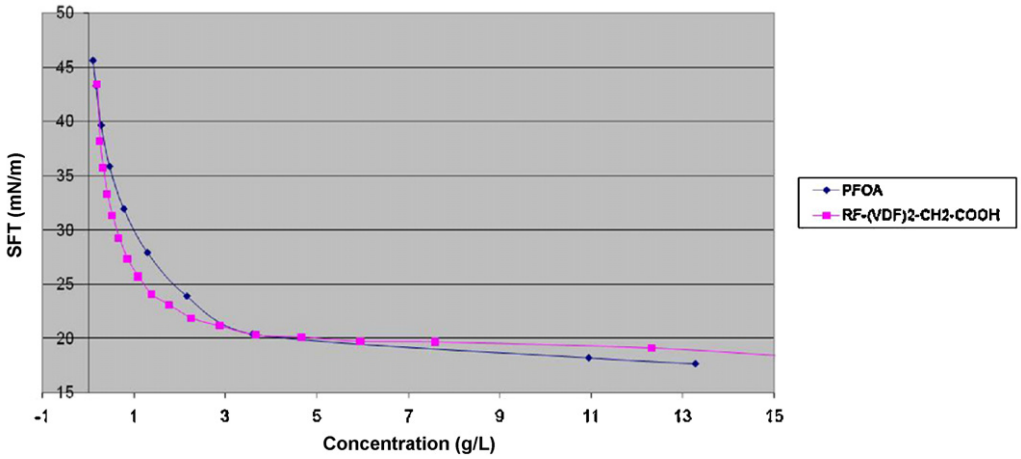

Fig. 4. Surface tension curves of 3,3,5,5,7,7,8,8,8-nonafluorooctanoic acid compared to that of perfluorooctanoic acid (PFOA).

methylene site of VDF. The ethylenation of these VDF telomers was achieved in the presence of peroxypivalate or peroxydicarbonate initiators with a quantitative conversion of the ω-iodide VDF-containing reactants. Though the chemical change of $R_F(VDF)_xC_2H_4I$ into $R_F(VDF)C_2H_4OH$ led to two product the formiate by-product was converted into the alcohol in high yield in a second step. Suitable conditions were found to avoid any dehydrofluorination of the VDF telomeric chain. Oxidation of these fluorinated alcohols in the presence of H_2SO_4/CrO_3 mixture led to the corresponding $C_nF_{2n+1}(VDF)_xCH_2CO_2H$ carboxylic acids, obtained in ca. 20–25% overall yield from 1-iodoperfluoroalkanes. Such fluorinated VDF-containing carboxylic acids exhibit very interesting surfactant behaviours. Indeed, their surface tensions reached 19.8 mN m^{-1} for a surfactant concentration of 5 g L^{-1}, and low critical micellar concentration (1.4 g L^{-1} at room temperature) showing similar values as that of commercially available perfluorooctanoic acid (PFOA).

4. Experimental

4.1. Materials

Vinylidene fluoride (or 1,1-difluoroethylene, VDF) and 1,1,1,3,3-pentafluorobutane were kindly donated by Solvay S.A. (Tavaux, France and Brussels, Belgium). 1-Iodoperfluorobutane (C_4F_9I, purity 95%) was generously supplied by Atofina (now Arkema, Pierre-Benite, France) while C_2F_5I was supplied by Clariant. It was treated with sodium thiosulfate and then distilled prior to use. *Tert*-butylperoxypivalate (TBPPI) (purity 75%) and *tert*-butyl cyclohexyl peroxydicarbonate were gifts from AkzoNobel, Chalons sur Marne, France used as supplied. Acetonitrile, dimethylformamide (DMF), tetrahydrofuran (THF), methanol, methylethylketone and dimethylacetamide (DMAc) of analytical grade were purchased from Aldrich Chimie, 38299 Saint Quentin-Fallavier, France.

4.2. Analyses

Gas chromatography analyses (GC) were achieved by means of a Delsi (Model 330) apparatus equipped with a flame ionization detector, and a 3-m-long and 1/8th inch diameter SE30 column (10% over chromosorb WHP 80/100). Vector gas was nitrogen at 0.5 bar-pressure and the detector and injector temperatures were 260 and 255 °C, respectively. The temperature programme was 15 °C/min from 50 to 250 °C. Chromatograms were recorded on a Hewlett-Packard (Model 3390) integrator which determined automatically each peak area on the chromatogram.

The compositions and the structures of the different iodinated or functional telomers were determined by *^{19}F and ^{1}H NMR spectroscopies*. The NMR spectra were recorded on Bruker 400 (400 MHz) instruments, using deuterated acetone and deuterated chloroform as the solvents and tetramethylsilane (TMS) (or $CFCl_3$) as the references for ^{1}H (or ^{19}F) nuclei. Coupling constants and chemical shifts are given in Hz and ppm, respectively. The experimental conditions for ^{1}H (or ^{19}F) NMR spectra were the following: flip angle 90° (or 30°), acquisition time 4.5 s (or 0.7 s), pulse delay 2 s (or 5 s), number of scans 16 (or 128), and a pulse width of 5 (s for ^{19}F NMR. Letters s, d, t, qi and m correspond to singlet, doublet, triplet, quintet and multiplet, respectively.

Infra red spectra were recorded on a Nicolet 510P Fourier transform infrared (FTIR) spectrometer from KBr pellets (10 wt%), and the intensities of the absorption bands (cm^{-1}) were labeled strong (s), medium (m), or weak (w). The accuracy was ±2 cm^{-1}. s, vs, m stand for strong, very strong, medium, respectively.

The characterization of the *surface tension* was carried out on a Dataphysics DCAT tensiometer equipped with a Wilhelmy plate, made of a platinum–iridium alloy. To assess the surface tension (SFT), the tensiometer first detected the surface of the test liquid (50 mL) by moving the sample vessel with the liquid up to the balance detects a weight difference (since the probe is getting lighter when it dips into the liquid). The data is acquired as the position where the plate meets the surface. Then, the plate dips into the liquid to the defined position (immersion depth). The stage moved down to the stored position of the surface and waited until a constant SFT value was reached. Each concentration was prepared at least 24 h prior to measurement. The solution was allowed to equilibrate in the apparatus and the surface tension was considered stable when the difference was less than 0.03 dyn/cm. The critical micellar concentration (CMC) was calculated as the intersection between the two straight lines emerging from high and low concentrations.

4.3. Reaction in autoclave: telomerization of VDF with $C_nF_{2n+1}I$

Radical telomerizations of VDF were performed in the presence of 1-iodopentafluoroethane or 1-iodoperfluorobutane as the degenerative chain transfer agents (CTAs) and initiated by *tert*-butylperoxypivalate (TBPPi) at 75 °C or *tert*-butylcyclohexyl peroxydicarbonate at 60 °C. A typical experiment is reported below with molar feed $[C_nF_{2n+1}I]_0/[VDF]_0 = 0.50$ and $[TBPPi]_0/[VDF]_0 = 0.13$.

A 100-mL Hastelloy (HC-276) autoclave, equipped with inlet and outlet valves, a manometer and a rupture disc, was degassed and pressurized with 30 bar of nitrogen to check for eventual leaks. Then, a 20 mmHg vacuum was imposed for 30 min. Under vacuum, were transferred into the autoclave 2.31 g (13.3 mmol) of *tert*-butylperoxypivalate (TBPPI), 12.31 g (0.05 mol) of 1-iodoperfluoroethane (C_2F_5I) and 45.0 g of 1,1,1,3,3-pentafluorobutane. Then, by double weighing, 6.4 g (0.10 mol) of VDF were introduced in the mixture. Then, the autoclave was slowly heated to 75 °C. A low exotherm of ca. 8 °C was observed and then a sharp drop of pressure from 10 bar to 1 bar. After 6 h-reaction, the autoclave was placed in an ice bath for about 30 min and unreacted VDF was progressively released. After opening the autoclave, about 50.0 g of a yellow liquid was obtained. The solvent and traces of monomers and CTA were removed by distillation at 60 °C under reduce pressure (P = 20 mmHg), to obtain a viscous and yellow product in yield = 68%. The telomer was characterized first by gas chromatography, the chromatogram of which exhibited a classical telomeric distribution (ca. 16% of monoadduct, 49% of diadduct, 18% of triadduct, 9% of tetradduct and 5% of higher telomers) and then by ^{19}F (Fig. 1) and ^{1}H NMR and IR spectroscopies.

When the reaction was initiated by *tert*-butyl cyclohexylperoxydicarbonate at 60 °C for 7 h, an exotherm of ca. 5 °C was noted (with an increase of about 9 bar) from 55 °C. After reaction, the autoclave was cooled in an ice bath for about 30 min and 2 g of unreacted VDF were vented off. After distillation, both mono- and diadduct were distilled and the overall yield were obtained 76%.

1-Iodo-1,1,3,3,5,5,6,6,6-nonafluorohexane:

^{19}F NMR ($CDCl_3$) δ (ppm): −39 ppm (–CH_2CF_2I end-group, 2F), −82.1 (C**F$_3$**– end-group 3F); −90 to −93.5 (CH_2–**CF_2**CH_2, 2F); −113.5 (m, CF_3C**F_2**CH_2, 2F).

^{1}H NMR ($CDCl_3$) δ (ppm): 2.8–3.25 (m, –C**H$_2$**CF_2–, 4H); absence of signal in the 2.2–2.5 (m, –CF_2C**H$_2$**C**H$_2$**CF_2–).

Similar conditions were used for the radical telomerization of VDF with C_4F_9I to lead to 1-iodo-1,1,3,3,5,5,6,6,7,7,8,8,8-tridecafluorooctane after distillation as a pink liquid (b.p. = 85 °C/23 mmHg).

^{19}F NMR ($CDCl_3$) δ (ppm): −39 ppm (–CH_2CF_2I end-group, 2F), −82.1 (C**F$_3$**– end-group 3F); −90 to −93.5 (CH_2–C**F_2**CH_2, 2F); −113.5 (m, C_3F_7C**F_2**CH_2, 2F); −122 to −127 (m, CF_3C_2**F_4**CF_2, 4F).

^{1}H NMR ($CDCl_3$) δ (ppm): 2.8–3.25 (m, –C**H$_2$**CF_2–, 4H); absence of signal in the 2.2–2.5 (m, –CF_2C**H$_2$**C**H$_2$**CF_2–).

4.4. Ethylenation of VDF telomers

A 100-mL Hastelloy (HC-276) autoclave, equipped with inlet and outlet valves, a manometer and a rupture disc, was degassed and pressurized with 30 bar of nitrogen to check eventual leaks. Then, a 20 mmHg vacuum was operated for 30 min. Under vacuum, were transferred into the autoclave 3.34 g (1.44×10^{-2} mol) of *tert*-butylperoxypivalate (TBPPi), 25 mL of *tert*-butanol and 21.7 g (0.058 mol) of C_2F_5(VDF)$_2$–I. Then, by double weighing, 4.0 g (0.14 mole) of ethylene (E) were introduced in the mixture and the autoclave was progressively heated to 70 °C. An exotherm of ca. 10 °C was observed followed by an increase of pressure from 7 bar up to 17 bar and then a drop of pressure to 6 bar in 8 h. After reaction, the autoclave was placed in an ice bath for about 30 min and 1.0 g of unreacted E was progressively released (the conversion of E was 75 wt%). After opening the autoclave, about 55.1 g of a yellow liquid were obtained. The latter was transferred to a separating funnel, added distilled water and shaken. Two phases were obtained: aqueous and organofluorine one. The upper phase consisted of an aqueous solution of *tert*-BuOH while the lower phase was the organofluorinated one. This operation was repeated twice. Then, the organofluorinated phase was dried over $MgSO_4$ and filtered. The total organofluorinated mixture was distilled and the fractions were analyzed by gas chromatography. That shows almost the quantitative conversion of the iodofluorinated precursor into ethylene end-capped one and the pure fractions were characterized by ^{1}H and ^{19}F NMR spectroscopy. The yield of $C_2F_5CH_2CF_2CH_2CF_2CH_2CH_2I$ was 78 wt%.

1-Iodo-3,3,5,5,7,7,8,8,8-nonafluorooctane:

^{19}F NMR ($CDCl_3$) δ (ppm): absence of signal at −39 ppm, −85.1 (C**F$_3$**– end-group 3F); −91 to −97.5 (CH_2–C**F_2**CH_2–C**F_2**CH_2–, 4F); −114.2 (CF_3C**F_2**CH_2–, 2F).

^{1}H NMR ($CDCl_3$) δ (ppm): 3.25–3.41 (t, –CH_2**CH_2**I, 2H); 2.8–3.25 m, (–C**H$_2$**CF_2–, 4H); 2.6–2.8 (m, –C**H$_2$**CH_2I, 2H).

Ethylenation of $C_4F_9CH_2CF_2CH_2CF_2I$ was achieved according to the same procedure and led to $C_4F_9CH_2CF_2CH_2CF_2CH_2CH_2I$ in 82% yield.

1-Iodo-3,3,5,5,7,7,8,8,9,9,10,10,10–tridecafluorodecane:

^{19}F NMR ($CDCl_3$) δ (ppm): absence of signal at −39 ppm, −82.1 (C**F$_3$**– end-group 3F); −92 to −97.5 (CH_2–C**F_2**CH_2–C**F_2**CH_2–, 4F); −113.2 (C_3F_7C**F_2**CH_2–, 2F); −125 to −126.6 (m, –(C**F_2**)$_2$$CF_3$, 4F).

The ^{1}H NMR spectrum is similar to that of the above one.

4.5. Hydrolysis of ethylenated VDF telomers

In a two-necked round-bottomed flask equipped with a double condenser and magnetic stirrer were introduced 25.1 g (0.05 mole) of ethylenated diadduct telomer, 44.5 g (0.6 mole) of DMF and 1.75 g (0.1 mol) of H_2O. Then, the mixture was purged by argon for 15 min, heated up to 120 °C and stirred. The reaction was monitored every 2 h by sampling and FTIR analysis of the characteristic frequency –OH at 3000–3600 cm^{-1}. After 6 h, the reaction was stopped and the medium was cooled down to room temperature. The reaction mixture was washed up 3 times with distilled hot water (ca. 80 °C) in separated funnel and the organofluorinated phase (lower phase) was dried over $MgSO_4$ and filtered. *Caution*: Do not try to evaporate DMF via rotary evaporator since the fluorinated alcohol evaporates too. Instead, gas chromatography analyses revealed the presence of two products: the first one with a retention time, RT = 18.9 min was assigned to the fluorinated alcohol while the second one corresponded to the formiate (RT = 21.1 min). Both hydrolyzed ethylenated products (yield 75 wt%) were characterized by ^{1}H, ^{19}F and ^{13}C NMR spectroscopy. NMR analyses confirmed both products: the produced alcohol with a characteristic signal (centered at 3.8 ppm assigned to **CH_2**OH) and the formiate (for which the methylene group and H end atom in CH_2OCHO led to signals centered at 4.5 and 8.1 ppm, respectively).

The ^{19}F NMR spectra of $C_4F_9CH_2CF_2CH_2CF_2CH_2CH_2OH$ (and $C_4F_9CH_2CF_2CH_2CF_2CH_2CH_2OCOH$) and $C_2F_5CH_2CF_2CH_2CF_2CH_2CH_2$ OH (and $C_2F_5CH_2CF_2CH_2CF_2CH_2CH_2OCOH$) are similar to the above iodofluoro ethylene end-capped VDF telomers.

^{1}H NMR of both above derivatives based on C_2F_5 or C_4F_9 ($CDCl_3$) ((ppm): 3.8 (t, –CH_2**CH_2**OH, 2H); 2.7–3.4 [m, **CH_2**CF_2, 4H]; 2.2–2.4 (m, –C**H$_2$**CH_2OH, 2H); 4.5 (t, CH_2**CH_2**OCHO, 2H; 8.1 s, proton of formiate, 1H).

4.6. Saponification of the fluorinated formiate

In a 250 cm^3 two-necked-round-bottom flask equipped with a double condenser and magnetic stirrer were inserted 15.7 g (0.04 mole) of hydrolyzed derivative produced synthesized above, 7.8 g (0.08 mole) of H_2SO_4 and 40 cm^3 of CH_3OH. Then, the mixture was purged by argon for 15 min at 25 °C and stirred. The reaction was controlled every hour by sampling and FTIR analysis enabled to monitor that saponification by checking the characteristic –OH at 3000–3600 cm^{-1} and the vanishing of formiate at 1712 cm^{-1}. After 4 h, the reaction was stopped. The reaction mixture was washed up 3 times with distilled hot water (ca. 80 °C) in a

separated funnel and the organofluorinated phase was dried over $MgSO_4$ and then filtered. The total organofluorinated mixture was purified by evaporation of traces of MeOH at 40 °C under 22 mmHg and characterized by gas chromatography. Only one fraction was distinguished with RT = 18.9 min, i.e. the fluorinated diol. The hydrolyzed ethylenated product (yield 75 wt%) was analyzed by ^1H, ^{19}F and ^{13}C NMR spectroscopy.

^1H NMR spectrum enabled to check the total consumption of the formiate by the absence of signal centered at 8.1 ppm.

3,3,5,5,7,7,8,8,8-Nonafluorooctanol or 3,3,5,5,7,7,8,8,9,9,10,10,10-tridecafluorodecanol:

The ^{19}F NMR spectra were similar as those of the above mixtures.

^1H NMR ($CDCl_3$) *(* (ppm): 3.8 (–C**H**$_2$OH, shifted to 4.7 ppm in the presence of Cl_3CNCO); 2.8 (–O**H**, shifted with dilution, 2H); 2.6–3.4 (AA′ system –**CH**$_2$CF$_2$–**CH**$_2$CF$_2$, 4H); 2.2–2.4 (–C**H**$_2$CH$_2$OH, 2H).

4.7. Oxidation of 3,3,5,5,7,7,8,8,8-nonafluorooctanol into 3,3,5,5,7,7,8,8,8-nonafluorooctanoic acid

In a 250 cm^3 two-necked round bottomed flask equipped with a double condenser and a magnetic stirrer were introduced 175.1 g (44.6 mmol) of 3,3,5,5,7,7,8,8,8-nonafluorooctanol, 691.3 g of acetone and 206.5 g of diethyl ether. Into that mixture the Jones catalyst [composed of 25 ml of pure sulfuric acid in a mixture of 25 g (164 mmol) of chromium oxide and 70 ml of water] was stepwise added at room temperature until a brown orange color of that mixture became persistent. After 1 h-stirring, the total product mixture was worked up with two water washings and the fluorinated organic phase was extracted with diethyl ether, dried over $MgSO_4$ filtered and concentrated. The fluorinated acid was purified by distillation (108–112 °C/4 × 10^{-2} mbar), the ^1H NMR spectrum of which showed the absence of the signal centered at 3.8 ppm assigned to methylene C$\underline{H}_2$OH of the fluorinated alcohol and the presence of a signal centered at 2 ppm assigned to the methylene group adjacent to the carboxylic acid. The yield was 72%.

3,3,5,5,7,7,8,8,8-Nonafluorooctanoic acid: $C_2F_5CH_2CF_2CH_2CF_2CH_2CO_2H$ **F-surf 2,2**:

^{19}F NMR (CD_3COCD_3) *(* (ppm): −86.5 (C**F$_3$**– end group, 3F); −90 to −92.5 (CH_2**CF$_2$**–, 4F); −116.1 (CF_3**CF$_2$**(VDF)$_2$, 2F).

^1H NMR (CD_3COCD_3, Fig. 2) *(* (ppm): 9.3 broad signal (CO_2H); 3.2 (C_2F_5**CH$_2$**, qi, $^3J_{HF}$ = 10 Hz, 2H); 2.7–3.0 (**CH**$_2$CF$_2$–**CH**$_2$CO$_2$H, 4H).

The same procedure was utilized for the synthesis of **F-surf 4,2** surfactant and the yield was 69%.

3,3,5,5,7,7,8,8,9,9,10,10,10-tridecafluorodecanoic acid (or 2H, 2H. . .-Pefluorodecanoic acid):

2H,2H,4H,4H,6H,6H-Perfluorodecanoic acid $C_4F_9CH_2CF_2CH_2CF_2CH_2CO_2H$:

^{19}F NMR (CD_3COCD_3) *(* (ppm): of −83.5 (C**F$_3$**– end group, 3F); −91 to −93.5 (CH_2**CF$_2$**–, CH_2**CF$_2$**, 4F); −112.5 (C_3F_7**CF$_2$**(VDF)$_2$, 2F); −122 to −126.6 (m, CF_3–(**CF$_2$**)$_2$$CF_2$–, 4F).

^1H NMR (CD_3COCD_3) slightly similar to the ^1H NMR spectrum above.

^{13}C NMR ($CDCl_3$, Fig. 3) *(* (ppm): 172 (CO_2H); 110–125 (CF_3 and CF_2 groups in C_4F_9); 42 (q, $^2J_{CF}$ = 32 Hz, C_4F_9–**CH$_2$**CF_2); 38 (t, $^2J_{CF}$ = 30 Hz, C_4F_9–CH_2CF_2–**CH$_2$**CF_2); 32 (t, $^2J_{CF}$ = 29 Hz, **CH$_2$**CO_2H).

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