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Original Fluorinated Surfactants Potentially Non-Bioaccumulable

ABSTRACT

This minireview updates non-exhaustive recent strategies of synthesis of original fluorosurfactants potentially non-biodegradable. Various strategies have been focused on: (i) the preparation of CF_3-X-$(CH_2)_n$-SO_3Na (with X=O, C_6H_4O or $N(CF_3)$ and n=8-12), (ii) the oligomerization of hexafluoropropylene oxide (HFPO) to further synthesize oligo(HFPO)-$CF(CF_3)CO$-R_H (where R_H stands for an hydrophilic chain); (iii) the telomerization of vinylidene fluoride (VDF) with 1-iodopentafluoroethane or 1-iodononafluorobutane to produce C_nF_{2n+1}-$(VDF)_2$-CH_2CO_2R (n=2 or 4, R=H or NH_4), (iv) the radical telomerization of 3,3,3-trifluoropropene (TFP) with isoperfluoropropyliodide or diethyl hydrogenophosphonate to prepare $(CF_3)_2CF(TFP)_x$-R_H or CF_3-CH_2-CH_2-$(TFP)_y$-$P(O)(OH)_2$, and (v) the radical cotelomerization of VDF and TFP, or their controlled radical copolymerization in the presence of $(CF_3)_2CFI$ or a fluorinated xanthate. In most cases, the surface tensions versus the surfactant concentrations have been assessed. These above strategies led to various highly fluorinated (but yet not perfluorinated) telomers whose chemical changes enabled to obtain original surfactants as novel alternatives to perfluorooctanoic acid (PFOA), ammonium perfluorooctanoate (APFO), or perfluorooctylsulfonic acid (PFOS) regarded as bioaccumulable, persistent, and toxic.

INTRODUCTION

A surfactant is an amphiphilic molecule bearing both an hydrophobic and a hydrophilic parts. Surfactants are valuable compounds, being either cationic, anionic, amphoteric or non-ionic.[1] Among them, fluorinated surfactants have found much interest since very low critical micellar concentration values have been assessed. Various commercially available compounds have been marketed by Asahi Glass, Atofina, Daikin, and DuPont, under the Surlyn®, Forafac®, Unidyne®, and Zonyl® trademark, respectively, to name a few.

Fluorinated surfactants are more efficient than hydrogenated homopolymers since their surface tensions are lower. They are usually composed of a perfluorinated chain and a hydrophilic group [2-4] and the most known are perfluorooctanoic acid ($C_7F_{15}CO_2H$, PFOA), ammonium perfluorooctanoate (APFO), and perfluorooctane sulphonate ($C_8F_{17}SO_3X$, with X= K, Na, H, PFOS). They are found in more than 200 applications[1,5] including soil and stain-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* and *bioaccumulable*[6-8] because of the too stable perfluorinated chain which cannot degrade under enzymatic or metabolic decomposition.[9] Indeed, because of their ubiquitous occurrence, they are found all over our planet (surface waters of Atlantic and Pacific Oceans[10], coastal waters, rivers, drinking and rain waters, fresh water ecosystems air[11], urban centers, soils, sediments[12,13] high Arctic ice caps, and dust in Canadian homes[14,15], in the blood of many animal species (fish, rodents[5], birds, dolphin, mammals and even livers of polar bears[16]) and the general human population worldwide, as well-reported in an extensive review from Kovàrovà and Svobodovà[5]. In fact, perfluoroalkyl substances have been detected worldwide in human blood/serum, with PFOS being the most prevalent compound in humans, followed by PFOA[17].

For these above reasons, in 2002, the major manufacturer of PFOS, decided to phase out the production of this surfactant (while its production and use at the end of the 80ies was estimated at 3,500 tons annually). Indeed, in 2005, PFOS underwent risk management evaluation by U.S. Environmental Protection Agency (U.S. EPA)[18] and from 2006, EPA launched the PFOA Stewardship Program[19] (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. Attempts to degrade PFOA and PFOS was suggested by Parsons et al.[20] 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. In an interesting review, Lehmler[21] reported various strategies to synthesize PFOA, PFOS and other fluorinated surfactants.

The objectives of this minireview concern various strategies for synthesizing non-bioaccumulable alternatives to PFOA. Five main families are considered: (i) those bearing either a CF_3O or $(CF_3)_2N$ end-groups, (ii) arising from oligo(hexafluoropropylene oxide); (iii) those produced from the telomerization of vinylidene fluoride with short perfluoroalkyliodide; (iv) 3,3,3-trifluoropropene telomers from either perfluoroalkyliodides or other chain transfer agents, and (v) surfactants obtained by cotelomerization or by controlled radical copolymerization of vinylidene fluoride and 3,3,3-trifluoropropene.

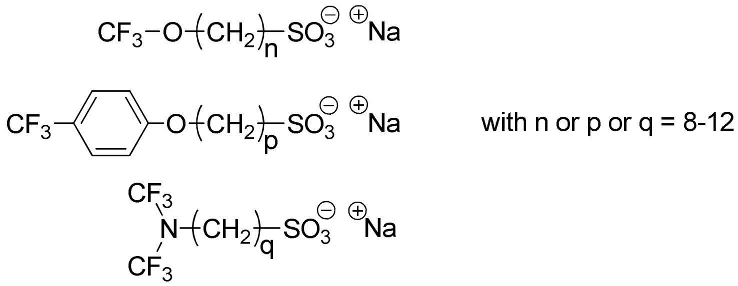
In addition, though academic surveys have been reported[9-15], industries are also active in that field. For example, the 3M Company[21] reported the synthesis of original surfactants containing C_4F_9 end group.

In this minireview, we consider water-surfactants only, and not surfactants for supercritical CO_2 in which usually a (per)fluorinated sequence is CO_2-philic while other block (or sequence such as polystyrene) is CO_2-phobic.[22]

RESULTS AND DISCUSSION

1 Fluorosulfonates.

The Merck company has recently investigated the synthesis of three key molecules bearing either a CF_3 or $(CF_3)N$ fluorinated end-group, and a sodium sulfonate at the other extremity:

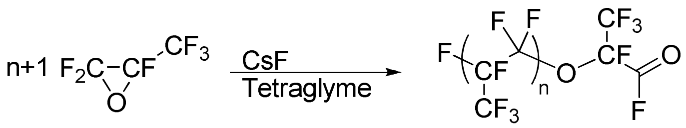


Sodium 10-(trifluoromethoxy)decane-1-sulfonate was prepared in several steps from 10-bromo-decan-1-ol. This molecule showed biomineralization and its biodegradability was evaluated. [23] It was possible to distinguish between two major degradation pathways of the fluorinated alkylsulfonate derivative: (i) a desulfonation and subsequent oxidation and degradation of the alkyl chain being predominant and (ii) an insertion of oxygen with a subsequent cleavage and degradation of the molecule. The utilized trifluoromethoxy end-group resulted in instable trifluoromethanol after degradation of the alkyl chain, which led to a high degree of mineralization of the molecule.

Indeed, $CF_3O(CH_2)_{10}SO_3Na$ compound exhibit only three fluorine atoms but still keeps a good surface efficiency though a bit lower than that of PFOA (for example, it is 25 $mN.m^{-1}$ at 0.01 wt.% in water, while for the same concentration, that of PFOA is 19 $mN.m^{-1}$).

2 Surfactants from the chemical modification of oligo(HFPO)

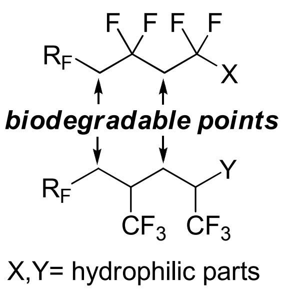
Oligo(hexafluoropropylene oxide) oligomers have shown to be degraded but their synthesis is difficult. They are usually produced by anionic ring opening oligomerization of hexafluoropropylene oxide (HFPO) (Scheme 1).[24-27] In addition, oligo(hexafluoropropylene oxide)s have been claimed to be not bioaccumulable and not persistent,[28] and various companies producing such perfluoropolyethers (PFPEs) Krytox®[29] or similar oligomers such as $(CF_2O)_x(C_2F_4O)_y$, Fomblin®[30,31], or $(CF_2CF_2CF_2O)_n$, Demnum® have also been active in synthesizing either anionic surfactants (such as oligo(HFPO)CO_2NH_4,[32], oligo(HFPO)P(O)$(OH)_2$[29] or functionalizing into PFPE-$CONHC_3H_6Si(OCH_3)_3$ [33] or leading to block cooligomers based on PFPE and hydrophilic sequences.[34,35]



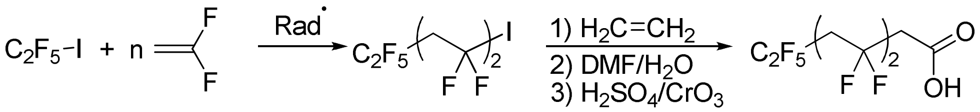
Scheme 1. Anionic ring-opening polymerization of hexafluoropropylene oxide

3 Radical Telomerization of VDF and surfactants there from

Potential degradability of surfactants can be possible if these compounds contains "weak" points which may undergo enzymatic or bio-degradation. For example, a methylene of methyne group can be of interest and this is considered when surfactants bear oligo(vinylidene fluoride) or oligo(3,3,3-trifluoropropene) chains as follows:



Recently, Kappler and Lina[36] have claimed the synthesis of $C_2F_5(VDF)_n$-CH_2CO_2H prepared in four steps from the radical telomerization of VDF with C_2F_5I. Although the radical telomerization of VDF with perfluoroalkyliodides is well-known (and extensively reviewed [37]), that patent unfortunately lacks of suitable characterizations of all the intermediates which have all been clearly identified by ^1H and ^{19}F NMR spectroscopy in a recent investigation,[38] summarized as in Scheme 2:



Scheme 2: Telomerization of vinylidene fluoride (VDF) with 1-iodoperfluoroethane followed by ethylene end-capping for the preparation of an alternative to PFOA

The produced 3,3,5,5,7,7,8,8,8-nonafluorooctanoic acid contains the same number of carbon atoms.[38] The overall yield from C_2F_5I is 32 %. The same strategy has also been successfully achieved from C_4F_9I.[38]

Figure 1 here

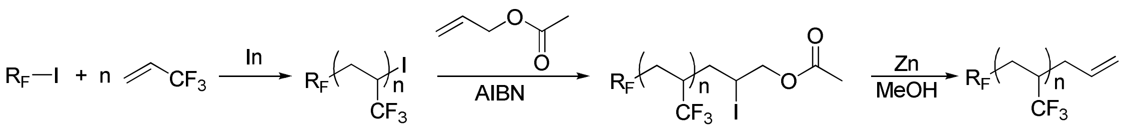
Interestingly, the surface tension of this VDF-containing surfactant which is a C10 derivative (i.e. 2 carbon atoms higher than PFOA) is similar to that of PFOA (Figure 1).

4 Radical telomerization of TFP and surfactants there from

Another interesting (but less used) fluoroolefin is the 3,3,3-trifluoropropene (TFP). In contrast to vinylidene fluoride, this fluoroalkene has not been involved in so many fluorocarbon thermoplastics or elastomers, though it is the precursor of fluorosilicone such as poly(3,3,3-trifluoropropyl-methyl siloxane). These fluorosilicones are marketed under the Silastic® tradename by the Dow Corning Company[39], and more recently produced by the Momentive Performance Materials Company[40]. These represent more than 96 % of the worldwide production of fluorosilicones.

4.1 Telomerization of TFP with perfluoroalkyliodides

Though the telomerizations of TFP with various chlorinated or brominated chain transfer agents were achieved by Vasil'eva et al.[41-44], Terent'ev et al.[45], or Zamyslov et al.[46,47], few works have been reported on the radical cotelomerization of TFP with perfluoroalkyliodides.[48-50] Recently, we revisited this reaction to produce TFP telomers with longer chain lengths that those achieved by Haszeldine[48,49] from CF_3I as the chain transfer agent, and for obtaining original TFP-based monomers as in Scheme 3.[50]



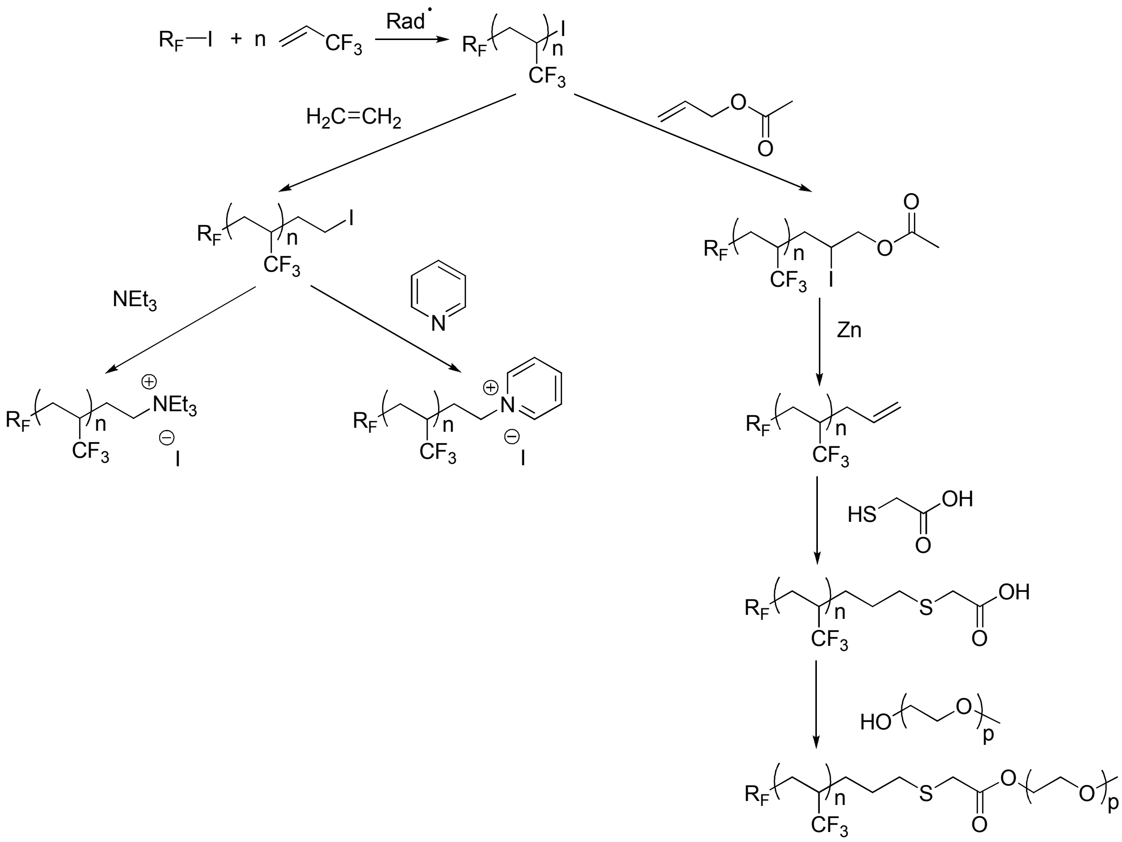
R_F= C_4F_9 or iC_3F_7

Scheme 3: Radical telomerization of 3,3,3-trifluoropropene (TFP) in the presence of perfluoroalkyliodides followed by a radical addition of these resulting TFP telomers onto allyl acetate to produce ω-unsaturated TFP telomers.

Indeed, these TFP-containing allylic derivatives were achieved in similar overall yields (ca. 65 %) from R_F-(TFP)$_n$-I as those obtained for the synthesis of $C_nF_{2n+1}CH_2CH=CH_2$ (where n=6 or 8) from $C_nF_{2n+1}I$.[51]

All the intermediates have carefully been characterized by NMR spectroscopy.[50]

These telomers have further been chemically modified into cationic surfactants according to the strategy shown in Scheme 4:



Scheme 4. Preparation of various 3,3,3-trifluoropropene-based cationic and non-ionic surfactants

The shortest pathways involve the ethylene end-capping in satisfactory yield (>70 %) [52] followed by nucleophilic substitution under mild conditions to avoid any dehydroiodination, as we could recently overcome in poly(CTFE-*alt*-IEVE) copolymers [53] where CTFE and IEVE stand for chlorotrifluoroethylene and 2-iodoethylvinyl ether, respectively.

The longest procedure requires mercaptoethanoic acid (or thioglycolic acid) under either photochemical initiation or initiated by peroxide or *tert*-butylperoxypivalate[54] to lead to original non-ionic surfactants after the esterification with oligo(ethylene oxide). The overall yield starting from R_FI is 35 %

Figure 2 here

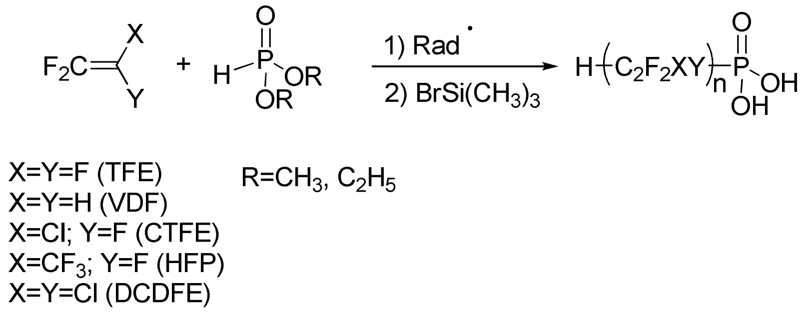
The evolution of the surface tension of these three different surfactants (although that of $(CF_3)_2CFCH_2CH(CF_3)C_3H_6SCH_2CO_2H$ has not yet been studied) has been compared to that of PFOA (**Figure 2**) and it is observed that the surface tensions are only slightly higher than that of PFOA for surfactant concentrations lower than 4-4.5 $g.L^{-1}$or even better for the cationic surfactants bearing ammonium polar head.

Physicochemical properties (mainly inertness to acids and bases) of these TFP-containing surfactants are supplied in Table 1. The oligo(TFP-*co*-VDF)-*b*-PEO has the best chemical inertness. They also show satisfactory solubility in water and methanol but are insoluble in diethylether or benzene.

Table 1 here

4.2 *Telomerization of TFP in the presence of diethyl hydrogenophosphonate*

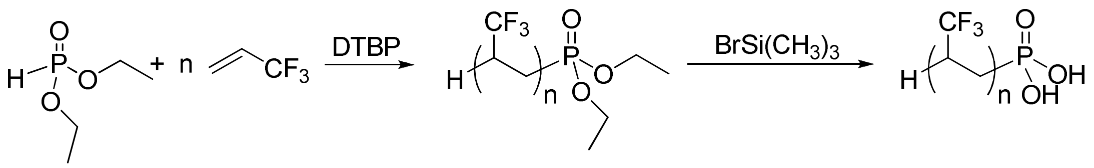
Less known fluorosurfactants can exhibit phosphonic acid end-groups as the polar hydrophilic part after the hydrolysis of the corresponding fluoro-phosphonates. These latters can be produced by the radical telomerization of various fluoroalkenes (tetrafluoroethylene, hexafluoropropylene, vinylidene fluoride, chlorotrifluoroethylene, dichlorodifluoroethylene),[55-63] with dialkyl hydrogenophosphate as listed in **Table 2** and Scheme 5:



Scheme 5. Phosphonic acid-containing fluorosurfactants achieved by radical telomerization of fluoroalkenes with dialkyl hydrogenophosphate followed by hydrolysis

Table 2 here

However, few reactions that involve TFP have been reported and more recently, di*tert*-butylperoxide was shown to be the most efficient initiator. The reaction is as displayed in Scheme 6: [62]



Scheme 6. Radical telomerization of 3,3,3-trifluoropropene (TFP) with diethyl hydrogenophosphonate followed by hydrolysis.

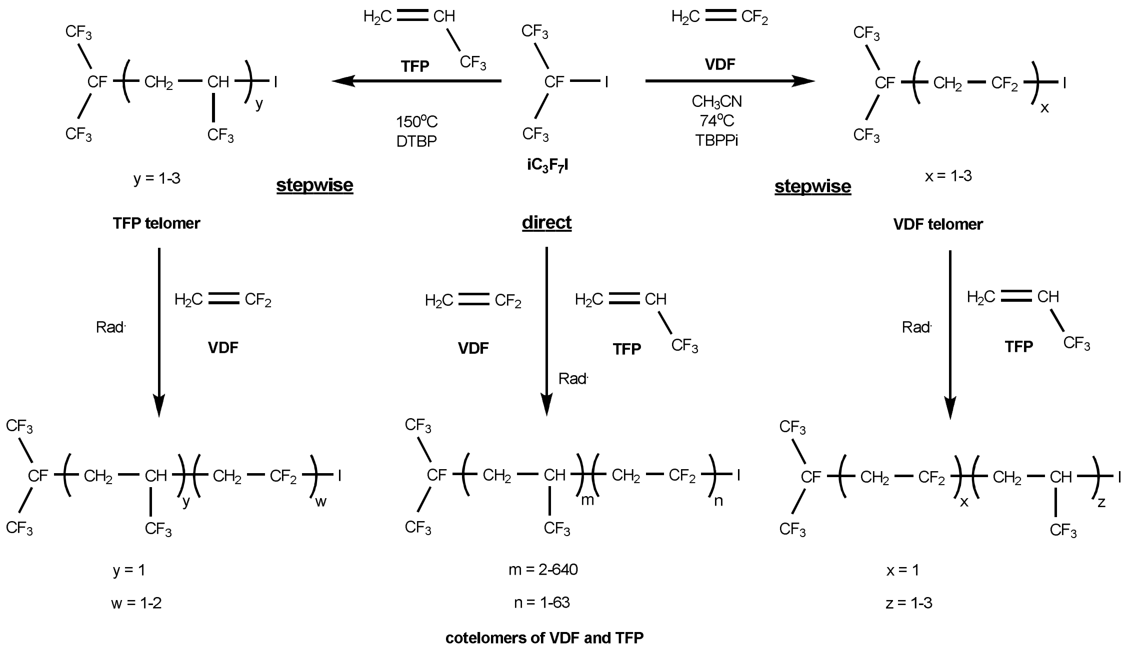
The hydrolysis was carried out refluxing $BrSi(CH_3)_3$ and led to 55 % yield of $CF_3CH_2CH_2(TFP)_x$-$P(O)(OH)_2$, whose surface properties are under investigation.

Although the degradation of these surfactants containing VDF and TFP have not been achieved, these compounds are very interesting, and simple reactions have been carried out in satisfactory yields. Thus, it was of interest to synthesize original surfactants containing both VDF and TFP units.

5 Conventional or controlled radical cotelomerization of VDF and TFP with suitable chain transfer agents, and chemical modification of the resulting poly(VDF-*co*-TFP) cotelomers or copolymers

5.1 Radical cotelomerization of VDF and TFP in the presence of perfluoroalkyliodides

Interestingly, the radical cotelomerizations of both the above fluoroalkenes have also led to novel fluorinated surfactants. A first step concerns the cotelomerization and we have chosen two strategies to achieve this goal: by sequential and direct cotelomerization as indicated in Scheme 7.[64]



Scheme 7. Sequential and random cotelomerizations of vinylidene fluoride (VDF) and 3,3,3-trifluoropropene (TFP) with isoperfluoropropyl iodide

The direct cotelomerization led to both higher yields and molecular weights while the stepwise enabled a better control over the structure.[64] Direct emulsion cotelomerization also led to telomers with molecular weights up to 66,000 g.mol^{-1}, which can be used as elastomers.

These original poly(VDF-*co*-TFP) copolymers (Scheme 7) have been characterized by ^{1}H, ^{13}C and ^{19}F NMR spectroscopies to evidence (i) the molecular weights ranging between 425 and 66,000 g.mol^{-1}, (ii) the mol. contents of both VDF and TFP comonomers (6-81 % and 19-96 %, respectively), (iii) the VDF and TFP defects of chainings, and (iv) the end-groups of the chains. Identifications for $–CH_2F_2$-I and –

CF_2CH_2-I are crucial since the former isomer is able to reinitiate a chain, hence leading to block copolymers, in contrast to the latter one which is inactive under radical initiation to insert another sequence or to react onto a double bond. These reactivities have been extensively reported earlier,[65,66] even involving C_6F_{13}-CH_2CF_2-I and HCF_2-CF_2CH_2-I models for the iodine transfer polymerization of VDF.

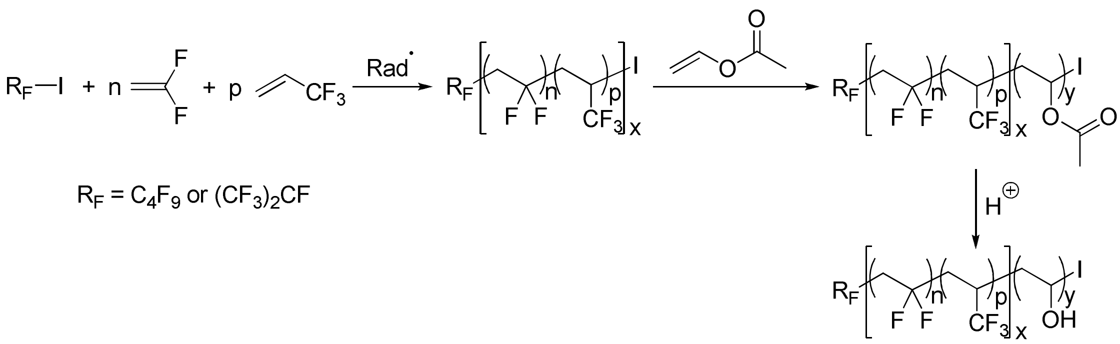
5.2 Iodine transfer copolymerization of VDF and TFP

This iodine transfer copolymerization was optimized for achieving the preparation of block copolymers based on VDF and TFP.

As for -TFP-I end-group, a previous study has shown that –$CH_2CH(CF_3)$-I is able to react onto allyl acetate[50], and a recent work[52] has shown that it is also reactive onto ethylene producing –$CH_2CH(CF_3)$-CH_2CH_2-I leading to various surfactants as shown in section 4.1. Such an original end-group leads to a wide range of functional groups by nucleophilic substitution such as: OR (R=H, Ac), CO_2H, N_3,…

Since both –CH_2CF_2-I and –$CH_2C(CF_3)$-I are able to react onto monomers, we have chosen vinyl acetate for two reasons: (i) VAc is able to be polymerized under iodine transfer polymerization[67] and (ii) the hydrolysis of an oligo(VAc) produces oligo(vinyl alcohol) which brings the hydrophilic counter-part in the structure of the resulting surfactant.

Hence, poly(VDF-*co*-TFP)-I was involved as the chain transfer agent in the iodine transfer polymerization of vinyl acetate (Scheme 8).[54] This reaction was monitored by size exclusion chromatography (SEC) (showing a shift to higher molecular weights when the oligo(VAc) was inserted) and by ^{1}H NMR spectroscopy (from the integrals of the signals centered at 2.9-3.2, 4.4, and 2.05 ppm assigned to the methylene group of VDF, the methyne group of TFP, and methyl groups of acetate, respectively). Molecular weights were ranging from 600 to 10,000 g.mole^{-1}. Hydrolysis of the oligo(VAc) sequence was carried out under acidic conditions (Scheme 8).[54] Usually, such a hydrolysis occurs in the presence of base which is obviously a non suitable procedure in this present case, since the VDF units in the poly(VDF-*co*-TFP) block are base sensitive.

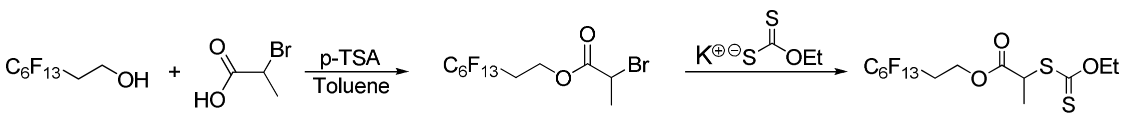


Scheme 8. oligo(VDF-*co*-TFP)-*b*-oligo(vinyl acetate) block cotelomers, and their hydrolysis to obtain surfactants.

5.3 Controlled radical copolymerization of VDF and TFP in the presence of Xanthate

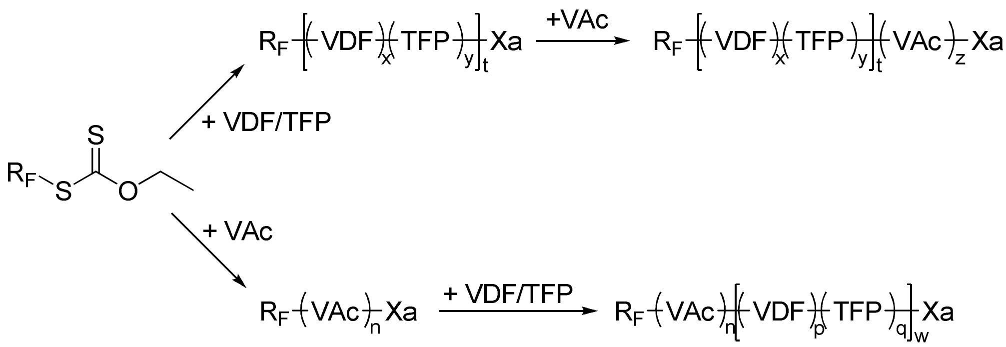
Macromolecular design via the interchange of xanthates (MADIX) has been invented by the Rhodia Company for controlling the radical polymerization of vinyl acetate (VAc).[68-70] On the other hand, a few investigations[71,72] dealing with the radical (co)polymerization of fluoroolefins controlled by hydrogenated xanthates have been realized. The first original fluorinated xanthate (bearing a CF_3 group) was reported by

Monteiro et al[73]. More recently,[74] an original fluorinated xanthate was prepared from the esterification of $C_6F_{13}CH_2CH_2OH$, as displayed in Scheme 9:

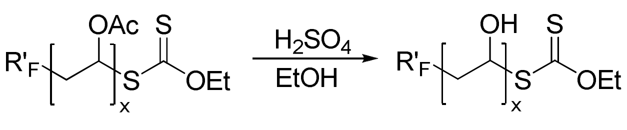


Scheme 9. Preparation of the fluorinated xanthate from 1H,1H,2H,2H-perfluorooctanol (p-TSA stands for *para*-toluene sulfonic acid).

This original fluorinated xanthate was used for the controlled radical copolymerization of VDF and TFP followed by the insertion of a second oligo(vinyl acetate) block (Scheme 10) or from a first sequence of VAc followed by the insertion of the second oligo(VDF-*co*-TFP) block.[75]



Hydrolysis



Scheme 10. Oligo(VDF-*co*-TFP)-*b*-oligo(VAc) block cooligomers obtained by MADIX technology, and their hydrolysis into fluorinated surfactants (where Xa = SC(S)OEt).

All the structures obtained were characterized by NMR spectroscopy and size exclusion chromatography showing a shift toward higher molecular weights after the insertion of the second block. The poly(VAc) block was then successfully hydrolyzed to yield a hydrophilic vinyl alcohol block enabling the molecule to get a surfactant character. The surface tension was examined (Figure 3) and compared to that of APFO.

Figure 3 here

CONCLUSIONS

Except oligo(HFPO)-based and CF_3-X-$(CH_2)_n$-SO_3Na (X=O, C_6H_4O,CF_3N and n=8-12) surfactants, which have been mainly investigated in industry, few attractive surfactants endowed with potential non-bioaccumulation can be synthesized from the radical cotelomerization or controlled radical cooligomerization of VDF and TFP.
Searching other chain transfer agents which bear a polar group is still useful to investigate other families of surfactants, under investigation. For example, diethyl hydrogenophosphonate is an efficient chain transfer agent for developing telomers bearing a phosphonic acid group, and the surface properties of the resulting surfactants are under investigation.

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FIGURES

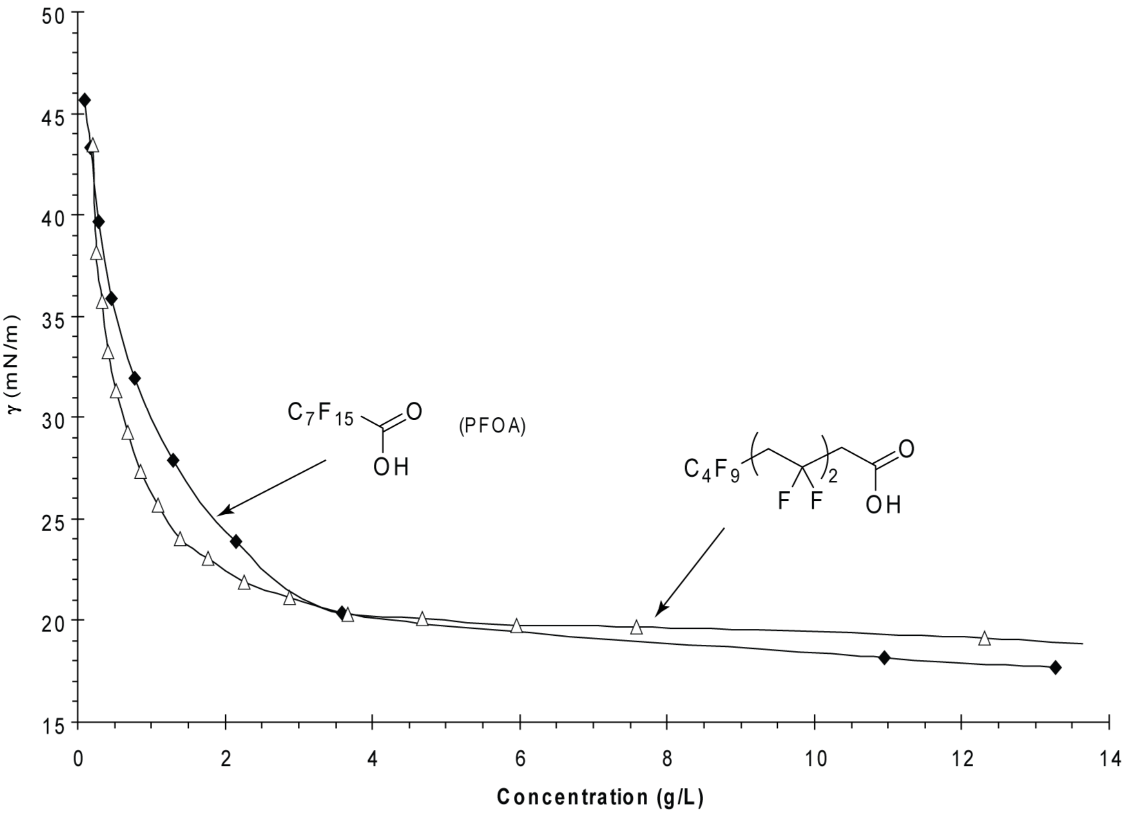

Figure 4: Surface tension measurement of C_4F_9-$(VDF)_2$-CH_2-COOH (white triangles) compared to PFOA (black diamonds).

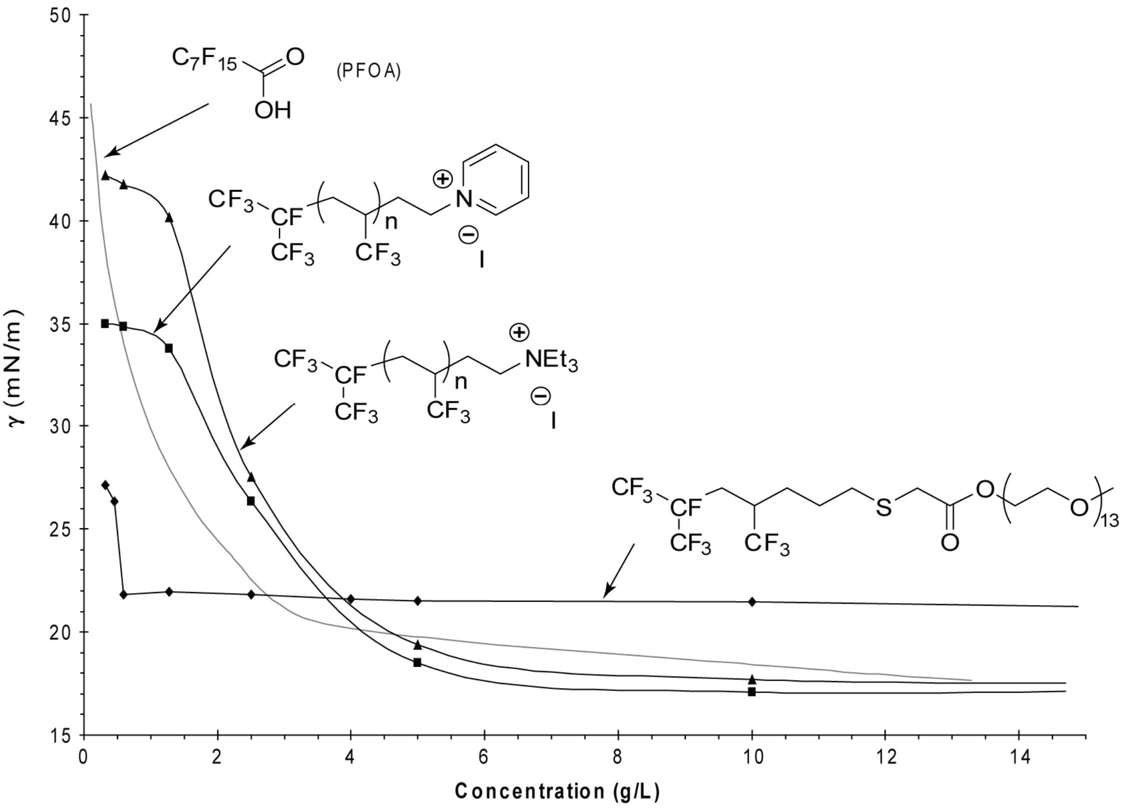

Figure 5. Surface tension versus the concentration of TFP-based surfactants compared to that PFOA.

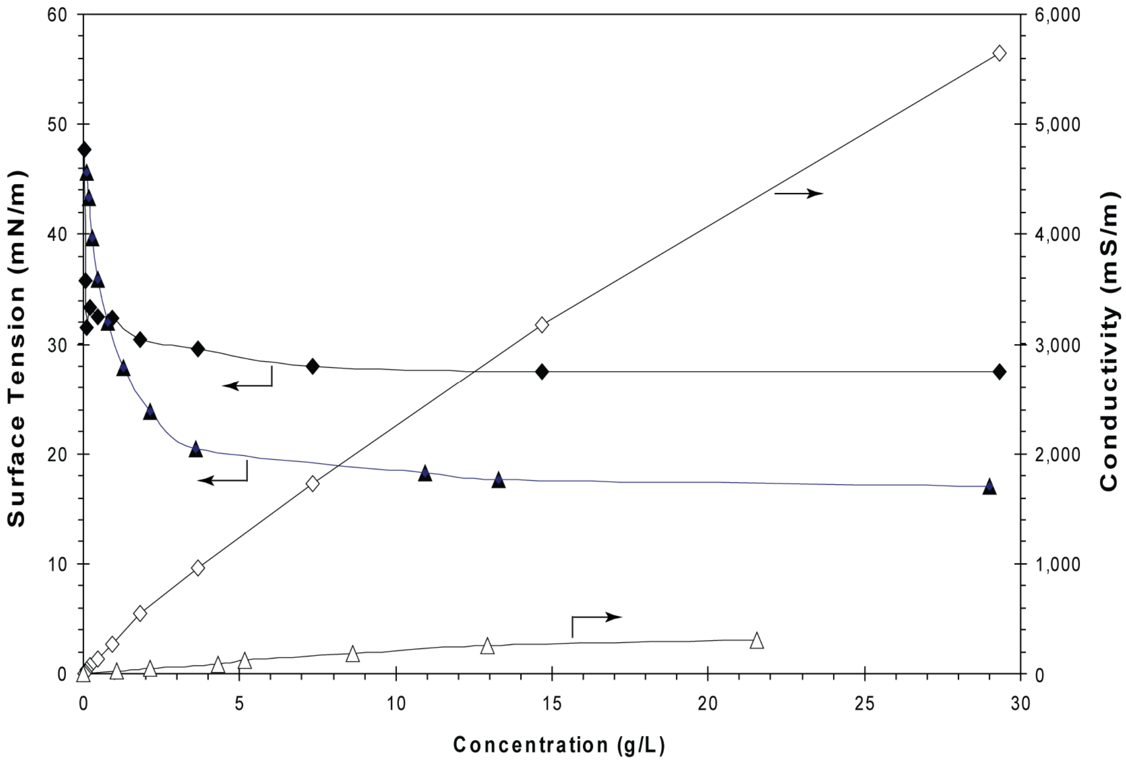

Figure 6. surface tension and conductimetry curves of poly(VDF-*co*-TFP)-*b*-poly(VA) block cooligomers (diamonds) compared to those of APFO (triangles). (VDF, TFP, and VA stand for vinylidene fluoride, 3,3,3-trifluoropropene, and vinyl alcohol, respectively)

SCHEME CAPTIONS

Scheme 1. Anionic ring-opening polymerization of hexafluoropropylene oxide

Scheme 2: Telomerization of vinylidene fluoride (VDF) with 1-iodoperfluoroethane followed by ethylene end-capping for the preparation of an alternative to PFOA

Scheme 3: Radical telomerization of 3,3,3-trifluoropropene (TFP) in the presence of perfluoroalkyliodides followed by a radical addition of these resulting TFP telomers onto allyl acetate to produce ω-unsaturated TFP telomers.

Scheme 4. Preparation of various 3,3,3-trifluoropropene-based cationic and non-ionic surfactants

Scheme 5. Phosphonic acid-containing fluorosurfactants achieved by radical telomerization of fluoroalkenes with dialkyl hydrogenophosphate followed by hydrolysis

Scheme 6. Radical telomerization of 3,3,3-trifluoropropene (TFP) with diethyl hydrogenophosphonate followed by hydrolysis.

Scheme 7. Sequential and random cotelomerizations of vinylidene fluoride (VDF) and 3,3,3-trifluoropropene (TFP) with isoperfluoropropyl iodide

Scheme 8. oligo(VDF-*co*-TFP)-*b*-oligo(vinyl acetate) block cotelomers, and their hydrolysis to obtain surfactants.

Scheme 9. Preparation of the fluorinated xanthate from 1H,1H,2H,2H-perfluorooctanol (p-TSA stands for *para*-toluene sulfonic acid).

Scheme 10. Oligo(VDF-*co*-TFP)-*b*-oligo(VAc) block cooligomers obtained by MADIX technology, and their hydrolysis into fluorinated surfactants (where Xa = SC(S)OEt).

Table 1. Physicochemical characteristics of the surfactants based on TFP

Conditions	Weight losses (%)		
	$iC_3F_7(TFP)(CH_2)_3SCH_2CO_2(PEO)CH_3$	$iC_3F_7(TFP)(CH_2)_2N^+C_5H_5,I^-$	$iC_3F_7(TFP)(CH_2)_2N^+(CH_3)_3,I^-$
(1) Base-acid resistance			
98 % H_2SO_4 25 °C; 7 days	0.0	<1.2	0.0
60% HNO_3 25 °C; 7 days	-	>40.0	<20
37% HCl 25 °C; 7 days	0.0	>15.0	0.0
40% NaOH 25 °C; 7 days	0.0	0.0	0.0
(2) Solubility in selected solvents		**Solubility (g/100mL)**	
Water 25°C; 3 days	>10	>10	>10
Methanol 25°C; 3 days	>10	>10	>10
Diethyl ether 25°C; 72 hrs	<1	<1	<1
Benzene 25°C; 3 days	<2	<2	<2
Acetone 25°C; 3 days	<10	<10	<10

Table 3. Physicochemical characteristics of the surfactants based on TFP

Fluoroalkene	Initiation conditions	$R_o^{a)}$	$\overline{DP}_n$	C_T^{∞} b)	Reference
$F_2C=CF_2$	AIBN	0.1-2	n = 1-10	n.d.	[55]
	Peroxide	-	n = 1-6	n.d.	[56]
$F_2C=CFCF_3$	peroxide, therm.	-	n = 1	n.d.	[57]
$F_2C=CFCl$	Peroxides, 140°C	0.3-2.0	n = 1-10	0.34	[58]
$F_2C=CH_2$	DTBP, 140°C DBP, 92°C AIBN, 80°C	0.1-2.0	n = 1-15	0.34	[59]
$FClC=CFCl$	γ-rays, 9.3 days	3.0	-	n.d.	[60,61]
$F_2C=CCl_2$	γ-rays, 16 days	2.1	-	n.d.	[60,61]
$CFCl=CCl_2$	γ-rays, 15 days	2.0	-	n.d.	[60,61]
$H_2C=CHCF_3$	DTBP, 130°C	1.0	monoadduct 39%	n.d	[57]
	DTBP, 140°C	variable	n = 1-8	0.75	[62]
$H_2C=CHR_F$	Peroxide, AIBN	1.0	n = 1-3	n.d.	[63]

a) $R_o = [HP(O)(OR)_2]_o/[Fluoroalkene]_o$

b) $\overline{DP}_n$ means average degree of telomerization

c) C_T means the infinite transfer constant to $HP(O)(OR)_2$

Table 2. Radical telomerisation of various fluoroalkenes with dialkyl hydrogen phosphonate and characteristics (n.d. stands for not determined).