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A new oligo(hexafluoropropylene oxide)-*b*-oligo(ethylene oxide) diblock surfactant obtained by radical reactions

Jiří Lapčík [1,2], Olinda Gimello[2], Vincent Ladmiral[2], Chadron Mark Friesen[3*], and Bruno Ameduri[2*]

[1]Department of Organic Chemistry, Institute of Chemical Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic, [2]Ingenierie et Architectures Macromoleculaires, Institut Charles Gerhardt, Ecole Nationale Supérieure de Chimie de Montpellier (UMR5253-CNRS), 8, rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France; [3]Department of Chemistry, Trinity Western University, Langley, British Columbia, V2Y 1Y1, Canada

Abstract

The synthesis and characterization of a new oligo(hexafluoropropylene oxide)-*b*-oligo(ethylene oxide), oligo(HFPO)-*b*-oligo(PEG), diblock co-oligomer are presented. First, the model reactions dealing with the radical addition of 1-iodoperfluorohexane ($C_6F_{13}I$) onto allyl alcohol and allyl-O-PEG-OCH_3 were optimized in terms of choices of the initiator (azobisisobutyronitrile [AIBN], *tert*-butylperoxypivalate [TBBPi], and benzoyl peroxide [BPO]) and of the solvent, temperature, and time. Allyl-O-PEG-OCH_3 was obtained from the etherification of ω-hydroxy-PEG with allyl bromide. End-capping of oligo(HFPO) with PEG was successfully achieved by the radical addition of 1-iodoperfluoropropyl-2-oligo(hexafluoropropylene oxide) [oligo(HFPO)-$CF(CF_3)CF_2I$] onto allyl-O-PEG-OCH_3 using the best conditions of the model reactions. Although TBPPi failed and led to oligo(HFPO)-*iso*butyl iodide, AIBN and BPO yielded oligo(HFPO)-CH_2CHICH_2-oligo(PEG). The selective reduction of the latter compound led to oligo(HFPO)-*b*-oligo(PEG) in 77%-yield, the surface tension properties of which were compared to those of commercially available ammonium perfluorooctanoate (APFO) and perfluorooctanoic acid (PFOA). Its critical micelle concentration was 0.04 $g \cdot mol^{-1}$. All models, intermediates, and diblock co-oligomers were characterized by ^1H, ^{19}F, and ^{13}C NMR spectroscopy as well as matrix assisted laser desorption ionization (MALDI) and Atmospheric pressure Solids Analysis Probe (ASAP) Time-Of-Flight mass spectrometry (TOF-MS).

Correspondence: chad.friesen@twu.ca, bruno.ameduri@enscm.fr

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1. Introduction

Polyfluorinated compounds (PFCs) are useful chemicals involved in a wide range of products. Among them, molecules that bear both fluorinated hydrophobic moieties and hydrophilic parts, called "surfactants" [1,2,3,4] are valuable compounds. Surfactants are being used in more than 200 applications [5,6,7,8,9,10] ranging from the protection of surfaces (textile, paper, carpets, masonry, metal, leather), as stimulating fluids for oil recovery, fire-fighting foam, skin protection from chemical agents, soil and stain-repellents, plane hydraulic fluids,[1,11] paints, lubricants, electroplating, photographic emulsifiers, pressure sensitive additives, pharmaceuticals, insecticides, or involved in cosmetic formulations. Perfluorooctanoic acid (PFOA), for example, is frequently used as surfactant in the aqueous media (co)polymerization of hydrophobic monomers, (e.g. fluorinated monomers [5,12] PFOA and perfluorooctane sulfonic acid (PFOS) are the most used fluorosurfactants. Their surface tensions and critical micelle concentrations are very low.[1,2] They feature both pronounced hydrophobicity and oleophobicity and display high chemical and thermal resistance. They can be synthesized either by electrochemical fluorination (ECF)[13]or by telomerization. [14] The former process leads to ca. 70% straight chain PFOS along with 30% of branched and cyclic isomers. [15] PFOA is being used in fast food packaging (≥300 µg kg $^{-1}$) for its water and oil repellencies.[4b]

Telomerization reactions[14] are straightforward and the most representative example is the radical telomerization of tetrafluoroethylene (produced industrially by various chemical industries) that generated telomers containing a hydrophobic perfluorinated C_nF_{2n+1} end-group (where n is an even number).[5,14] D'Eon and Mabury[16] reported the fluorotelomer production values from 1970 to 2020. Telomeric alcohols have been widely used for polymers and surface coatings with an estimated annual production of ca. 12,000 t/year in 2004.7 In spite of its

remarkable properties and wide range of applications, PFOS was listed in Annex B of the Stockholm convention as a persistent organic pollutant in 2009.[17] As research has demonstrated that many of the long-chain PFCs are toxic, persistent, and bioaccumulative, government and regulatory agencies have been working toward agreements and regulations to limit the production of some PFCs.[10,18] These three health and environment severe issues arise from the high stability of the perfluorinated chains which are not degraded either by enzymes or metabolic processes.[19] In addition, PFCs bioaccumulate in the food chains and have long half-lives in human blood:[16] 3.6, 5.4,[20,21,22] and 8.5 years for PFOA, PFOS and perfluorohexane sulfonate, respectively.[23] Other severe limitations are the foetal development toxicity, the immunotoxicity, and the effects on thyroidal hormones.[24] PFOS itself is quite stable in the environment, with no known natural mechanism of degradation.[24] Attempts to degrade PFOA and PFOS were suggested by Parsons et al.[22] PFOS remains the predominant PFC found in all living species, tissues, and locations analyzed around the world.[25] PFOA and PFOS accumulations in marine mammals (e.g., >1200 ng/g in liver) are common all over the Northern hemisphere.[11,16,26] In a recent review, Fromme *et al*. [27] evaluated potential PFC exposures from indoor and outdoor air, house dust, drinking water, and food [28] and concluded that median uptakes of PFOS and PFOA were on the order of 2–3 ng/kg/day, with food being responsible for greater than 90% of this exposure.[29] However, with the wide variety of foods consumed and the difficulty in establishing sensitive analytical methods that accurately measure contaminants, there is still a great deal of uncertainty about the role of food as an exposure route.[30] An increasing number of studies has suggested that fish from contaminated water bodies may be the prevailing source of exposures to PFOS and possibly other long-chain perfluorocarbon acids (PFCAs).[26,31] In addition, the consumption of contaminated drinking water[15] has been linked with an increased surfactant amount in blood, as reviewed by Lindstrom *et al*. [15]

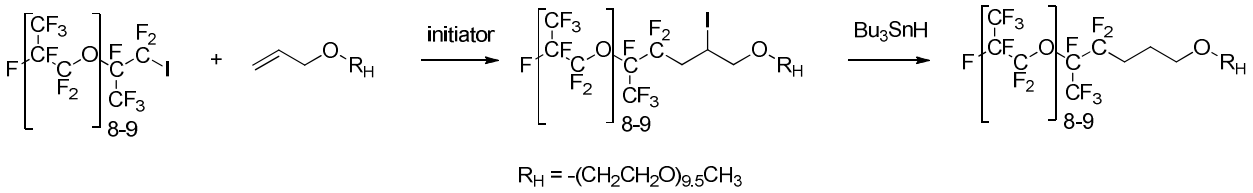
Indeed, in 2006, the European Union set out a ban on the use of PFOS in a number of goods. However, PFCs are still produced and released into the environment[16] and have been quoted as the "*PCBs of the XXIst century*". In the same time, EPA launched the 2010/2015 PFOA Stewardship Program[32] to reduce emissions and residual content of PFOA and long-chain PFCAs by 95% by 2010, with the goal to eliminate long chain PFCs by 2015. While there has been some

success with voluntary controls for some PFCs,[32] limited incentive for companies to join in these voluntary agreements was noted. Hence, a growing interest for the synthesis of short perfluoroalkyl chain surfactants was noted,[33,34,35,36] especially since the 3M company developed perfluorobutane sulfonyl compounds.[37,38,39]

Various strategies to synthesize potentially non-bioaccumulable alternatives to PFOA have been reported: [40] (1) Chemicals bearing either a CF_3O or $(CF_3)_2N$ end-groups,[41] (2) Compounds produced from small perfluorinated chain with non-ionic oligoethylene oxide or carbohydrate,[36,42] (3) carboxylate gemini surfactants,[43,44] (4) vinylidene fluoride (VDF) telomers with short 1-iodoperfluoroalkane where methylene groups may act as "weak" degradable points,[45,46] (5) 3,3,3-trifluoropropene (TFP) telomers from either 1-iodoperfluoroalkanes or other chain transfer agents,[47] (6) VDF and TFP cotelomers ,[48] and (7) compounds derived from oligo(hexafluoropropylene oxide), oligo(HFPO).[49] Interestingly, these perfluorooligoethers were shown to be non toxic and non bioaccumulable[50] and thus offer further opportunities to synthesize more environmentally friendly fluorinated surfactants. For example, Li et al.[51] reported the synthesis of oligo(HFPO)-CO_2-PEG from the esterification of trimer(HFPO)C(O)F with HO-PEG leading to a surfactant that possesses a critical micelle concentration of 0.6 g/L. However, the ester group induces limitations in some applications due to their stability and polarity. The objective of this article is thus to overcome this issue. It describes the use of longer oligo(HFPO)-based novel surfactants. Oligo(HFPO) iodide was reacted under radical conditions with ω-unsaturated oligo(ethylene oxide) to yield the desired oligo(HFPO)-based surfactants.The study of their surface tension properties is also presented.

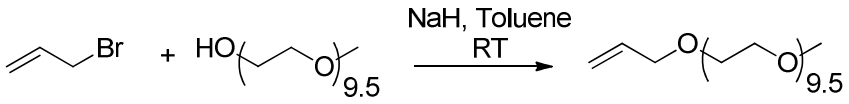
2. Results and discussion

The purpose of this work was to explore conditions that were favorable in converting 1-iodo perfluorooligoalkane ether, specifically oligo(hexafluoropropylene oxide) [oligo(HFPO)] primary iodide, into diblock surfactants using polyethylene glycol (PEG) as the hydrophilic sequence. This oligo(HFPO)-*b*-Oligo(EG) diblock surfactant was achieved by the radical addition of [oligo(HFPO)] primary iodide onto allyl-PEG followed by a selective reduction of the iodine atom (Scheme 1).



Scheme 1. Synthesis of oligo(hexafluoropropylene oxide)-*b*-polyethylene glycol, oligo(HFPO)-*b*-PEG diblock surfactant by radical addition of [oligo(HFPO)] primary iodide onto allyl PEG followed by a selective reduction of the iodine atom.

Earlier work had demonstrated that the synthesis of an oligomeric diblock was possible with aromatics and oligo(HFPO)-$CF(CF_3)CF_2I$.[52] Other studies reported that perfluoroalkyl iodides can be added onto alkenes in high yields[53] under radical conditions, as well as act as efficient chain transfer agents in iodine transfer copolymerization of vinylidene fluoride (VDF) and hexafluoropropylene (HFP).[54] The radical addition process was considered the best route to forming a diblock of perfluoroalkyl or 1-iodo perfluorooligoalkane ether with polyethylene glycol (PEG).[9] Indeed, other types of linkages such as esters or amides are likely to hydrolyze over time and thus prone to degradation. The synthesis of target amphiphilic diblock proceeded in two steps: i) the introduction of an allylic ether on the hydroxyl end-group of mono methyl ether polyethylene glycol *via* Williamson ether syntheses (**Scheme** 2), and ii) the radical addition of the iodide precursor onto the allylic moiety. Depending on the conditions used, a reduction step was achieved.



Scheme 2. Synthesis of allyl oligo(ethylene oxide) allyl-O-PEG-OCH_3 from the etherification of HO-PEG-OCH_3 with allyl bromide .

The yield in allyl-O-PEG-OCH_3 was found to be ca. 65%. The ^{1}H NMR spectrum (Figure S1) displays the expected multiplets assigned to the three ethylenic protons centered at 5.11, 5.20,

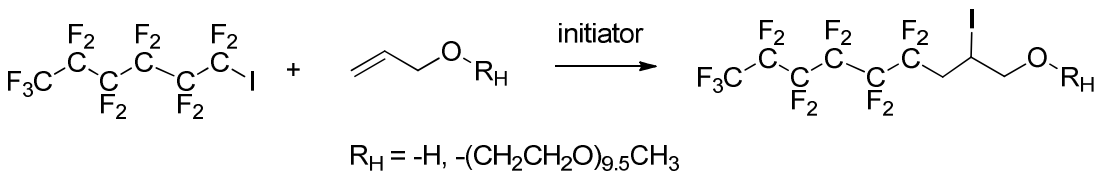
and 5.85 ppm while the signals assigned to the methylene groups adjacent to oxygen atoms in oligo(ethylene oxide) chain and a characteristic of CH_3O end-group are located at 3.96 ppm and a singlet centered at 3.31 ppm, respectively. The ^{13}C NMR spectrum (Figure S2) confirms its structure from the signals centered at 136 and 116, 70.7, and 59 ppm assigned to both ethylenic carbon atoms, methylenes in ethylene oxide units, and the $-OCH_3$ end-group, respectively. The synthetic strategy for this work relies on the radical addition of 1-iodoperfluoroalkane or 1-iodoperfluoroalkylether [oligo(HFPO)-$CF(CF_3)CF_2I$] onto an alkene compound such as above allyl-O-PEG-OCH_3.

To explore the appropriate and best conditions to prepare oligo(HFPO)-*b*-oligo(PEG) diblock co-oligomers in high yield using radical initiators, a systematic study was undertaken. This article reports the study of five systems: 1) short 1- iodoperfluoroalkane ($C_6F_{13}I$) reacting with a model alkene [e.g., allyl alcohol], 2) small perfluorinated alkyl iodides reacted with a polymeric alkene [e.g., allyl-O-PEG-OCH_3], 3) polymeric fluorinated iodides [oligo(HFPO)-$CF(CF_3)CF_2I$] with a simple alkene [e. g., allyl alcohol], 4) polymeric fluorinated iodides with a polymeric alkene, and 5) small molecule and polymeric fluorinated iodides reacted strictly with three radical initiators: azobisisobutyronitrile [AIBN], *tert*-butylperoxypivalate [TBBPi], and benzoyl peroxide [BPO]) to observe potential by-product formation.

2.1. Radical addition of 1-iodoperfluorohexane ($C_6F_{13}I$) onto unsaturated alkenes (allyl alcohol and allyl ether, allyl-O-PEG-OCH_3).

2.1.1 Radical Addition onto allyl alcohol

The radical addition of 1-iodoperfluoroalkanes onto unsaturated derivatives has been reported in many reviews and articles, involving thermal and photochemical initiations, metallic salts and radical initiators.[55] The model reaction with 1-iodoperfluorohexane ($C_6F_{13}I$) with allyl alcohol (a simple functional alkene compound), initiated by azobisisobutyronitrile, AIBN, *tert*-butylperoxypivalate, TBBPi, or benzoyl peroxide, BPO (**Scheme** 3), was an important starting point to further explore the use of oligo(HFPO) diblocks.



Scheme 3. Radical reaction of 1-iodoperfluorohexane with allyl alcohol (initiated by azobisisobutyronitrile AIBN, *tert*-butylperoxypivalate, TBBPi, and benzoyl peroxide, BPO).

The reaction temperatures were first adjusted so the half-lives of the initiators were approximately one hour (Table 1). The reactions were initially monitored by gas chromatography/mass spectrometry (GC/MS) to determine reaction times. After the reaction and removal of trace of unreacted reactants, the total product mixture was characterized by the ^{1}H ^{19}F, and ^{13}C NMR spectroscopies to determine the reaction yield. In all cases, $C_6F_{13}I$ conversion was higher than 93%. The first ^{1}H NMR spectrum (Figure S3) did not display any signals at ca. 5.5-7.0 ppm range assigned to the ethylenic protons of allyl alcohol (Figure S4) but instead showed complex systems at 2.95 and 2.65 ppm and 4.3 ppm attributed to $C_6F_{13}CH_2$- and –CHI-, respectively. ^{19}F-NMR spectrum (Figure S5) showed the high field shift of the signal assigned initially to -CF_2I (-59 ppm, Figure S6) to that of -CF_2CH_2- (-112 ppm) as a characteristic AB system. All other signals such as the CF_3- centered at -83 ppm, and those in the -123 to -128 ppm range assigned to the $(CF_2)_n$-, remained relatively unchanged compared to those of the spectrum of $C_6F_{13}I$. Finally, the ^{13}C NMR spectrum (Figure S7) exhibited a doublet of triplets, and both singlets centered at 37.18, 67.8, and 20.4 ppm assigned to the methylene groups in -$CF_2\underline{C}H_2$-, -$\underline{C}H_2OH$, and the methine -$\underline{C}HI$- group, respectively. This ^{13}C NMR spectrum did not show any signal assigned to -CF_2I at 110 pm (Figure S8) for potentially remaining $C_6F_{13}I$ and displayed minimal amount of unreacted ally alcohol (Figure S9). Electron Impact mass spectrometry (Figure S10) was also useful in detecting the formation of the iodhydrin characterized by the molecular ion at m/z= 504 (M+ =$C_6F_{13}CH_2CHICH_2OH$), and characteristic fragments at m/z = 377 (M-I), and m/z = 357 (M-I-HF).

However, it is worth noting that conversion of the alkyl iodide does not necessarily equate to product yield. In all cases, complete conversion of the iodide took place within 8 to 9

hrs. Both TBPPI and AIBN were suitable in yielding the desired iodhydrin adduct. In contrast, benzoyl peroxide did not yield any product (yield= 0%, Table 1).

2.1.2 Radical Addition onto Allyl-O-PEG-OCH_3

The radical addition of $C_nF_{2n+1}I$ (n = 6 or 8) onto allyl oligo(ethylene oxide) (with average repeating units of 2, 3 or 4), reported by Koplanik et al.[9a], initiated by AIBN or sodium dithionite, led to the expected iodinated product in 87-96% yield. However, in contrast to our present study, the chain length chosen by these authors was much shorter. Using similar conditions to those of section 2.1.1, for the radical addition of $C_6F_{13}I$ onto an allyl-O-PEG-OCH_3, a striking difference was noted between the three initiators (Table 1). As reported by Koplanik et al.[9a], AIBN led to the iodinated diblock co-oligomers, but only in fair yield (37%) probably because of the long chain length. However, TBPPI enabled the reaction to achieve the highest yield of C_6F_{13}-CH_2CHICH_2-O-PEG-OCH_3. One possible explanation for such a feature is the higher amount of radicals produced (the reactions were carried out at 90 °C). 84% of the converted iodide resulted in the desired product using TBPPI (69% yield) whereas, in the case of AIBN, 51% conversion and 37% yield were observed. In the ^{1}H-NMR spectrum (Figure S11), the multiplet centered at 4.35 ppm indicates the methine -CHI- formed by the radical addition of $C_6F_{13}I$ onto the allyl-O-PEG-OCH_3. The ^{19}F-NMR spectrum (Figure S12) is the most useful for demonstrating connectivity. It clearly shows the AB system for the $-CF_2CH_2$- group centered at around -118 ppm. In the ^{13}C-NMR spectrum (Figure S13), the difluoromethylenes are hidden in the background noise but the triplet centered at 37.3 ppm and the signal at 14.38 ppm were assigned to the -CF_2CH_2- and -*C*HI, respectively. Under further examination between TBPPI and AIBN initiated-reactions, a substantial difference is noted in initiator/$C_6F_{13}I$ ratio: a 0.6 ratio for TBPPI and only 0.03 for AIBN. Again, benzoyl peroxide was able to convert $C_6F_{13}I$ but did not lead to the desired product. The GC/MS (Figure S14A) exhibits that BPO converts the $C_6F_{13}I$ into an aromatic adduct. Retentions times of 7.9, 8.2, and 8.5 min show that the major products formed are the ortho, meta, and para isomers of $C_6F_{13}PhI$.[52a] This can be easily identified by the mass spectrometry with m/z fragments at 126, 252, and 522 m/z assigned to the $PhCF_2$+, I-Ph-CF_2+, and the molecular weight of $C_6F_{13}PhI$ fragments, respectively (Figure S14B).

Table 1: Model Reactions: Radical addition of $C_6F_{13}I$ onto allyl compounds.

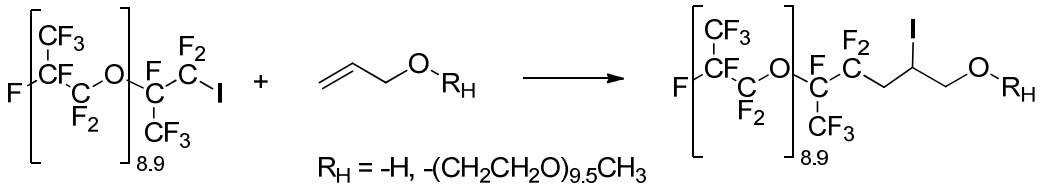
Rxn #	Allyl Compound	$C_6F_{13}I$ (mmol)	Allyl (mmol)	Initiator (mmol)	Initiator	*t* (hr)	T (°C)	Conv. $C_6F_{13}I$ (%)	Yield (%) ^{19}F-NMR
1[a]	Allyl Alcohol	1.150	1.875	0.152	TBPPI	2	75	>99	>99
2[a,b]	Allyl Alcohol	1.120	1.484	0.023	AIBN	4	90	93	92
3	Allyl Alcohol	1.120	1.680	1.008	BPO	8	90	100	0
4	Allyl-O-PEG-OCH_3	0.359	0.417	0.217	TBPPI	4	90	84	69
5[c]	Allyl-O-PEG-OCH_3	0.209	0.417	0.006	AIBN	4	90	51	37
6	Allyl-O-PEG-OCH_3	0.093	0.417	0.310	BPO	8	90	100	0

Note: initiator for reactions 1-6 was only added once at the beginning of the reaction. a) reference 56, b) reference 57, c) reference 9a; AIBN, TBPPi, and BPO stand for azobisisobutyronitrile, *tert*-butylperoxypivalate, and benzoyl peroxide, respectively; d) assessed from ^{19}F NMR.

2.2. Radical addition of 1-iodoperfluoropropyl-2-oligo(hexafluoropropylene oxide) onto unsaturated alkenes (allyl alcohol and ether).

2.2.1. Radical Addition onto Allyl alcohol

The analysis of the results of the reaction of polymeric iodides [1-iodo-2-oligo(hexafluoropropylene oxide) perfluoropropane] with allyl alcohol (Scheme 4) showed a considerable increase in time necessary to form the iodhydrin when similar molar scale as $C_6F_{13}I$ was used. These reactions required five times longer than in the case of $C_6F_{13}I$.



Scheme 4. Radical reaction of 1-iodoperfluoropropyl-2-oligo(hexafluoro-propylene oxide) onto allyl alcohol and allyl-O-PEG-OCH_3 (initiated by AIBN, TBPPI, and BPO).

The progress of the reaction was monitored by the decrease of the starting iodide (Figure S15) and the formation of the product (Figure S16) using gas chromatography/mass spectrometry

(GC/MS). The spectrum showed that 38 to 72 hours were necessary to reach the desired yields (> 80%). The ^{1}H NMR spectrum of the iodhydrin based on oligo(HFPO) (Figures S17 or S18) exhibited the characteristic signals for -CHI- group at 4.31 and 4.15 ppm resulting from the -$CF_2CH_aH_b$- at 2.84 and 2.54 ppm, respectively. The respective methylene in -CH_2OH and the -OH are noted at 3.66 and 3.99 ppm, respectively (Figure S18). The ^{19}F-NMR spectra (**Figure 1 A & B**) show the absence of the characteristic triplet of doublets centered at -58 ppm (**Figures 1 A** and S19) assigned to CF_2I end-group in oligo(HFPO)-$CF(CF_3)CF_2I$. Instead, a high field shifted signal centered at -112 ppm and resulting from a complex AB system containing two stereo centers (**Figure 1 B** and S20). The ^{13}C-NMR spectrum (Figure S21) exhibits the absence of triplet of doublets at 91.3 ppm, which is normally present in the iodide (Figure S22). Typical signals of oligo(HFPO)-$CF(CF_3)CF_2$ were observed in the 124 ppm to 98 ppm range, while those of iodhydrin can be noted at 66.32, 36.52 and 18 ppm attributed to the -$\underline{C}H_2OH$, -$CF_2\underline{C}H_2$-, and –$\underline{C}HI$ groups, respectively.

Atmospheric pressure solids analysis probe (ASAP) time-of-flight mass spectrometry (TOF-MS) spectrum in negative ion mode for oligo(HFPO)-$CF(CF_3)CF_2I$ (Figure S23) displays one distribution between 2400 and 4200 m/z corresponding to oligo(HFPO)-based polymers as evidenced by the m/z difference between two consecutive oligomeric peaks (Δ m/z = 166 Da) which corresponds to the HFPO repeat unit mass. This distribution is attributed to the deprotonation molecular ion of ($F[CF(CF_3)CF_2O]_nCF(CF_3)CF_2I + CH_3OH - H)^-$ when methanol is present in the probe. In addition, fragments of $F[CF(CF_3)CF_2O]_nCF(CF_3)O^-$ were observed between 184 and 1845 m/z. In negative ion mode, MALDI-TOF-MS spectrum of oligo(HFPO)-$CF(CF_3)CF_2I$ (Figure S24) shows one distribution between 2300 and 4400 m/z . This distribution corresponds to the deprotonation of oligo(HFPO)-I with formic acid ($F[CF(CF_3)CF_2O]_n CF(CF_3)CF_2 I+HCOOH-H)^-$. The repeat units Δm/z = 166 Da confirms the presence of oligo(HFPO). In the ASAP-TOF-MS spectrum of $F[CF(CF_3)CF_2O]_n CF(CF_3)CF_2CH_2CHICH_2OH$ iodhydrin (Figure S25) in positive ion mode a main distribution of $M^{+\circ}$= ($F[CF(CF_3)CF_2O]_n CF(CF_3)CF_2CH_2CHICH_2)^{+\circ}$ cation radical was observed. The loss of OH group is possible in this ionization mode. A second distribution corresponding to the radical cation $M^{+\circ}$ with acetonitrile from the probe and a few fragments that may arise from the main compound were also observed. The MALDI-TOF-MS

spectrum of $F[CF(CF_3)CF_2O]_nCF(CF_3)CF_2CH_2CHICH_2OH$ iodhydrin (Figure S26) highlights the positive ion of $F[CF(CF_3)CF_2O]_nCF(CF_3)CF_2CH_2CHICH_2OH$. One distribution was detected between 1400 and 3000 m/z. This corresponds to $(F[CF(CF_3)CF_2O]_nCFCF_3CF_2CH_2CHICH_2O + Li)^+$ lithium adduct. The repeat units of 166 m/z indicates that oligo(HFPO) was present, whereas several fragmentations of this compound were observed between 400 and 3000 m/z.

The reaction of oligo(HFPO)-$CF(CF_3)CF_2I$ with allyl alcohol carried out on the same scale (0.56 mmole) initiated by TBPPI (0.5 mole ratio to the iodide) was almost twice faster than with AIBN (0.6 mole ratio to the iodide). It is believed that the rate of the reaction was increased with a higher amount of formed free radicals. TBPPI produces $tBu^\bullet$ while $t\text{-}BuO^\bullet$ initially generated also released $CH_3^\bullet$ at more elevated temperatures.[58] On the contrary, AIBN only produces two $(CH_3)_2(CN)C^\bullet$. Once again, BPO[52b] did not form any of the desired iodhydrin although it produces two radicals as well: $Ph^\bullet$ or $PhC(O)O^\bullet$ (Table 2).

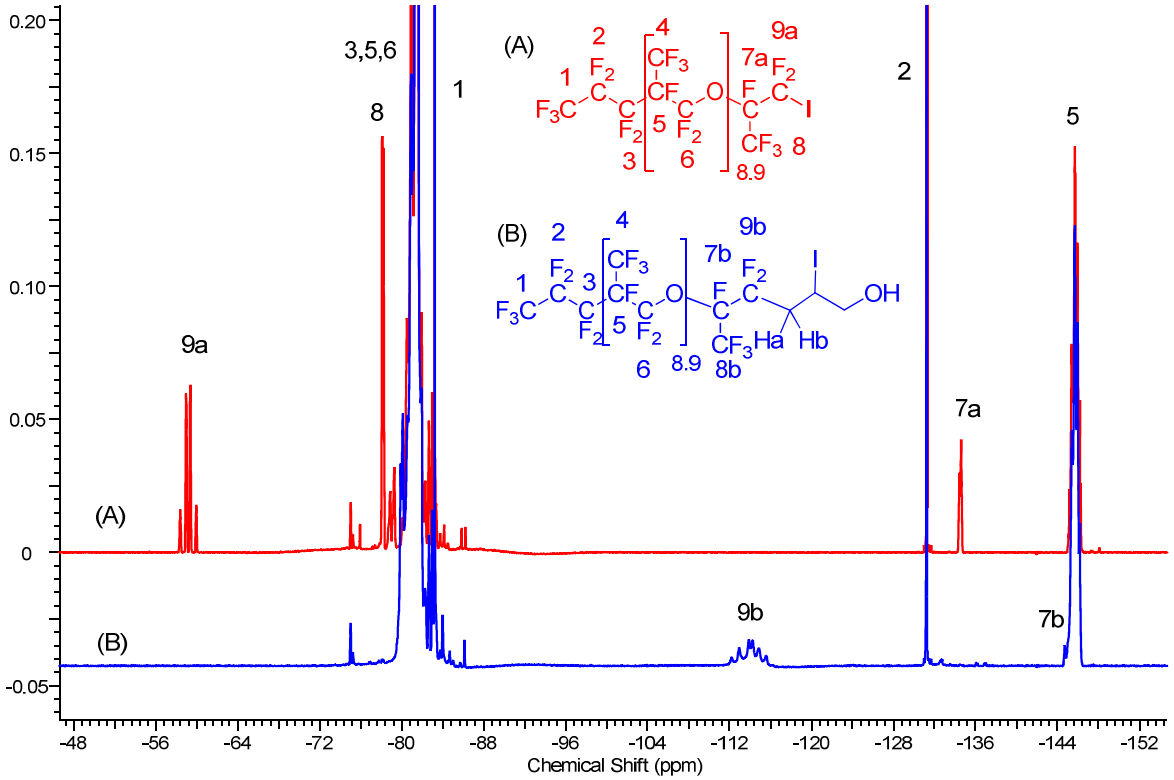
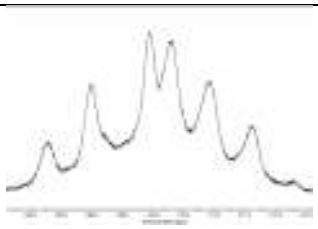
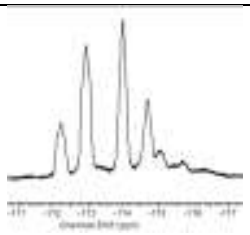
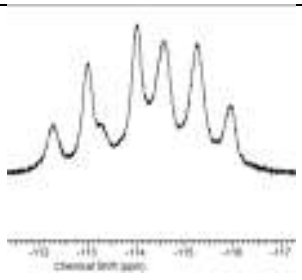
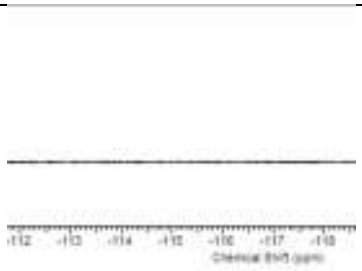


Figure 1: ^{19}F-NMR spectra of 1-iodo-2-oligo(hexafluoropropylene oxide)perfluoropropane ($F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2I$) (A) and $F[CF(CF_3)CF_2O]_{8.9}CH_2CHICH_2OH$ (B).

The reactions with allyl alcohol are difficult to reproduce due to the biphase nature of the reaction media, the reactants being immiscible and it is expected that reaction most likely occurred at the interface of both liquid phase (Table 2, RXNs 9 and 10). Because of such a non-homogeneous medium, a situation may be created in which the radicals react more easily with oligo(HFPO)-$CF(CF_3)CF_2I$. The abstraction of iodine atom in oligo(HFPO)-$CF(CF_3)CF_2I$ from the radical initiators leads to oligo(HFPO)-$CF(CF_3)CF_2^{\bullet}$ macroradical that may recombine with itself. But this observation was not noted in any of the MALDI-TOF-MS spectra. [59] However, this macroradical could trap a radical initiator fragment or add onto an aromatic decomposition product. The product corresponding to that latter hypothesis was detected by ^{19}F NMR spectroscopy (**Figure 2**) as evidenced by the presence of the broad signal centered at -116.3 ppm. This signal is in close agreement with oligo(HFPO)-$CF(CF_3)CF_2$-C_6H_5 structure previously reported. [52b] The difluoromethylene attached to benzene gives a complex multiplet from -110.76 to -113.67 ppm, an upfield shift to -116 ppm is probably with an activated group such as iodine attached to the benzene ring. The ^{1}H-NMR spectrum (Figure S27) does indicate the presence of aromatic compounds in the mixture ranging from 7.5 to 8.5 ppm.

RXN 9  **10 g scale oligoHFPO-I + Allyl-OH + TBPPi**	RXN 25  **oligoHFPO-I + TBPPi**
RXN 12  **10 g scale oligoHFPO-I +Allyl-OH + AIBN**	RXN 26  **oligoHFPO-I +AIBN**

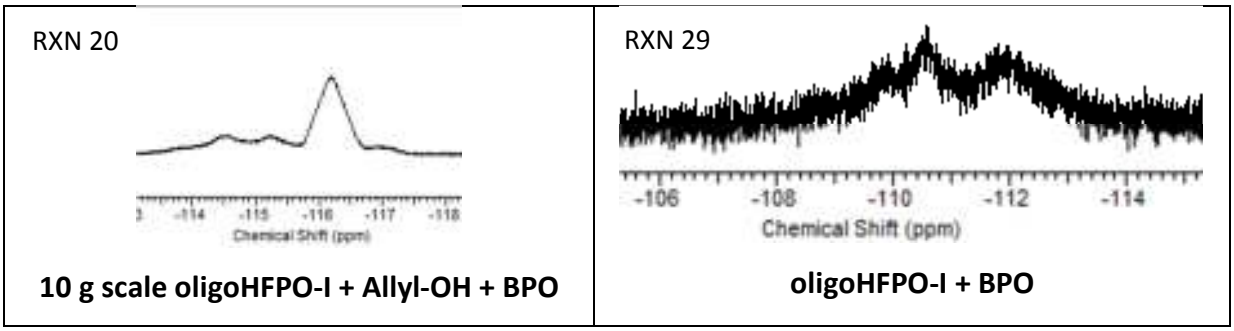


Figure 2: Comparison of the ^{19}F-NMR expansions of ^{19}F NMR spectra the reaction of oligo(HFPO)-CF(CF_3)CF_2I with the initiator (TBPPi, AIBN, BPO) (right column) and initiator with allyl alcohol (left column).

2.2.2. Radical Addition onto Allyl-O-PEG-OCH_3

The results of the reactions of polymeric 1-iodoperfluoroalkane (oligo(HFPO)-CF(CF_3)CF_2I) with allyl-PEG-OCH_3 (Scheme 4, Table 2) were very surprising. The best yields in oligo(HFPO)-*b*-PEG diblock co-oligomer were achieved using benzoyl peroxide (71%), followed by AIBN (48%), and lastly by TBPPI (0%) from respective $[initiator]_o/[oligo(HFPO)\text{-}CF(CF_3)CF_2I]_o$ initial ratios of 6.0, 4.0, and 0.4. All three initiators almost completely converted all the iodide into product or byproducts (Table 3). Two important differences in these reactions, compared to previous ones, were: i) the absence of a hydroxyl functional group and ii) more sterically hindered iodide and allyl derivative. This combination of these structural changes can greatly affect the solubility of the reactants.

Table 2: Radical addition of oligo(HFPO)-CF(CF_3)CF_2I onto allyl compounds.

Rxn #	Allyl Compound	HFPO-I (mmol)	Allyl (mmol)	Initiator (mmol)	Initiator	*t* (hr)	T (°C)	Conv. HFPO-I (%)	1° HEC (%)	Yield (%) 19F-NMR
7	Allyl Alcohol	0.564	5.279	0.080	TBPPI	48	75	100	2.3	88
8		0.564	16.357	0.284		38	90	94.5	4	80
9		5.640	30.120	7.293		32	75	73	2.5	0
10	Allyl Alcohol	1.147	12.162	0.180	AIBN	64	90	100	1.12	86
11		0.564	1.510	0.203		72	90	100	3	86
12		5.640	112.861	4.056		72	90	100	2.5	89
13	Allyl Alcohol	0.564	1.119	0.845	BPO	8	90	68	2.7	0
14		0.564	2.256	3.619		8	90	95.5	6.5	0
15	Allyl-O-PEG(450)-OCH_3	0.564	0.862	0.230	TBPPI	80	75	96.5	8.1	0
16		5.640	17.239	18.365		64	75	99.0	4	0

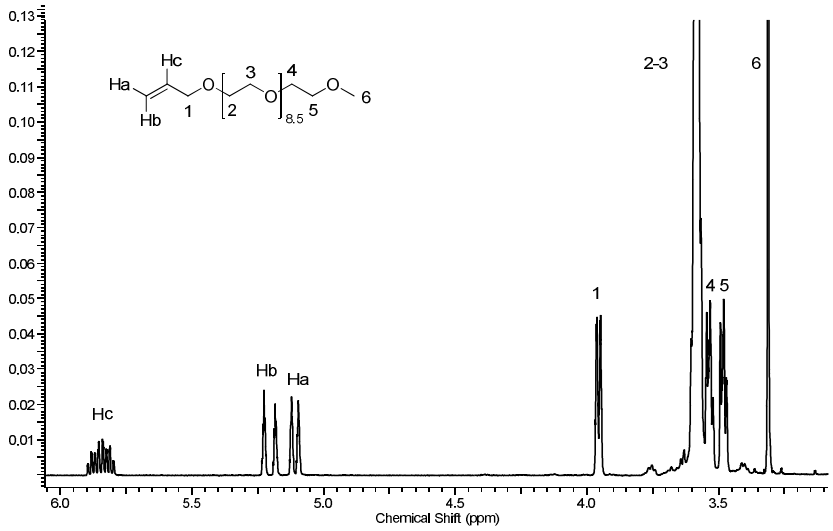
17	Allyl-O-PEG(450)-OCH_3	0.564	2.586	2.326	AIBN	80	90	100	25	48
18		5.640	23.015	23.997		172	90	100	24	50
19	Allyl-O-PEG(450)-OCH_3	0.564	2.761	2.343	BPO	16	90	100	6	71
20		5.640	11.280	23.618		48	90	97.0	19	51

Note: additions beyond the first amount of initiator - 7) 6 additions, 8) 18 additions, 9)16 additions, 10) 7 additions, 11) 17 additions, 12)35 additions, 13) 0 addition, 14) 1 addition, 15) 19 additions, 16) 15 additions, 17) 20 additions, 18) 86 additions, 19) 1 addition, 20) 5 additions; c) calculated using ^{19}F NMR.

Figure 3 compares the ^{1}H NMR spectra of allyl-PEG-OCH_3 (**Figure 3A**) with the resulting iodinated diblock co-oligomer (**Figures 3B or S28**). It is noted that the ethylenic protons initially located at 5.11, 5.20, and 5.85 ppm have disappeared and were replaced by an AB system and two multiplets centered at 2.55 and 3.05 ppm, 3.79, and 4.36 ppm assigned to methylene groups in $-CF_2CH_aH_b$, $-CH_2OH$, and -CHI-, respectively.

As expected, the ^{19}F NMR spectrum exhibits the high field shift from -60 ppm (assigned to CF_2I end-group in the iodinated precursor) to -112 to -117.5 ppm in the diblock co-oligomers (Figure S29).

A)



B)

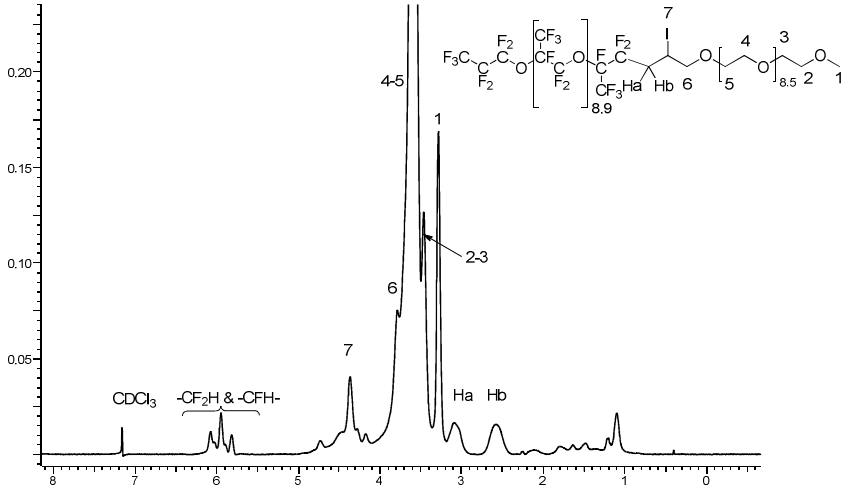


Figure 3: ^{1}H-NMR spectra of A) CH_2=CH-$CH_2O(CH_2CH_2O)_{9.5}CH_3$, allyl-PEG-$OCH_3$ and B) $F[C(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2CH_2CHICH_2O(CH_2CH_2O)_{9.5}CH_3$.

The ^{13}C NMR spectrum (Figure 4 or S30) also shows the absence of ethylenic carbon atoms at 116 and 136 ppm and the presence of fluorinated groups in the 100-125 ppm range, and of the methylene groups in PEG at 70.54 ppm.

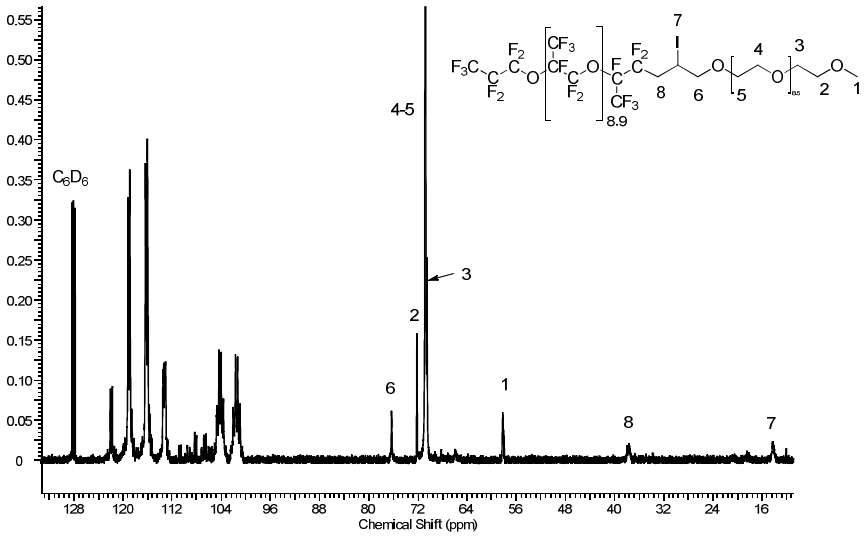


Figure 4: ^{13}C-NMR spectrum of $F[C(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2CH_2CHICH_2O(CH_2CH_2O)_{9.5}CH_3$

ASAP (Figure 5 or S31) and MALDI (Figure S32) spectra were critical to determining the coupling of the two oligomers. ASAP was more helpful in determining whether the iodo-diblock co-oligomer based on oligo(HFPO) and PEG was formed. In other experiments, it was observed

that ASAP ionization caused the fragmentation of polymers.[60] The desorption temperature, ranging from 50 to 650 °C, plays an important role since the high temperature may also induce a thermal degradation. The analyses using ASAP ionization of oligo(HPFO) oligomers thus led to molecular weights lower than those assessed by MALDI-TOF-MS. In ASAP ionization, the main distribution was observed between 1090 and 2700 m/z which corresponds to $F[CF(CF_3)CF_2O]_nCF(CF_3)CF_2CH_2CHICH_2O(OCH_2CH_2)_4CH_3$+ radical cation. This distribution displays a 166 m/z-repeat unit as well as a 44 m/z-repeat units characteristic of HFPO and EG, respectively (**Figure 5**). In positive ion mode, MALDI-TOF-MS spectrum of $F[CF(CF_3)CF_2O]_nCF(CF_3)CF_2CH_2CHICH_2O(OCH_2CH_2)_{9.5}CH_3$ exhibits only one distribution between 1500 and 3200 m/z for the adduct $(M+Li)^+$ (Figure S32).

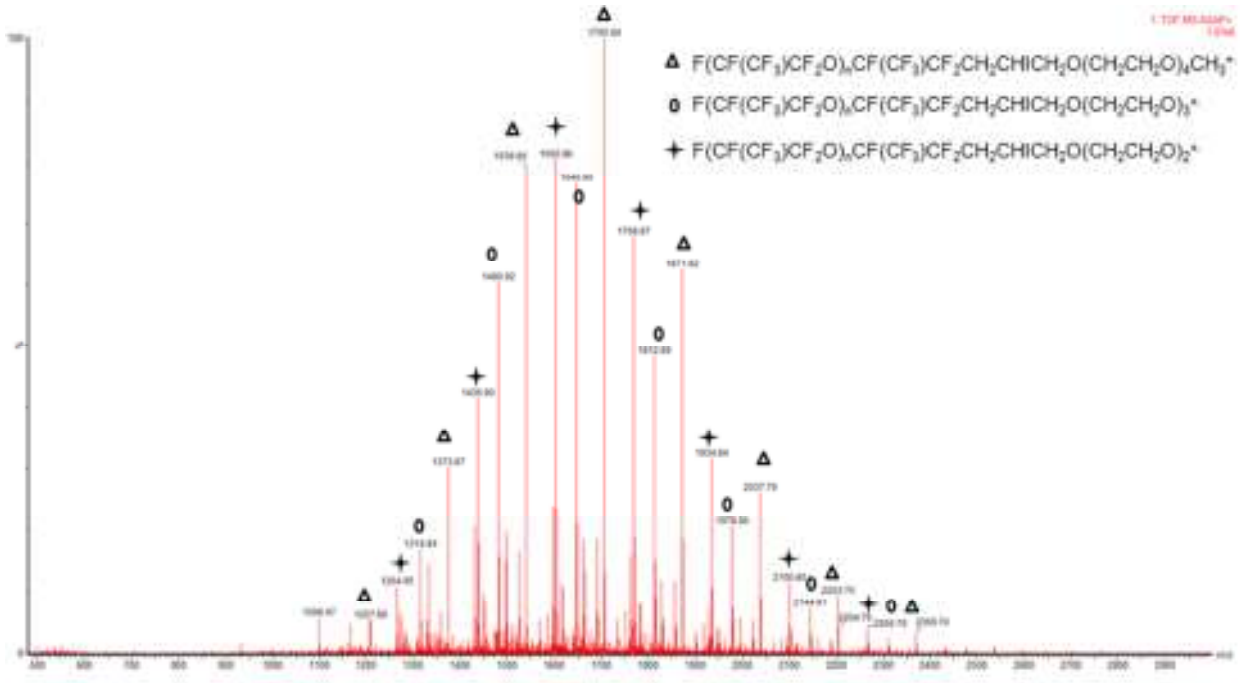


Figure 5: Positive mode Atmospheric pressure Solids Analysis Probe (ASAP) time-of-flight mass spectrometry (TOF-MS) spectrum of $F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2CH_2CHICH_2O(CH_2CH_2O)_{9.5}$-$CH_3$ (initiated with BPO). 166 m/z is the repeat unit for HFPO $[CF(CF_3)CF_2O]$ and 44 m/z is the repeat unit for ethylene oxide (CH_2CH_2O).

Table 3: Conversions of 1-iodoperfluorohexane and oligo(HFPO)-$CF(CF_3)CF_2I$ and the formation of the undesired hydrogen end-capped (HEC) compound for the radical addition of

1-iodoperfluoro(alkoxy)alkanes onto allyl alcohol and allyl-O-PEG-OCH_3. Experimental conditions of runs are detailed in Tables 1 and 2.

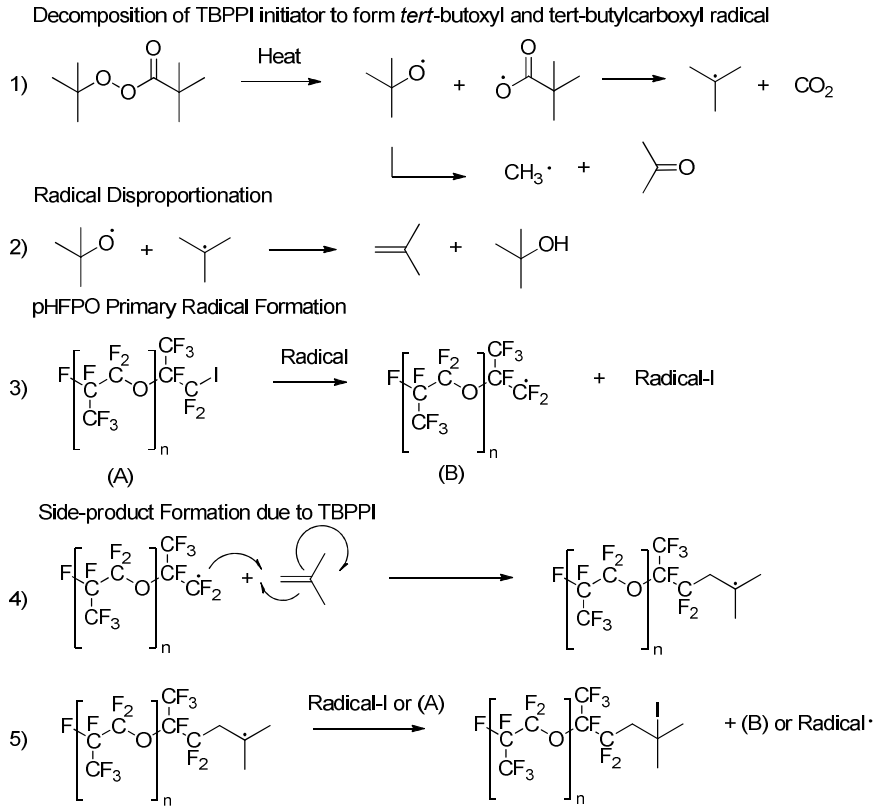
Rxn #	Initiator Type	Catalyst/Solvent	1^o HEC (%)	Conv. 1^o iodide (%)
1,4,7-9,15-16	TBPPI	none	2.3-8.1	94.5-100
3,6,13-14, 19-20	BPO	$Cu(OAc)_2$	2.7-19	68-100
2,5, 10, 12, 17-18	AIBN	none	1.12-25	100
11	AIBN in $CHCl_3$	none	3	100

Note: 1^o HEC = $C_6F_{13}H$ or oligo(HFPO)-$CF(CF_3)CF_2H$

2.3. Radical reactions of 1-iodoperfluorohexane and 1-iodoperfluoro-propylene-2-oligo(hexafluoropropylene oxide) with various initiators (TBPPi, AIBN, and BPO)

In all radical reactions involving an allyl reagent, an almost complete conversion of the fluorinated iodides was observed [seen in the ^{19}F-NMR spectra (Figures 2 and S33-35)]. However, this did not necessarily imply the formation of the desire product. Thus, it was worth studying the nature of radical initiators to understand their role in the production of undesired side-products. As expected, AIBN did not add onto any of the fluorinated alkyl iodides both in the case of neat addition (RXN 22 and 26, Table 4) or in the presence of sodium dithionite (RXN 28) or when chloroform was used as a solvent (RXN 23 and 27). In the presence of radicals, chloroform normally generates $CCl_3^{\bullet}$ or $HCCl_2^{\bullet}$, but the ^{13}C-NMR spectrum did not show any chemical shifts ranging between 80 and 100 ppm.[61] On the contrary, TBPPI and BPO formed side-products with both fluorinated alkyl iodides, $C_6F_{13}I$ and oligo(HFPO)-$CF(CF_3)CF_2I$. When $C_6F_{13}I$ reacted with TBPPi (RXN 21), the ^{19}F NMR spectrum (Figure S33) shows complex signals ranging between -112.3 and -113.6 ppm assigned to the by-product and a signal at -112 ppm characteristic of -C$\underline{F}_2CF_2I$ in the remaining $C_6F_{13}I$. C_4F_9I is known to react with aryl-compounds evidenced by a ^{19}F-NMR chemical signal centered at ca. -111 ppm assigned to a -CF_2-Aromatic group.[62] The ^{19}F-NMR spectrum of RXN 24 (Figure S33) displays two signals in this same area. These signals were also present in the case of radical reactions of $C_6F_{13}I$ onto ally compounds (Figures S33-34), while both other initiators are more efficient in product formation (yield = 37 to 99%).

As mentioned earlier, BPO produces aromatic side-products. The structures of these side-products were observed by GC/MS (Figure S14). From the reaction of 1-iodoperfluorohexane with BPO, the prevailing aromatic products were iodobenzene (4.8 min, 77 and 204 m/z), benzoic acid (7.1 min, 77, 105, 122 m/z), ortho, meta, para isomers of perfluorohexyl iodobenzene (7.9, 8.1, and 8.5 min; 126, 253, and 522 m/z, respectively) and the minor products arising from the addition of perfluorohexyl radical onto biphenyl (7.4 and 7.8 min) and benzoic acid (9.77 and 10.2 min). Therefore, it is believed that the dominating side-product in the case of reaction between BPO and the 1-iodoperfluoroalkanes (Table 4) is an iodobenzene perfluoroadduct.



Scheme 5. Conversion of poly(hexafluoropropylene oxide) primary iodide to undesired side-product using TBPPI as the radical initiator.

The same radical reactions were studied in the presence of oligo(HFPO)-CF(CF_3)CFI. Surprisingly, this iodo compound shows a different behavior to that of $C_6F_{13}I$. It was noted that neither AIBN (RXN 26) nor BPO (RXN 29) led to any new signals in the -112 to -118 ppm range in

the ^{19}F-NMR spectra (Figure S35). In contrast, TBPPi converted all the iodide into the undesired side-product. ^{13}C-NMR spectroscopy (APT, Figure S36) and ASAP mass spectrometry (Figure S37) were instrumental in identifying the main side-product using TBPPi. The side-product arises from the addition of the 1-iodoperfluoroalkane onto 2-methyl-propene (**Scheme** 5), a decomposition product from TBPPi. This was evidenced in the ^{13}C NMR spectrum (Figure S36) by the presence of the characteristic triplet ($^{2}J_{CF}$= 19 Hz) of doublets ($^{3}J_{CF}$= 8 Hz) centered at 47.5 ppm and assigned to -$\underline{C}H_2CF_2$-. The two other signals which can be seen at 36.1 and 32.0 ppm are attributed to the methyl groups in *iso*-butyl and the tertiary carbon atom connected to the iodine atom, respectively. It is known that TBPPi generates two radicals: *tert*-butoxyl$^{\bullet}$ and *tert*-butyl-$CO_2^{\bullet}$.[58,63] The positive mode in ASAP analysis also confirms the addition of oligo(HFPO)-I onto 2-methyl-propene with the main distribution observed between 900 and 1950 m/z corresponding to $(F[CF(CF_3)CF_2O]_nCF(CF_3)CF_2CH_2C(CH_3)_2^{o}+ CH_3CN)+$ radical cation formed with acetonitrile in the probe.

This work carried out with the 1-iodoperfluoroalkanes and initiators provide a clear explanation for the results listed in Table 2. Most reactions were biphasic due to the immiscibility of the reactants. During the reaction with allyl alcohol and BPO in acetic acid, a dominating amount of iodobenzene was formed and could be more soluble in oligo(HFPO)-$CF(CF_3)CF_2I$ or $C_6F_{13}I$ than acetic acid. This led to a perfluoroalkyl iodide conversion into an aromatic side-product by reaction of the oligo(HFPO)-$CF(CF_3)CF_2I$- or $C_6F_{13}I$-derived radicals onto the iodobenzene. As for reactions with allyl-O-PEG-OCH_3 initiated by BPO, the solubility of the iodobenzene in $C_6F_{13}I$ is higher than that of the allyl-PEG. This difference in solubility may explain the failure of the reactions (yield = 0%). In the reaction involving oligo(HFPO)-$CF(CF_3)CF_2I$, allyl-O-PEG-OCH_3 may have some partial solubility in the fluorinated ether which reduced the production of iodobenzene and thus minimized side-products. In summary, BPO only formed by-products with $C_6F_{13}I$, but not with oligo(HFPO)-$CF(CF_3)CF_2I$ (at least not detectable at the scale of the reactions).

In the case of the reactions involving oligo(HFPO)-$CF(CF_3)CF_2I$ and allyl-O-PEG-OCH_3, if TBPPi was used as the initiator, 2-methylpropene was quickly released at 90 ^{o}C (Scheme 5) and

oligo(HFPO)-CF(CF_3)CF_2I reacted faster with the smaller 2-methylpropene rather than with the bulky and sterically hindered allyl-O-PEG-OCH_3.

2.4. Reduction of oligo(HFPO)-CH_2CHICH_2-oligo(PEG) using tributyltin hydride

Koplanik et al. [9a] reported the formation of ω-perfluorohexyl poly(ethylene oxide) diblocks co-oligomer [$C_6F_{13}CH_2CHICH_2$PEG] by the reduction of the iodine atom in the presence of zinc, $NiCl_2 \cdot 6H_2O$ in THF/H_2O in 62% yield. The present study used tributyltin hydride which was efficient in previous works to achieve the desired reduction.[64,65] The successful reduction can be evidenced from the ^{1}H-NMR spectrum (Figure S38) with the high field shift from 4.36 ppm (assigned to -CHI-, Figure S28) to 1.89 ppm characteristic of the central -CH_2- group. The ^{19}F-NMR spectrum (Figure S39) is similar to the iodide-containing diblock cooligomer.

Table 4: Radical reactions of $C_6F_{13}I$ and oligo(HFPO)-CF(CF_3)CF_2I with only radical initiator (TBPPi, AIBN, and BPO).

Rxn #	1° iodide	Initiator Type	Catalyst/Solvent	1° HEC (%)	Conv. 1° iodide (%)
21	$C_6F_{13}I$	TBPPI	none	0	92
22	$C_6F_{13}I$	AIBN	none	0	0
23	$C_6F_{13}I$	AIBN ($CHCl_3$)	none	0	0
24	$C_6F_{13}I$	BPO	$Cu(OAc)_2$	0	100
25	oligoHFPO-I	TBPPI	none	4.5	95.5
26	oligoHFPO-I	AIBN	none	0	0
27	oligoHFPO-I	AIBN ($CHCl_3$)	none	0	0
28	oligoHFPO-I	AIBN	$Na_2S_2O_4$	0	0
29	oligoHFPO-I	BPO	$Cu(OAc)_2$	0.5	7.5

The ^{13}C-NMR spectrum (Figure S40) exhibits the absence of the signal assigned to the methine –CHI- at 18 ppm that underwent a low field shift to 20.55 ppm for the new central methylene group. In addition, the methylene group in -CF_2CH_2 shifted from 37.65 to 27.80 ppm due to the reduction of the iodine atom. The yield of this reaction was 77%. The positive mode of ASAP and MALDI-TOF-MS spectra (**Figures 6** and S41-42) also confirmed the reduction of the material and showed the connectivity of oligo(HFPO) to oligo(PEG) evidenced by the presences of a 166 and 44 m/z- for HFPO and ethylene oxide repeat units, respectively.

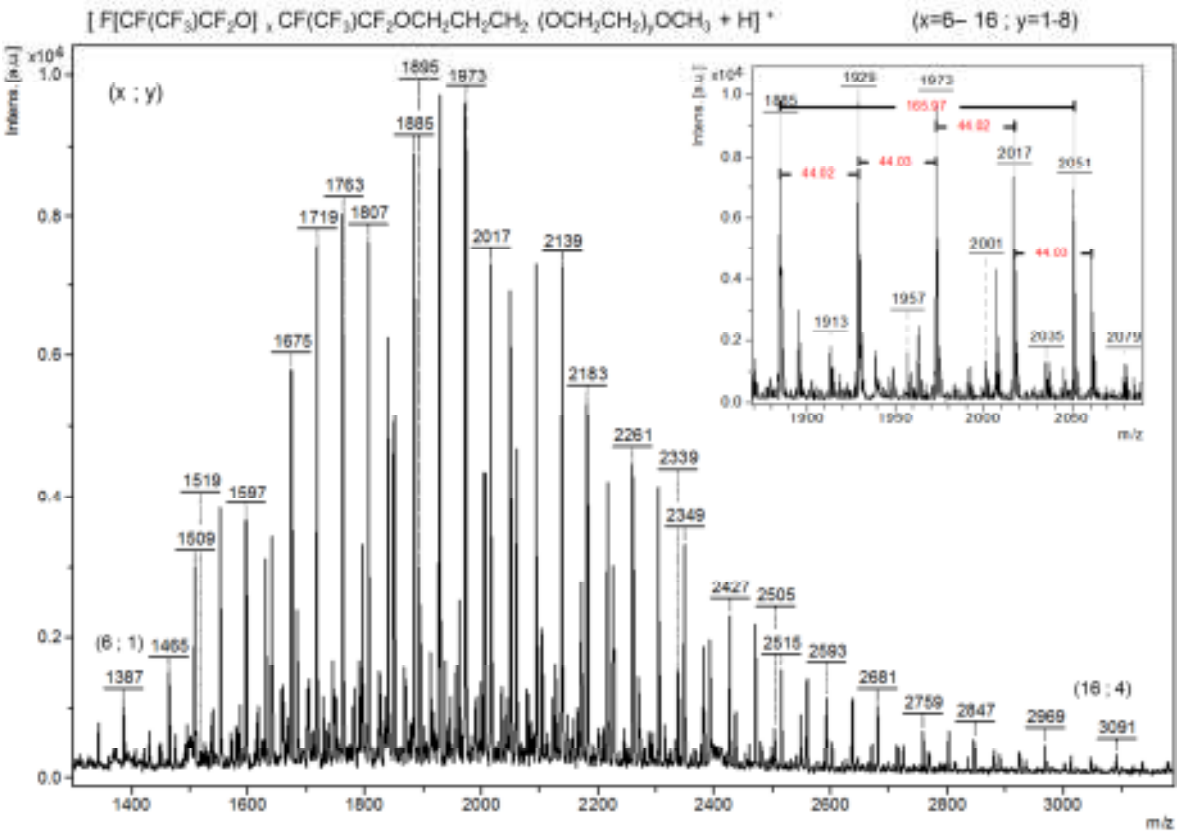


Figure 6: Positive ion mode MALDI-TOF-MS spectrum of oligo(HFPO)-$CH_2CH_2CH_2$-oligo(PEG) (using as matrix DCTB and LiCl as the cationizing agent), 1807 m/z is x =8 and y = 5. The insert expansion *m/z* between 1850 and 2100 displays 166 and 44 m/z-repeat units for HFPO [$CF(CF_3)CF_2O$] and ethylene oxide (CH_2CH_2O), respectively.

2.5. Surface Tension Measurements (critical micellar concentration, CMC)

Oligo(HFPO)-*b*-oligo(PEG) diblock co-oligomer is as an attractive amphiphilic molecule, the surfactant behavior of which deserves to be studied. It is partially water-soluble up to ca. 0.3 g/L. Surface tension properties of this diblock co-oligomer were assessed by tensiometry and compared to the surface tension of commercially available ammonium perfluorooctanoate (APFO). Three surfactants were measured for comparison: APFO, oligo(HFPO)-CH_2CHICH_2-oligo(PEG) and oligo(HFPO)-*b*-oligo(PEG) diblock cooligomers. APFO, a commonly used surfactant, was regarded as a reference and was measured to have a surface tension of 37.7 mN/m at the critical micellar concentration (CMC) of 3.77 g/L (Figure S43). Oligo(HFPO)-CH_2CHICH_2-oligo(PEG) and oligo(HFPO)-*b*-oligo(PEG) diblocks were measured to have surface tensions of 38.5 mN/m and 43.5 mN/m at the cmc of ca. 0.13 g/L and 0.04 g/L, respectively.

The plot of their surfaces can be seen in **Figure 7**. Interestingly, it can be noted that the surface tension properties of such a diblock co-oligomeric surfactant are much better than those of APFO in terms of the amount of material required to reach the critical micellar concentration. The oligo(HFPO)-*b*-oligo(PEG) diblock's cmc is ca. 94 times better than that of APFO and 3 times smaller than that of oligo(HFPO)-CH_2CHICH_2-oligo(PEG). In comparison, the cmcs of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) are 4.45 and 15.70 g/L, respectively.[66] At room temperature, oligo(HFPO)-*b*-oligo(PEG) diblock co-oligomer is a potential surfactant, competitor to APFO.

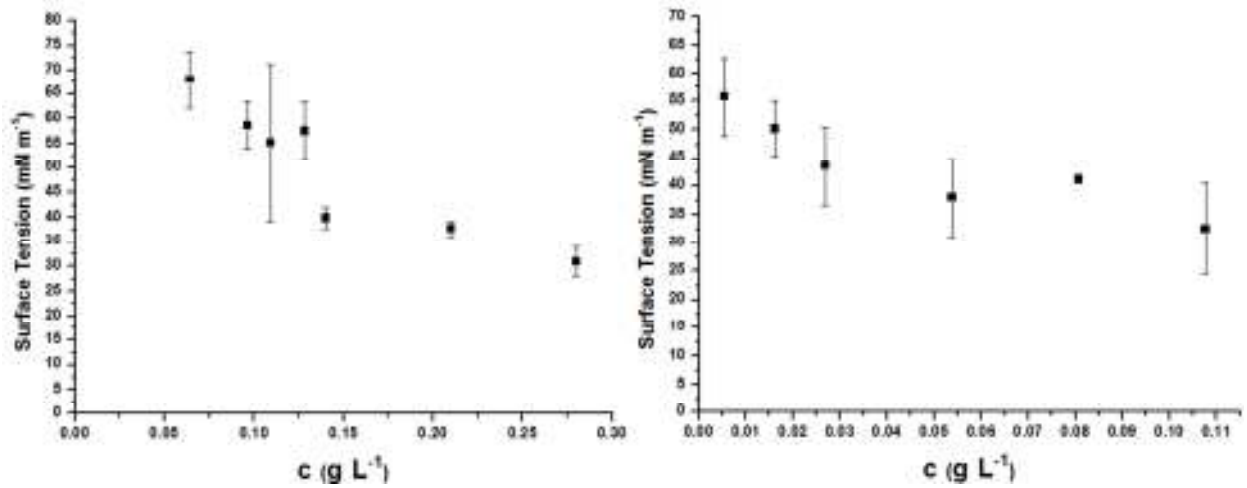


Figure 7: Surface tension measurements of new surfactant (Left) oligo(HFPO)-CH_2CHICH_2-oligo(PEG) [CMC = 0.13 g/L] (and Right) oligo(HFPO)-*b*-oligo(PEG)[CMC = 0.04 g/L]. Reference: APFO [CMC = 3.77 g/L] (Figure S42)

3. Conclusion

An original diblock co-oligomer based on oligo(hexafluoropropylene oxide) and oligo(ethylene oxide) was successfully synthesized by the radical addition of oligo(HFPO)-$CF(CF_3)CF_2I$ onto an allyl-O-PEG-OCH_3 derivative followed by the selective reduction of the iodine atom. Careful optimization of the experimental conditions such as the nature of the initiators (TBPPi, AIBN, or BPO), temperature, and reaction time was required to synthesize the desired diblock co-oligomer. BPO was shown to be the most efficient source of radicals with regards to both yield and reaction time. The best overall yield obtained from the oligo(HFPO)-$CF(CF_3)CF_2I$ precursor

was 71%. The oligo(HFPO)-*b*-oligo(PEG) diblock co-oligomer exhibits very interesting surfactant behavior. Indeed, the surface tension of water reached 32.5 mN/m for a surfactant concentration of 0.11 g/L and low critical micellar concentration (0.04 g/L at room temperature). This newly formed diblock molecule has demonstrated relevant properties compared to those of the commercially available ammonium perfluorooctanoate (APFO). Further works dealing with the synthesis of homologue surfactants containing various oligo(HFPO) and PEG chain lengths delving into deeper surface activity studies, absorption kinetics, and static and dynamic interfacial properties, as well as their bioaccumulation, decomposition and micellar behavior in solution are under progress.

4. Experimental Details

4.1. Materials

All materials were used without further purification or drying. Krytox® primary iodide, 1-iodoperfluoropropyl-2-oligo(hexafluoropropylene oxide) (oligo(HFPO)-$CF(CF_3)CF_2I$) and Freon 113, was kindly offered by DuPont, (Wilmington, USA) and Iodoperfluorohexane ($C_6F_{13}I$, purity 95 %) was generously supplied by Atofina (now Arkema, Pierre-Benite, France). Ammonium perfluoro-octanoate (Daikin Industries, LTD.), allyl alcohol and anhydrous copper (II) acetate (Fluka, 98%), tributyl stannane (Sigma Aldrich, 97%), sodium dithionite ($Na_2S_2O_4$, Fisher Chemical), chloroform (Sigma Aldrich, 98%), recrystallized Azobisisobutyronitrile (AIBN) in methanol (Fluka Analytical), *tert*-butyl peroxypivalate (TBPPi, TRIGONOX 25-C75, 75% TBPPi diluted to 63% in isodecane, Akzo Nobel), di-benzoyl peroxide (BPO) (Sigma Aldrich), polyethylene glycol methyl ether (Fluka Analytical, 500 amw), and allyl bromide (Sigma Aldrich).

4.2. Analyses

Gas Chromatography (GC) Mass Spectrometry (MS): The total product mixture was analyzed by a Shimadzu GC (GC-2010 Plus) and a quadripole MS (GCMS-QP2010 SE) equipped with a Zebron ZB-5ms column, 20 m x 0.18 mm id, 0.18 μm df. The detector and the injector temperatures were 200 °C and 280 °C, respectively. The temperature program started from 50 °C with a 2 min hold then the heating rate was 25 °C/min until reaching 250 °C and holding at 250 °C for 2

minutes. The total pressure 108 kPa, total flow was 25.9 mL/min, column flow 0.74 mL/min, purge flow 3mL/min, linear velocity 38.2 cm/s, and a split injection of 30:1.

Atmospheric pressure Solids Analysis Probe (ASAP)-Time-Of-Flight mass *spectrometry (TOF-MS):* Full MS analyses were performed on a SYNAPT G2 HDMS QTOF Mass Spectrometer fitted with an Atmospheric Solids Analysis Probe (Waters Corp., Manchester, UK). The samples were applied directly to the exterior of glass capillary that is attached to the ASAP probe. The sample in the gas phase was ionized by the proximity to a corona discharge needle. Ions were then passed from the atmospheric pressure region to the mass spectrometer. ASAP mass spectra were acquired in positive and negative ion modes over the m/z 50-4500 range for 3 min for MS spectra. A nitrogen gas flow of 500 L h^{-1} was ramped from 50 °C to 650 °C at 200°C/min for thermal desorption. The corona discharge voltage was 4 µA and the sampling cone voltage was 40 V.

Matrix Assisted Laser Desorption Ionization-Time-Of-Flight mass spectrometry (MALDI-TOF-MS): Experiments were determined with a Bruker Ultraflex III with a positive ionization method for compounds containing a higher content of hydrocarbons and a negative ionization method for compounds higher in fluorocarbon content. For sample preparation, samples were 1/50 diluted in CH_2Cl_2. 1 mL of LiCl/MeOH (10 mg/mL) was deposited on the target first, and dried. Then, 0.5 mL of sample solution was spotted on top of the LiCl layer and dried, and finally 0.5 mL of trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) matrix was applied on top and dried.

Nuclear Magnetic Resonance (NMR) spectroscopy: The structure of the products was determined by NMR spectroscopy at room temperature (25 ^{o}C). NMR spectra were recorded on Bruker AC-400 instruments using deuterated benzene or dimethylformamide capillary as internal references, respectively. The experimental conditions were accomplished using TopSpin 2.1 operating at 400.13 (^{1}H), 376.46 (^{19}F), 100.62 (^{13}C) MHz. Flip angle 90° for ^{1}H and ^{13}C and 30° for ^{19}F-NMR); acquisition time 3.96 s (^{1}H), 0.87 s (^{19}F), 1.36 s (^{13}C); pulse delay 2 (^{1}H), 4 s (^{19}F and ^{13}C); scans 128 (^{1}H), 16 (^{19}F), 6144 (^{13}C); and pulse width of 12.50 (^{1}H), 13.0 (^{19}F), and 9.0 (^{13}C) µs . The letters s, d, t, q, and sext stand for singlet, doublet, triplet, quartet, and sextet, respectively.

Surface tension for critical micelle concentration (CMC): The characterization of the surface tension was carried out on a Dataphysics DCAT tensiometer equipped with a DuNouy ring made of a platinum-iridium alloy. To assess the surface tension (SFT), the tensiometer first detected the surface of the test liquid (30 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 ring meets the surface. Then, the ring 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. The solution was allowed to equilibrate in the apparatus and then surface tension measurements were accomplished. The critical micelle concentration (CMC) was calculated as the intersection between the two straight lines emerging from high and low concentrations.

4.3. Syntheses

4.3.1. Synthesis of $C_6F_{13}CH_2CHICH_2OH$ [56,57]

Note: Oxygen was removed from the reactants (1-iodoperfluoroderivatives and allyl) by bubbling nitrogen through the systems for several minutes.

RXN #1: A round-bottomed flask (10 mL) was charged with $C_6F_{13}I$ (0.5135 g, 1.15 mmol), allyl alcohol (0.1089 g, 1.87 mmol) TBPPi (0.0264 g, 0.152 mmol), heated to 75°C, for 2 hr. After elimination of unreacted reactants by rotary evaporator, the total product mixture was dissolved in $CDCl_3$ for NMR analysis. Yellow solid, yield by ^{19}F-NMR = >99% yield, with >99% purity.

RXN #2: A round-bottomed flask (10 mL) was charged with $C_6F_{13}I$ (0.501 g, 1.12 mmol), allyl alcohol (0.0667 g, 1.148 mmol) AIBN (0.0037 g, 0.0225 mmol), $Na_2S_2O_4$ (0.0503 g, 0.289 mmol), H_2O (0.0663 mL), heated to 90°C for 4 hr. Product was dissolved in $CDCl_3$. Slightly yellow solid, yield by ^{19}F-NMR = 92% yield, with 93% purity.

RXN #3: A round-bottomed flask (10 mL) fitted with a reflux condenser was charged with $C_6F_{13}I$ (0.501 g, 1.12 mmol), allyl alcohol (0.0976 g, 1.68 mmol), BPO (0.2442 g, 1.008 mmol), copper (II) acetate (0.0102g, 0.055 mmol), glacial acetic acid (0.3 mL), heated to 90°C for 8 hr. Product was dissolved in $CDCl_3$. Yellow solid, yield by ^{19}F-NMR = 0% yield.

Characterization: (TBPPI)^{1}H NMR (400 MHz, $CDCl_3$, 25°C) (Figure S3): δ = 4.31 (quin, -$CH_2C\underline{H}ICH_2OH$, $^{3}J_{HH}$=6.57 Hz, 1H), 3.80, 3.74 (-$CH_2CHIC\underline{H_a}H_bOH$, $^{2}J_{HaHb}$=12.13 Hz, 1H), 3.78, 3.73(d, -$CH_2CHICH_a\underline{H_b}OH$, $^{2}J_{HbHa}$=12.13 Hz, 1H) 3.01 (m, -$CF_2C\underline{H_a}H_bCHI$-, 1H), 2.65 (m, -$CF_2CH_a\underline{H_b}CHI$-, 1H), 2.95(-$CH_2O\underline{H}$, 1H); ^{19}F NMR (376.41 MHz, $CDCl_3$, 25°C) (Figure S5): δ = -81.06 ($C\underline{F}_3$-, $^{3}J_{FF}$=10.33, $^{4}J_{FF}$=2.30 Hz, 3F), -126.36 (m, $CF_3C\underline{F}_2(CF_2)_4CH_2$-, 2F), -123.77 (m, -$C\underline{F}_2(CF_2)_3CH_2$-, 2F), -123.05 (m, -$C\underline{F}_2(CF_2)_2CH_2$-, 2F), -121.97(m, -$C\underline{F}_2CF_2CH_2$-, 2F), -113.17, -114.20 (dm, -$C\underline{F}_2CH_2$-, $^{2}J_{FF}$ =144.68 Hz, 2F); ^{13}C NMR (101 MHz, $CDCl_3$, 25°C)); (Figure S7): δ = 118.49 (qt, $\underline{C}F_3CF_2$- $^{1}J_{CF}$ = 288.34 Hz, $^{2}J_{CF}$= 33.66 Hz), 117.70 (tt, -$CF_2\underline{C}F_2CH_2$-, $^{1}J_{CF}$=257.61 Hz, $^{2}J_{CF}$ = 32.20 Hz), 110.87 (m, $CF3(\underline{C}F_2)_4CF_2$-, 4C), 67.78 (s, -$\underline{C}H_2OH$, 1C), 37.18 (t, -$CF_2\underline{C}H_2CHI$-, $^{2}J_{CF}$ = 20.49 Hz, 1C), 20.4 (s, -$CH_2\underline{C}HICH_2OH$, 1C).

4.3.2. *Synthesis of Allyl-Polyethylene glycol [PEG]- methyl ether (CH_2=$CHCH_2O[CH_2CH_2O]_{9.5}CH_3$)*

The same equipment as above was used and dried and the reactions were carried out under a nitrogen atmosphere. To the three neck round-bottomed flask (100 mL) containing a magnetic stirrer, sodium hydride (80% by mass) in mineral oil (0.5125 g, 17.129 mmol) was weighed, dissolved in dry toluene (5 mL) and placed in an ice bath. A mixture composed of PEG_{500} (5.004 g, 10.58 mmol) in 50 mL toluene (dried by distillation) was added drop-wise into the reaction medium under vigorous stirring and then stirred for 2 hrs over room temperature. Then, the total product mixture was cooled in an ice bath and allyl bromide (3.849 g, 31.81 mmol) was slowly added. Mixture was stirred at room temperature for 24 hr. The resulting mixture was filtrated over silica gel. Liquid part was dissolved in 100 mL water and extracted four times with 20 mL portions of ether. Product was dried on high vacuum (0.128 x 10^{-3} mBar). Product was a colourless liquid; isolated yield was 3.5044 g, 65%.

Characterization: ^{1}H NMR (400 MHz, C_6D_6, 25°C) (Figure S1) δ = 5.85 (ddt, CH_aH_b=$C\underline{H_c}CH_2$-, $^{3}J_{HcHb(trans)}$ = 17.34 Hz, $^{3}J_{HcHa(cis)}$ = 10.36 Hz, $^{3}J_{HcH(CH_2)}$ = 5.81 Hz, 1H), 5.20 (ddt, $CH_a\underline{H_b}$=CH_cCH_2-, $^{2}J_{HbHa}$ = 1.77 Hz, $^{3}J_{HbHc(trans)}$=17.18 Hz, $^{4}J_{HbH(CH_2)}$ = 1.77 Hz, 1H), 5.11 (dm, $C\underline{H_a}H_b$=CH_cCH_2-, $^{3}J_{HaHc(cis)}$=10.36 Hz, $^{2}J_{HaHb}$ = 1.77 Hz, 1H), 3.96 (dm, CH_aH_b=$CH_cC\underline{H_2}O$-, $^{3}J_{H(CH_2)Hc}$=5.56 Hz, 2H), 3.53 (t, -$OC\underline{H_2}CH_2OCH3$, $^{3}J_{HH}$ = 5.5 Hz, 2H), 3.55-3.61 (m,- CH_2O-, 19 X 2H), 3.31 (s, -OCH_3, $^{4}J_{HH}$ = 0.72

Hz, 3H), 3.48 (t, -C$\underline{H}_2$OCH$_3$, $^3J_{HH}$ = 5.5 Hz, 2H); ^{13}C NMR (101 MHz, C_6D_6, 25°C) (Figure S2) δ = 135.97 (s, –CH=, 1C), 116.0 (s, =CH$_2$, 1C), 72.07 (s, 1C, $\underline{C}$H$_2$-OCH$_2$CH=CH$_2$, 1C), 72.07 (s, 1C, $\underline{C}$H$_2$–OCH$_3$, 1C), 70.74 (s, -$\underline{C}$H$_2$-O, 19 X 1C), 58.65 (s, 1C, $\underline{C}$H$_3$).

4.3.3. *Synthesis of $C_6F_{13}CH_2CHICH_2O(CH_2CH_2O)_{9.5}CH_3$*

RXN #4: $C_6F_{13}I$ (0.160 g, 0.358 mmol), Allyl-O-PEG-OCH$_3$ (0.2112 g, 0.417 mmol) TBPPi (0.050 g, 0.1808 mmol), were heated to 75 °C in a round-bottomed flask. After 2 h, additional TBPPi was added to the reaction (0.01g, 0.057mmol) and the reaction was then stopped after 8hr. Product was dissolved in $CDCl_3$. Brown solid, yield by ^{19}F-NMR = 79% yield, with 84% purity.

RXN #5: $C_6F_{13}I$ (0.093g, 0.208 mmol), Allyl-O-PEG-OCH$_3$ (0.2113g, 0.417 mmol), AIBN (0.001 g, 0.0042 mmol), heated to 90°C for 8 hr. Product was dissolved in $CDCl_3$. Brown solid, yield by ^{19}F-NMR = 37% yield, with 51% purity.

RXN #6: A round bottom flask (50 mL) equipped with a reflux condenser contained $C_6F_{13}I$ (0.093 g, 0.2084 mmol), Allyl-O-PEG-OCH3 (0.2113 g, 0.417 mmol), benzoyl peroxide (0.101 g, 0.413 mmol), copper (II) acetate (0.0039g, 0.0214 mmol), glacial acetic acid (10 mL), heated at 90 °C for 8 hr. Product was dissolved in $CDCl_3$. Dark brown solid, yield by ^{19}F-NMR = 0% yield.

Characterization: ^{1}H NMR(400 MHz, DMSO capillary, 25 ^{o}C) (Figure S11): δ = 4.35 (m, -CH$_2$C$\underline{H}$ICH$_2$OH, 1H), 3.80, 3.74 (-CH$_2$CHIC$\underline{H_a}$H$_b$O-, $^2J_{HaHb}$=10.86 Hz, 1H), 3.65, 3.64(d, -CH$_2$CHICH$_a\underline{H_e}$OH, $^2J_{HbHa}$=10.86 Hz, 1H) 3.16 (s, -OCH$_3$, $^4J_{HH}$=0.72 Hz, 3H), 3.35 (t, -OC$\underline{H}_2$CH$_2$OCH3, $^3J_{HH}$=5.3 Hz, 2H), 3.33 (t, -C$\underline{H}_2$OCH$_3$, $^3J_{HH}$=6.3 Hz, 2H), 3.5-3.4 (m, -CH$_2$O-, 19 X 2H), 3.14-3.03 (m, -CF$_2$C$\underline{H}_a$H$_b$CHI-, 1H), 2.70-2.59 (m, -CF$_2$CH$_a\underline{H}_b$CHI-, 1H); ^{19}F NMR (376.41 MHz, DMSO capillary, 25°C) (Figure S12): δ = -80 (t, C$\underline{F}_3$-, $^3J_{FF}$ =9.4 Hz, 3F), -112.24 (d, -CF$_a$F$_b$CH$_2$- , $^2J_{FaFb}$=273.06 Hz, 1F),-112.83 (d, -CF$_a$F$_b$CH$_2$- , $^2J_{FbFa}$=273.06 Hz, 1F), 2F), -120.73 (m, -C$\underline{F}_2$CF$_2$CH$_2$-, 2F), -121.78(m, -C$\underline{F}_2$(CF$_2$)$_2$CH$_2$-, 2F),-122.62 (m, C$\underline{F}_2$(CF$_2$)$_3$CH$_2$-, 2F), -125.15 (s, CF$_3$C$\underline{F}_2$(CF$_2$)$_4$CH$_2$-); *impurity*: -63.78(m, CF$_2$I, 2F), -112.59(m, -C$\underline{F}_2$CF $_2$I, -120.08 (m, -(CF$_2$)$_2$I, 2F); ^{13}C NMR (101 MHz, CDCl3 capillary, 25°C) (Figure S13): δ = -122 to -104 (m, $\underline{C}_6F_{13}$, 6C), 76.05 (s, -CHI$\underline{C}$H$_2$O-, 1C), 71.85 (s, -$\underline{C}$H$_2$OMe, 1C), 70.47 (s, -O$\underline{C}$H$_2$-, 19 X 1C), 70.40 (s, -O$\underline{C}$H$_2$CH$_2$OMe), 58.92 (s, -O$\underline{C}$H$_3$, 1C), 14.39 (s, -CH$_2\underline{C}$HICH$_2$O-, 1C), 37.34 (t, $^2J_{CF}$ = 20.83 Hz,-CF$_2\underline{C}$H$_2$CHI-, 1C).

4.3.4. Synthesis of $F[CF(CF_3)CF_2O]_{8.9}CH_2CHICH_2OH$:

General Synthetic Procedure: 1-iodo-2 oligo(hexafluoropropylene oxide) perfluoropropane (oligoHFPO-I) (M =1773 g/mol), allyl alcohol, and initiator were weighed in their appropriate amounts. Oxygen was displaced by purging nitrogen into the reaction mixture for 10 minutes. All reactions were carried out under positive nitrogen pressure and heated using an oil bath. Initiators were added to the reaction mixtures in regular periods according to their half-lives and reaction temperatures. The progress of the reaction was monitored by GC/MS using the starting iodide as the reference. After reaction, all products were separated by an acetone extraction in the same reaction flask. The soluble side products were first separated by decantation, followed by filtration through a Teflon® filter (2 mm porosity). The final product was dried at ca. 40 ^{o}C under vacuum (ca. 140 X 10^{-3} mbar) for 20 minutes.

Initiator (*tert*-butyl peroxypivalate, TBPPi):

RXN #7: In a 10 mL round-bottomed flask, oligo(HFPO)-$CF(CF_3)CF_2I$ (1.006 g, 0.564 mmol), allyl alcohol (0.0438 g, 0.754 mmol), TBPPi (0.0020 g, 0.0113 mmol) was heated to 75 °C for 48 hrs. TBPPi was transferred (0.0020 g, 0.0115 mmol) every 4hr-period during the day for a total of six injections. Allyl alcohol (0.0438 g, 0.754 mmol) was also added 6 times. Reaction mixture was 3 times washed by 3 mL acetone and one time by 3 mL ethanol. Yellow liquid, yield by ^{19}F-NMR = 88%, with 98% purity.

RXN #8: In a 10 mL round-bottomed flask, oligo(HFPO)-$CF(CF_3)CF_2I$ (1.006 g, 0.564 mmol), allyl alcohol (0.0438 g, 0.754 mmol), TBPPi (0.00197g, 0.0113mmol) was heated to 90°C for 38 hrs. TBPPi was transferred (0.00263 g, 0.0151 mmol) every 4hr-period during the day for a total of 18 injections. Allyl alcohol (0.0503g, 0.867mmol) was also added 18 times. Reaction mixture was 3 times washed by 3 mL acetone and one time by 3 mL ethanol. Yellow liquid, yield by ^{19}F-NMR = 80%, with 90.5% purity.

RXN #9: In a 25 mL round-bottomed flask, oligo(HFPO)-$CF(CF_3)CF_2I$ (10.090 g, 5.694 mmol), allyl alcohol (0.438 g, 7.54 mmol), TBPPi (0.0020 g, 0.0113 mmol) was heated to 75°C for 32 hrs. TBPPi was transferred (0.0355 g, 0.204 mmol) every 4hr-period during the day for a total of 16 injections. Allyl alcohol (0.0820 g, 1.411 mmol) was also added 16 times. Reaction mixture was 3 times washed by 3 mL acetone and one time by 3 mL ethanol. Yield by ^{19}F-NMR = 0%.

Initiator (Azobisisobutyronitrile, AIBN):

RXN #10: 1^{o} oligo(HFPO)-$CF(CF_3)CF_2I$ (2.034 g, 1.147 mmol), allyl alcohol (0.0883 g, 1.52mmol), and AIBN (0.0037 g, 0.0226 mmol) was placed into a two necked pear-shaped flask (10 mL) and heated to 90 °C for 64 hrs. AIBN and allyl alcohol were both added 7 times at 4 hr-period intervals. When the reaction was complete, extraction of by-products were carried out with acetone washings (5 X 25 mL). Yield by ^{19}F-NMR = 86% yield, with 99% purity.

RXN #11: In a 10 mL-round bottomed flask, oligo(HFPO)-$CF(CF_3)CF_2I$ (1.004 g, 0.564 mmol), allyl alcohol (0.0437 g, 7.52 mmol), AIBN (20% in chloroform**,** AIBN (0.0019 g, 0.0116mmol) and chloroform (0.0074 g, 0.0620 mmol), heated to 90 °C for 72 hrs. AIBN in chloroform was added *via* a syringe 17 times every 4 hr while allyl alcohol was added once after 32 hr (0.044 g, 0.758 mmol). Extraction with acetone was achieved (5 times, 20 ml). Yield by ^{19}F-NMR = 86% yield, with 97% purity.

RXN #12: In a 250 mL-round bottomed flask, oligo(HFPO)-$CF(CF_3)CF_2I$ (10.040 g, 5.6402 mmol), allyl alcohol (0.0437 g, 7.52 mmol), AIBN (20% in chloroform**,** AIBN (0.0185 g, 0.0116mmol) and chloroform (0.074 g, 0.0620 mmol), heated to 90 °C for 72 hrs. AIBN in chloroform was added *via* a syringe 35 times with 4 hr-period allyl alcohol was added 1 time after 32 h (0.044 g, 0.758 mmol). Extraction with acetone was achieved (5 times 20 ml). Yield by ^{19}F-NMR = 89% yield, with 98% purity.

di-benzoyl peroxide (BPO):

RXN #13: In a three-necked round-bottomed flask (50 mL) equipped with a reflux condenser, oligo(HFPO)-$CF(CF_3)CF_2I$ (1.003 g, 0.564 mmol), allyl alcohol (0.065 g; 1.12 mmol), glacial acetic acid (solvent, 10 mL), copper(II) acetate (0.011 g, 0.0548 mmol), BPO (0.273 g; 1.128 mmol) was heated to 90 °C for 8hr. The contents were cooled and the acetic acid was evaporated. A one-time extraction with water (10 mL) followed by a 4x extraction with ethanol (10 mL) achieved the final material. Yield by ^{19}F-NMR = 0% yield.

RXN #14: In a three-necked round-bottomed flask (50 mL) equipped with a reflux condenser, oligo(HFPO)-$CF(CF_3)CF_2I$ (1.003 g, 0.564 mmol), allyl alcohol (0.1310 g, 2.2559 mmol), glacial acetic acid (solvent, 10 mL), copper(II) acetate (0.005 g, 0.02738 mmol), BPO (0.8767 g, 3.619 mmol) was heated to 90 °C for 8hr. The contents were cooled and the acetic acid was

evaporated. A onetime extracted was accomplished with water (10 mL), followed by a 4x extraction with ethanol (10 mL). Yield by ^{19}F-NMR = 0% yield.

Characterization: (TBPPI): ^{1}H NMR (400 MHz, C_6D_6 capillary, 25°C) (Figure S17): δ = 4.4 (s, -$CH_2C\underline{H}ICH_2OH$, 1H), 4.21(s,-$CH_2O\underline{H}$, 1H), 3.81 (-$CH_2CHIC\underline{H_2}OH$,2H), 2.98 (m, -$CF_2C\underline{H_a}H_bCHI$-, 1H), 2.72 (m, -$CF_2CH_a\underline{H_b}CHI$-, 1H); (AIBN): ^{1}H NMR (400 MHz, C_6D_6 capillary, 25°C) (Figure S18): δ = 4.31, 4.25 (s, -$CH_2C\underline{H}ICH_2OH$, 1H), 3.99(s,-$CH_2O\underline{H}$, 1H), 3.66 (-$CH_2CHIC\underline{H_2}OH$,2H), 2.84 (m, -$CF_2C\underline{H_a}H_bCHI$-, 1H), 2.54 (m, -$CF_2CH_a\underline{H_b}CHI$-, 1H); ^{19}F NMR (376.41 MHz, C_6D_6, 25°C) (Figure S20): δ = -80 to -85 (m, $CF(C\underline{F_3})C\underline{F_2}O$-), -80.15 (s, $C\underline{F_3}CF_2CF_2O$- , 3F), -81.80 (s, $CF_3CF_2C\underline{F_2}O$-, 2F), -110.92 (d, -$CF(CF_3)CF_aF_bCH_2$-, $^{2}J_{FF}$ = 262.73Hz), -112.54 (d, -$CF(CF_3)CF_aF_bCH_2$-, $^{2}J_{FF}$ = 237.49Hz), -113.99 (d, -$CF(CF_3)CF_aF_bCH_2$-, $^{2}J_{FF}$ = 261.58Hz), -129.80 (s, $CF_3C\underline{F_2}CF_2$-, 2F), -146.80 (m, -$C\underline{F}(CF_3)CF_2$-, 8.9 x 1F); ^{13}C NMR (101 MHz, DMSO/C_6D_6 capillary, 25°C) (Figure S22): δ = 118.0 (qd, $^{1}J_{CF}$ =290.9, $^{2}J_{CF}$ = 28.2 Hz –OCF($\underline{C}$F3)CF2-), 117.6 (qt, $^{1}J_{CF}$ = 286.15 Hz, $^{2}J_{CF}$ = 32.93 Hz, $\underline{C}F_3CF_2CF_2O$-, 1C), 117.5 (qd, $^{1}J_{CF}$ =286.15, $^{2}J_{CF}$ = 34.40 Hz, $CF_3CF_2\underline{C}F_2O$, 1C), 114.7 (td,$^{1}J_{CF}$ = 285.74, $^{2}J_{CF}$ = 31.26Hz,-$OCF(CF_3)\underline{C}F_2$-, 8.9 x 1C), 105.2 (tsext, $^{1}J_{CF}$= 267.03 Hz, $^{2}J_{CF}$ = 36.68 Hz, $CF_3\underline{C}F_2CF_2O$-, 1C), 101.8 (dsext, $^{1}J_{CF}$ = 270.7, $^{2}J_{CF}$ =36.7 Hz, –O$\underline{C}F(CF_3)CF_2$-), 66.32 (s, -$CH_2CHI\underline{C}H_2OH$, 1C), 36.52(m, -$CF_2\underline{C}H_2CHICH_2OH$, 1C), 18.09, 17.90 (s, -$CH_2\underline{C}HICH_2OH$, 1C).

4.3.5. *Synthesis of $F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2CH_2CH_2CH_2OH$* **Error! Bookmark not defined.**

To the three necked round-bottomed flask (250 mL), equipped with a dropping funnel and a reflux condenser, was added product from *RXN#12*, pHFPO-CH_2CHICH_2OH (10.012 g, 5.42 mmol), AIBN (0.3166 g, 1.928 mmol) dissolved in trifluorotoluene (20 mL). The medium was saturated by nitrogen by a 10 minute-bubbling. Reaction mixture was then heated at 80 °C. Tributhylthin hydride (2.435 g, 8.12 mmol) was added drop-wise for 5 minutes. Reaction was monitored by GC/MS at 2 hr and then at 5 hr. Then, AIBN (0.037 g, 0,226 mmol) was added followed by additional tributyltin hydride (0.369 g, 1.265 mmol) again drop-wise over 5 minutes. The reaction mixture was stirred at 80 °C for 5 hr and then cooled to room temperature. Then, trifluorotoluene was evaporated and the resulting product was extracted by acetone (10 mL) three times while the insoluble side products were decanted. The solid side

products were removed by filtration and then all solvents were evaporated under high vacuum. Isolated yield = 5.4438 g, 58% yield.

Characterization[65]: 1H NMR (400 MHz, $CDCl_3$) : δ = 3.8 (t, $^3J_{HH}$ = 5.6 Hz, -$CH_2C\underline{H}_2OH$), 2.3(m, -$CF_2C\underline{H}_2CH_2$-), 1.9(m, -$CH_2C\underline{H}_2CH_2$-)***;*** ^{13}C NMR (101 MHz, $CDCl_3$ capillary, 25°C) δ = 60.8 (s, -$\underline{C}H_2OH$, 1C), 27.9 (t, $^2J_{CF}$ = 24.3, -$CF_2\underline{C}H_2$-, 1C), 23.5 (s, -$CH_2\underline{C}H_2CH_2$-, 1C); the ^{19}F-NMR is similar to that of $F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2CH_2CHICH_2OH$. ASAP-TOF-MS spectrum (Positive and Negative, Figure S44-45).

4.3.6. Synthesis of $F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2CH_2CHICH_2O(CH_2CH_2O)_{9.5}CH_3$

General Procedure: 1-iodo-2-oligo(hexafluoropropylene oxide) perfluoropropane (oligo(HFPO)-$CF(CF_3)CF_2I$), polyethylene glycol allyl (allyl-O-PEG-OCH_3), and initiator were weighed in their appropriate amounts. Oxygen was displaced by purging nitrogen into the reaction mixture for 10 minutes. All reactions were carried out under positive nitrogen pressure and heated using an oil bath. Initiators were added to the reaction mixtures in regular periods according to their half-lives and temperatures. The progress of the reaction was monitored by GC/MS using the starting iodide as the reference. When the reaction was completed, the GC/MS showed no oligo(HFPO) iodide. After reaction, all products were separated by an acetone extraction in the same reaction flask. The soluble side products were first separated by decantation, followed by filtration through a Teflon® filter (2 mm porosity). The final product was dried at ca. 40 ^oC under vacuum (ca. 140 X 10^{-3} mbar) for 20 minutes and resulted in a light yellow oil.

Initiator (*tert*-butyl peroxypivalate, TBPPi):

RXN #15 In a 10 mL round-bottomed flask equipped with a reflux condenser, oligo(HFPO)-$CF(CF_3)CF_2I$ (1.0 g, 0.564 mmol), Allyl-O-PEG-OCH_3 (0.437 g, 0.8619 mmol), TBPPi (0.312 g, 1.13 mmol) was heated to 75 °C. TBPPi (3.202 g, 0.23 mmol) was added every 4 hr-period for a total of 19 additions. The product was wash 5x with ethanol (10 mL). A yellow liquid was obtained but yield by ^{19}F-NMR was 0% as well as from ^{19}F-NMR spectroscopy.

RXN #16: In a 3 neck 100 mL round-bottomed flask equipped with a reflux condenser, oligo(HFPO)-$CF(CF_3)CF_2I$ (10.008 g, 5.64 mmol), Allyl-O-PEG-OCH_3 (4.373 g, 8.61 mmol), TBPPi (0.312 g, 1.13 mmol) was heated to 75 °C for 64 hrs. TBPPi (0.312 g, 1.13 mmol) was added

every 4 hr-period for a total of 15 additions. The product was washed 3-times with ethanol (20 mL). Light yellow liquid, yield by ^{19}F-NMR = 0% yield.

Initiator (Azobisisobutyronitrile, AIBN):

RXN #17: In a 2 necked round-bottomed flask, oligo(HFPO)-CF(CF_3)CF_2I (1.005 g, 0.564 mmol), Allyl-O-PEG-OCH_3 (1.3110 g, 2.5858 mmol), AIBN (0.002 g, 0.012 mmol), heated to 90 °C for 80 hrs. 20 times added AIBN (0.02 g, 0.12 mmol) with 4 hr-period, 5 times extraction with acetone (10 mL), Light honey brown liquid, yield by ^{19}F-NMR = 48% yield, with 75% purity.

RXN#18: In a two-neck round-bottomed flask equipped with a Claisen condenser and magnetic stir bar was placed oligo(HFPO)-CF(CF_3)CF_2I (10.012 g, 5.64 mmol), allyl-O-PEG-OCH_3(3.8228 g, 7.54 mmol), AIBN (0.0185 g, 0.113 mmol) and chloroform (0.074 g, 6.197 mmol). The reaction mixture was bubbled for a ca. 10 minutes with nitrogen and then placed in an oil bath that was progressively heated up to 90°C. Additional allyl-O-PEG-OCH_3 (3.8228 g, 7.54 mmol) was transferred into the reaction mixture after 40 hrs. AIBN in chloroform (0.0185 g, 0.113 mmol, 0.074 g, 0.618 mmol) was 73 times in total with the additions occurring every 2 hr. Because complete conversion was not detected with NMR more allyl-O-PEG-OCH_3 was added (4.023 g, 7.93 mmol) and AIBN in chloroform (0.185 g, 1.13 mmol, 0.74 g, 6.197mmol) was added 14 times in total occurring every 2 hr. The product mixture was washed with 10 mL of water and then 3 times with 20 mL of acetone. The product was dried using a high-vacuum pump and filtrated through a ring filter. A yellow-brown oil was obtained.,The yield by ^{19}F-NMR = 50%, with 76% purity.

Initiator (di-benzoyl peroxide (BPO)):

RXN #19: In a two-neck 10 mL round-bottomed flask equipped with a reflux condenser, oligo(HFPO)-CF(CF_3)CF_2I (1.0007 g, 0.564 mmol), Allyl-O-PEG-OCH3 (1.4003 g, 2.7613 mmol), copper(II) acetate (0.0052 g, 0.0274 mmol), glacial acetic acid (3 mL) and BPO (0.5675 g, 2.343 mmol) were added and heated to 90 °C. After the reaction, the acetic acid was evaporated and washed 7 times with acetone (10 mL). Green oil, yield by ^{19}F-NMR = 51% yield, with 88% purity.

RXN #20: In a three-neck 100 mL round-bottomed flask equipped with a reflux condenser, oligo(HFPO)-CF(CF3)CF2I(10.007 g, 5.64 mmol), Allyl-O-PEG-OCH3 (4.291 g, 8.46 mmol), copper(II) acetate (0.052 g, 0.274mmol), glacial acetic acid (3 mL), and BPO (1.641 g, 6.77

mmol) were added and then heated to 90 °C. After 8 hrs, additional Allyl-O-PEG-OCH3 (1.431 g, 2.821 mmol) and BPO (1.192 g, 4.91 mmol) was added. The number of Allyl-O-PEG-OCH_3 and BPO additions were 5 times every 8 hr-period. After the reaction the acetic acid was evaporate, washed 7 times with acetone (10 mL). Dark green oil, yield by Yield by ^{19}F-NMR = 71% yield, with 94% purity.

Characterization: ^{1}H NMR(400 MHz, $CDCl_3$ capillary, 25 ^{o}C) (Figure S28): δ= 4.36 (b, -C*H*I-, 1H), 3.79 (b, -CHIC*H*$_2$O, 2H), 3.59 (b, -C*H*$_2$O, 19 x 1H), 3.46 (b, -C*H*$_2$C*H*$_2$$OCH_3$, 4H), 3.28 (s, C*H*$_3$O-, 3H), 3.09 (vb, -$CF_2$C*H*$_a$$H_b$CHI-, 1H), 2.58 (vb CF_2CH_a*H*$_b$CHI-, 1H); ^{19}F NMR (376.41 MHz, C_6D_6, 25°C) (Figure S29): δ = -80 to -84 (CF(C*F*$_3$)C*F*$_2$O-), -84.04 (C*F*$_3$$CF_2CF_2$O- , 3F), -82.37 ($CF_3CF_2$C*F*$_2$O-, 2F), -112 to -117.5 (b, -CF(CF3)C*F*$_2$$CH_2$CHI-, 2F), -132.03 (s, CF_3C*F*$_2$$CF_2$-, 2F), -146.54 (m, -C*F*(CF_3)CF_2-, 8.9 x 1F); ^{13}C NMR (101 MHz, C_6D_6, 25°C) (Figure S30): δ = 118.0 (qd, $^{1}J_{CF}$ =290.9, $^{2}J_{CF}$ = 28.2 Hz – OCF(*C*F3)CF2-), 117.6 (qt, $^{1}J_{CF}$ = 286.15 Hz, $^{2}J_{CF}$ = 32.93 Hz, *C*$F_3CF_2CF_2$O-, 1C), 117.5 (qd, $^{1}J_{CF}$ =286.15, $^{2}J_{CF}$ = 34.40 Hz, CF_3CF_2*C*F_2O, 1C), 114.7 (td,$^{1}J_{CF}$ = 285.74, $^{2}J_{CF}$ = 31.26Hz,-OCF(CF_3)*C*F_2-, 8.9 x 1C), 105.2 (tsext, $^{1}J_{CF}$= 267.03 Hz, $^{2}J_{CF}$ = 36.68 Hz, CF_3*C*F_2CF_2O-, 1C), 101.8 (dsext, $^{1}J_{CF}$ = 270.7, $^{2}J_{CF}$ =36.7 Hz, –O*C*F(CF_3)CF_2-), 76.27 (s, -CH_2CHI*C*H_2O-, 1C), 72.17 (s, *C*H_2–CH_2–OMe, 2C), 70.79 (s, 19 X 1C, -*C*H_2–O), 70.54 (s, -CH_2*C*H_2OMe, 1C) 58.65 (s, 1C, *C*H_3), 37.65 (m, -CF_2*C*H_2CHICH_2O-, 1C), 14.30 (s, -CH_2*C*HICH_2O-, 1C).

4.3.7. *Synthesis of F[CF(CF$_3$)CF$_2$O]$_{8.9}$CF(CF$_3$)CF$_2$CH$_2$CH$_2$CH$_2$O(CH$_2$CH$_2$O)$_{9.5}$CH$_3$*

To a 100 mL three neck round-bottomed flask equipped with a magnetic stirrer, reflux condenser and dropping funnel was placed the diblock iodo copolymer (RXN#20, 4.03 g, 1.6999 mmol), AIBN (0.1066 g, 0.649 mmol) and trifluorotoluene (6 mL). Oxygen was displaced from the reaction mixture by bubbling nitrogen gas through the reaction mixture for several minutes. The reaction mixture was placed in a 80 °C hot oil bath. Then tributyltin hydride 97% solution (0.505 mL, 1.8699mmol) was added drop by drop over 2 minutes. The colour of the reactant when from green to orange and then finally black. The reaction was stopped after 5 hrs. The product with the black suspension was centrifuged for 45 min at 8000 rpm at room temperature. The product was then decanted and finally filtrated. To the slightly yellow liquid was added KF (0.108 g, 1.8587mmol), and intensively stirred over 24 hrs at room temperature

(c.a. 25°C). Next 2 mL of Freon 113 was added and the contents were centrifuged for 45 min at 8000 rpm. The liquid product was decanted and filtrated through a ring filter (pore size 0.2 um, diameter 13mm). All solvents were removed under rotational evaporation (50 mbar, 60°C). The product was then filtered a final time with a ring filter. Final product was dried under high vacuum (800 X 10^{-3} mbar). The product is a light lemon yellow oil. Isolated yield 3.786 g, 77% yield.

Characterization: 1H NMR (400 MHz, $CDCl_3$ capillary, 25 ^{o}C) (Figure S35): δ= 3.5 9 (b, -C$\underline{H}_2$O, 23 x 1H), 3.40 (s, C$\underline{H}_3$O-, 3H), 2.20 (b, -$CF_2C\underline{H}_2CH_2$-, 1H), 1.89 (b, -$CF_2CH_2\underline{C}H_2$-, 1H); ^{19}F NMR (376.41 MHz, C_6D_6, 25°C) (Figure S36): δ = -80 to -84 (CF(C$\underline{F}_3$)C$\underline{F}_2$O-), -84.04 (C$\underline{F}_3CF_2CF_2O$- , 3F), -82.37 ($CF_3CF_2C\underline{F}_2O$-, 2F), -112 to -118 (b, -CF(CF3)C$\underline{F}_2CH_2CH_2$-, 2F), -131.56 (s, $CF_3C\underline{F}_2CF_2$-, 2F), -146.05 (m, -C$\underline{F}(CF_3)CF_2$-, 9.9 x 1F); ^{13}C NMR (101 MHz, C_6D_6, 25°C) (Figure S37): δ = 118.0 (qd, $^1J_{CF}$ =290.9, $^2J_{CF}$ = 28.2 Hz, –OCF(C$\underline{C}$F3)CF2-), 117.6 (qt, $^1J_{CF}$ = 286.15 Hz, $^2J_{CF}$ = 32.93 Hz, $\underline{C}F_3CF_2CF_2O$-, 1C), 117.5 (qd, $^1J_{CF}$ =286.15, $^2J_{CF}$ = 34.40 Hz, $CF_3CF_2\underline{C}F_2O$, 1C), 114.7 (td,$^1J_{CF}$ = 285.74, $^2J_{CF}$ = 31.26Hz,-OCF(CF_3)$\underline{C}F_2$-, 8.9 x 1C), 105.2 (tsext, $^1J_{CF}$= 267.03 Hz, $^2J_{CF}$ = 36.68 Hz, $CF_3\underline{C}F_2CF_2O$-, 1C), 101.8 (dsext, $^1J_{CF}$ = 270.7, $^2J_{CF}$ =36.7 Hz, –O$\underline{C}F(CF_3)CF_2$-), 69.42 (bs, -CH_2O-, 21 X 1C), 57.59 (s, $\underline{C}H_3$,1C), 27.80(m, -$CF_2\underline{C}H_2CH_2CH_2O$-, 1C), 20.55 (s, -$CH_2\underline{C}H_2CH_2O$-, 1C).

4.3.8. Initiator reactions

4.3.8.1. Model reactions of 1-iodoperfluorohexane with radical initiators

General Procedure: In a round-bottomed flask (10 mL), $C_6F_{13}I$ (0.5002 g, 1.12 mmol) and the appropriate initiator (TBPPi, AIBN, or BPO) was added to the flask. Oxygen was removed by purging the mixture with nitrogen gas for at least 10 minutes. The reaction mixture was heated at the required temperature.

RXN #21: TBPPi (0.6702 g, 2.42 mmol) was added to $C_6F_{13}I$ and heated at 75°C for 3 hrs. ^{19}F-NMR Yield = 92% $C_6F_{13}CH_2CI(CH_3)_2$.

RXN #22: AIBN in chloroform (0.2002 g, 1.21 mmol; 1.002 g, 8.37 mmol) was added to $C_6F_{13}I$ and heated to 90 °C for 3 hrs. No reaction.

RXN#23: AIBN in chloroform (0.3678 g, 2.24 mmol; 1.4712 g, 12.3 mmol), $Na_2S_2O_4$ (0.0436 g, 0.266 g), H_2O (0.108) was added to $C_6F_{13}I$ and heated to 90 °C for 3 hrs.

RXN#24: BPO (0.3315 g, 1,36 mmol), copper(II)acetate (0.0102 g, 0.056 mmol), acetic acid (1 mL) was added to $C_6F_{13}I$ heated to 90 °C for 3hrs. ^{19}F-NMR Yield = >99% C_6F_{13}-Aromatic Compounds (see Figure S14).

4.3.8.2. Model reactions of $F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2I$ with radical initiators

General Procedure: In a round-bottomed flask (10 mL) equipped with a condenser, oligo(HFPO)-$CF(CF_3)CF_2I$ (M=1773 g/mol, 1.003 g, 0.564 mmol) and the appropriate initiator (TBPPi, AIBN, or BPO) was added. Oxygen was removed by purging the mixture with nitrogen gas for at least 5 minutes. The reaction mixture was heated at the required temperature.

RXN#25 TBPPi (0.329 g, 1.154 mmol) was added to oligo(HFPO)-$CF(CF_3)CF_2I$ and heated to 75°C for 4 hrs. ^{19}F-NMR Yield = 95.5% of $F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2CH_2Cl(CH_3)_2$ and 4.5% $F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2H$

RXN# 26 AIBN (0.1895 g, 1.154 mmol) was added to oligo(HFPO)-$CF(CF_3)CF_2I$ and heated to 90 °C for 4 hrs. No reaction.

RXN#27 AIBN in chloroform (0.1895 g, 1.154 mmol; 0.9475 g, 7.94 mmol) was added to oligo(HFPO)-$CF(CF_3)CF_2I$ and heated to 90 °C for 4 hrs. No reaction.

RXN#28 AIBN in chloroform (0,1895g, 1,128 mmol; 0,742g, 6,22 mmol), $Na_2S_2O_4$ (0,0236g, 0,133g), H_2O (0,055ml) was added to oligo(HFPO)-$CF(CF_3)CF_2I$ and heated to 90 °C for 4 hrs. No reaction.

RXN#29 BPO (0.279 g, 1.154 mmol), copper (II)acetate (0.071 g, 0.389 mmol), acetic acid (0.3 ml), was added to oligo(HFPO)-$CF(CF_3)CF_2I$ and heated to 90 °C for 8 hrs. ^{19}F-NMR Yield = 7.5% $F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2$-Aromatics and 0.5% $F[CF(CF_3)CF_2O]_{8.9}CF(CF_3)CF_2H$.

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