Journal of Fluorine Chemistry 131 (2010) 844–851

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Synthesis and characterization of partially fluorinated ethers

A. Zaggia *, L. Conte, G. Padoan, F. Ceretta

Department of Chemical Processes of Engineering, University of Padova, Via Marzolo 9, 35131 Padova, Italy

ARTICLE INFO

Article history:
Received 15 March 2010
Received in revised form 16 April 2010
Accepted 19 April 2010
Available online 27 April 2010

Keywords:
Partially fluorinated ethers
Perfluorinated chains
Surface free energy

ABSTRACT

A series of partially fluorinated ethers PFE-*m*,*n* with general formula $F(CF_2)_mCH_2CH_2O(CH_2)_nH$ (*m* = 4, 6, 8 and *n* = 2, 3, 5, 8, 14, 18, 21) has been synthesized and characterized. The present work aimed to investigate the synthesis of PFE-*m*,*n* and evaluate some of their fundamental physico-chemical properties such as: specific gravity, refractive index, viscosity, solid–solid transitions, solubility and amphiphile surface activity in a variety of solvents. Further, a comparison between PFE-*m*,*n* and the well known semifluorinated *n*-alkanes $F(CF_2)_m$–$(CH_2)nH$ (FHm, *n*) with the same value of the *m*/*n* ratio have been reported.

1. Introduction

Partially or fully fluorinated hydrocarbon compounds exhibit outstanding chemical and thermal stability [1], high gas dissolving capacity [2], low solubility in water and excellent lubricating properties [3–7]. Partially fluorinated ethers (PFEs) have become increasingly important in many domains. Thanks to their almost zero ozone depletion potential (ODP) they are used as substitutes for ozone-depleting chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) [8]. Their ability to dissolve both hydrocarbons and flurocarbons makes them an ideal reaction solvent [9].

Herein, we describe the synthesis of a series of PFEs with general formula $F(CF_2)_m(CH_2)_2O(CH_2)_nH$ (*m* = 4, 6, 8 and *n* = 2, 3, 5, 8, 14, 18, 21) obtained by reaction of 1H,1H,2H,2H-perfluoro-1-alkanols with 1-bromoalkanes under basic conditions. These compounds were named PFE-*m*,*n*, where *m* is the number of carbon atoms in the perfluorinated moiety and *n* is the number of carbon atoms in the hydrocarbon segment.

PFE-*m*,*n* have been recently tested as long-term postoperative tamponade agents to aid retinal reattachment after surgery [10,11]. For this application there is the need for fluids that do not have the problems of buoyancy displayed by silicones and at the same time that are not as heavy as perfluorocarbons [12].

The present work aimed to give a straight and economical methodology for the preparation of highly pure PFE-*m*,*n* with different fluorocarbon–hydrocarbon ratio (*m*/*n*) and evaluate some physico-chemical properties such as specific gravity, refractive index, viscosity, solid–solid transitions, solubility and amphiphile surface activity in a variety of solvents. A comparison between PFE-*m*,*n* and semifluorinated *n*-alkanes with general formula $F(CF_2)_m$-$(CH_2)_nH$, (FH-*m*,*n*) allowed to investigate the role of both the ratio *m*/*n* and the ether linkage in determining the self-organizing behavior of these compounds.

2. Results and discussion

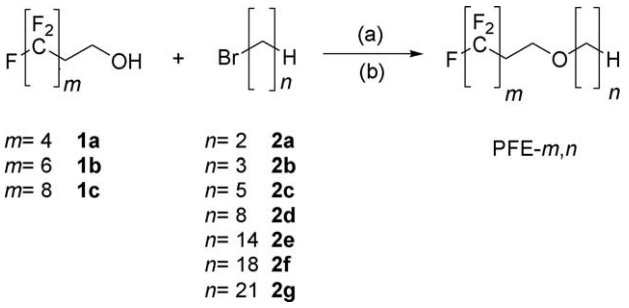
2.1. Synthesis

There are many methods reported in literature for preparing PFEs: addition of alcohols to fluorinated olefins under basic conditions [13,14], nucelophilic alkylation of fluorinated alkoxides [15], addition of perfluoroalkyl iodides to allyl ethers followed by reductive deiodination [16], reaction of a fluorinated alcohol with aldehydes under hydrogen pressure [17].

Huang et al. [18] have successfully synthesized PFE-*m*,*n* with varying *m*/*n* ratios reacting 1H,1H,2H,2H-perfluoro-*1*-alkanols $F(CF_2)_m(CH_2)_2OH$ and 1-bromoalkanes $Br(CH_2)_nH$ in aqueous solution of sodium or potassium hydroxide in the presence of a phase-transfer catalyst (tetrabutylammonium hydrogen sulfate or tetrabutylammonium bromide). These compounds were characterized by ^1H and ^{13}C nuclear magnetic resonance, infra red spectroscopy and elemental analysis; reaction by products were not identified; melting point, phase transition temperature, critical micelle concentration, micelle hydrodynamic radius were also determined by the authors. In a first test we applied the metodology described by Huang in order to synthesized PFE-*6*,*5* (**3h**); 50% aqueous solution of sodium hydroxide (10 ml) and tetrabutylammonium hydrogen sulfate (2 mmol) were added to a solution of 1H,1H,2H,2H-perfluoro-*1*-octanol (10.4 mmol) in a mixture of benzene (37 ml) and tetrahydrofuran (23 ml). The

* Corresponding author. Tel.: +39 049 827 25 55; fax: +30 049 827 25 57.
E-mail address: alessandro.zaggia@unipd.it (A. Zaggia).

0022-1139/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2010.04.003



Scheme 1. Step (a) N-methyl-2-pyrrolidone, 45% aqueous solution of potassium hydroxide, 50 °C, 5 h; followed by step (b) 70 °C, 2 h.

mixture was stirred for 1.7 h at 10 °C, followed by the addition of 1-bromopentane (31.2 mmol); the mixture was then stirred at room temperature for 4 days and PFE-*6,5*; after dilution with hexane and washing with water the crude product was dried over sodium sulfate, the solvent removed and PFE-*6,5* was recovered by distillation under reduced pressure at 65% yield. The use of phase-transfer catalyst gave long reaction times and low yields in agreement with data reported in literature [19]. Gas cromatography–mass spectrometry analysis performed on the crude product showed the formation of byproducts the most abundant of which was the symmetric fully hydrogented ether $H(CH_2)_5O(CH_2)_5H$. The phase transfer probably promotes a two step reaction involving first a nucleophilic substitution on a molecule of 1-bromoalkane with the formation of a linear alcohol which further reacts with a second molecule of 1-bromoalkane in a phase-transfer catalysed Williamson etherification. Given the central role reserved to the phase transfer in the formation of byproducts we developped a different synthesis methodology in order to eliminate this reactant (Scheme 1).

The reaction was performed by dropping a 45% aqueous solution of potassium hydroxide in a mixture composed by N-methyl-2-pyrrolidone, 1H,1H,2H,2H-perfluoro-*1*-alkanols (**1a**–**1c**) (100 mmoles) and 1-bromoalkane (**2a**–**2g**) (200 mmoles) at a temperature of 50–70 °C for 7 h. The yields in the desired PFE-*m,n* varied from 97% for PFE-*6,2* and PFE *8,2* (**3b**,**3c**) to 60% for PFE-*8,21* (**3z**) as reported in Table 1.

Under these conditions, we observed a remarkable increase in the reaction yield (due to the disappearance of the symmetric fully hydrogenated ether) and a shortening in the reaction time (less than 8 h).

2.2. Physico-chemical study

The molecular design of PFE-*m,n* gave the possibility to assess the role of both hydrocarbon and fluorocarbon chains, through the *m*/*n* ratio, in determining physical properties and surface activities.

Semifluorinated *n*-alkanes FH-*m,n* having *m* equal or nearly equal to *n* are known to undergo liquid crystal-liquid crystal termotropic transitions producing self-assembled nanostructures. DSC curves of FH-*m,n* having more than four fluorinated carbon atoms and at least 4–6 methylene units typically show two endoterms, one imputable to melting and the other to a solid–solid phase transition ascribable to a morphological change in the molecular assembling [20–23]; the heat of melting was found to be indipendent of the length of the hydrocarbon segment for $m \leq 14$ and growing nearly linearly with the number of methylene units for $m > 14$. Enthalpy and peak positions derived from DSC curves collected in the temperature range −80 °C to +80 °C on all the synthesized PFE-*m,n* (excepting ethers **3a**–**3f**) are given in Table 1. Compounds **3a**–**3f** were left out of the calorimetric investigation since their melting temperatures were below the lower instrumental limit of −80 °C. For all the synthesized compounds thermograms show a sharp endothermic melting peak. As clearly emerges from Table 1, keeping the number *n* of hydrogenated carbon atoms constant, the enthalpy of melting increases with the number of fluorinated carbon atoms m. For the same value of m the enthalpy of melting is rather independent of n until it reaches 18 units after which it starts to increase. Compounds **3h**, **3m** and **3n**, which have values of *m* and *n* equal or nearly equal, show a secondary endothermic peak. Comparing data obtained from thermograms (Fig. 1) it emerges that both the enthalpy of melting and the solid–solid transition of compounds **3h**, **3m** and **3n** are nearly independent of *n* and increase with increasing *m*.

Table 1
Values of reaction yield, refractive index, specific gravity, boiling/melting points, solid–solid phase transition temperatures and surface tension for PFE-*m,n* synthesized; n.a.: not available; n.o.: not observed. Compound identified by (*) have been previously described in Ref. [17], and (**) in Ref. [18].

Compound	Symbol	*m*	*n*	Yield	Refractive index	Specific gravity	Boiling point	Melting point	Enthalpy of melting	Solid–solid transition	Enthalpy of transition
				%	n_D^{20}		°C/mbar	°C	J/g	°C	J/g
3a	PFE-*4,2*	4	2	95	1.3121	1.12	56/760	< -80	–	n.a.	–
3b	PFE-*6,2*	6	2	97	1.3144	1.14	65/760	<−80	–	n.a.	–
3c	PFE-*8,2*	8	2	97	1.3157	1.21	72/760	<−80	–	n.a.	–
3d	PFE-*4,3*	4	3	84	1.3201	1.13	120/760	<−80	–	n.a.	–
3e	PFE-*6,3*	6	3	71	1.3245	1.18	145/760	<−80	–	n.a.	–
3f	PFE-*8,3*	8	3	82	1.3255	1.26	165/760	<−80	–	n.a.	–
3g	PFE-*4,5*	4	5	83	1.3267	1.21	90/12	−70.2	55.09	n.o.	–
3h	PFE-*6,5*	6	5	72	1.3385	1.23	110/6	−46.8	61.20	−72.6	4.81
3i	PFE-*8,5*	8	5	82	1.3399	1.31	130/7	−19.4	68.92	n.o.	–
3l	PFE-*4,8*	4	8	70	1.3691	1.28	125/5	−35.4	52.21	n.o.	–
3m (*)	PFE-*6,8*	6	8	71	1.3888	1.34	150/7	−21.2	57.34	−52.3	5.21
3n	PFE-*8,8*	8	8	72	1.3920	1.39	160/1	−8.5	67.42	−31.2	6.52
3o	PFE-*4,14*	4	14	71	n.a.	1.35	n.a.	14.5	54.32	n.o.	–
3p	PFE-*6,14*	6	14	68	n.a.	1.39	n.a.	19.2	59.21	n.o.	–
3q (**)	PFE-*8,14*	8	14	68	n.a.	1.41	n.a	27.1	68.32	n.o.	–
3r	PFE-*4,18*	4	18	65	n.a.	1.43	n.a.	18.5	55.28	n.o.	–
3s	PFE-*6,18*	6	18	67	n.a.	1.48	n.a.	27.4	60.56	n.o.	–
3t	PFE-*8,18*	8	18	65	n.a.	1.52	n.a.	39.7	69.02	n.o.	–
3u	PFE-*4,21*	4	21	69	n.a.	1.47	n.a.	31.7	64.56	n.o.	–
3v	PFE-*6,21*	6	21	67	n.a.	1.55	n.a.	40.8	75.25	n.o.	–
3z	PFE-*8,21*	8	21	60	n.a.	1.58	n.a.	58.1	83.21	n.o.	–

Table 2
Foaming tendency, solvent surface tension depression, solvent gel-phase formation and solubility in silicon oil for PFE-*m*,*n* synthesized.

Compound	Surface tension $mN\,m^{-1}$	Foaming tendency[a]			Solvent surface tension depression[b]			Solvent gel-phase formation[c]			Silicon oil solubility[d] (wt/wt) %
		n-Hexane	*n*-Dodecane	Perfluorodecalin	*n*-Hexane	*n*-Dodecane	Perfluorodecalin	*n*-Dodecane	Methanol	Perfluorodecalin	
3a	18.5	n.f.o.	n.f.o.	n.f.o.	18.2	25.2	19.1	n.g.o.	n.g.o.	n.g.o.	98
3b	18.0				18.3	24.9	19.4				64
3c	18.4				18.2	25.1	19.4				41
3d	19.0				18.1	25.1	18.9				96
3e	18.7				17.9	24.9	19.3				52
3f	18.2				17.8	23.1	19.4				35
3g	19.1				18.2	24.5	18.8				93
3h	18.7				18.1	23.9	18.7				43
3i	18.5				17.6	24.1	18.8				31
3l	19.7				17.5	24.5	19.1				91
3m	19.3				17.8	24.2	19.2				40
3n	18.8				17.6	23.9	18.9				28
3o	24.5				17.9	23.5	18.5				87
3p	24.0				18.1	23.9	18.6				38
3q	23.6				18.4	23.9	18.5				24
3r	28.9				18.5	24.3	18.9				78
3s	23.2				18.4	24.1	19.4				31
3t	21.4				18.6	24.2	19.5				23
3u	28.8				18.2	23.4	19.1				65
3v	22.5				17.9	22.9	19.3				21
3z	21.6				18.1	22.8	18.7				14

[a] 10-ml solution of 10 mM of PFE-*m*,*n*.
[b] 200 mM solutions of PFE-*m*,*n*; the reference value of surface tensions for the solvents were the following: $\gamma_{hex} = 18.4\,mN\,m^{-1}$, $\gamma_{dod} = 25.4\,mN\,m^{-1}$; $\gamma_{perfdec} = 19.4\,mN\,m^{-1}$.
[c] Composition of mixtures tested: 10 ml of solvent per gram of PFE-*m*,*n*, cooling rate 2 °C/min.
[d] the values refers to the percentages of PFE-*m*,*n* in RS-OIL 5000 at which the onset of turbidity (@ 25 °C) is observed; n.f.o.: no foam observed; n.g.o.: no gel observed.

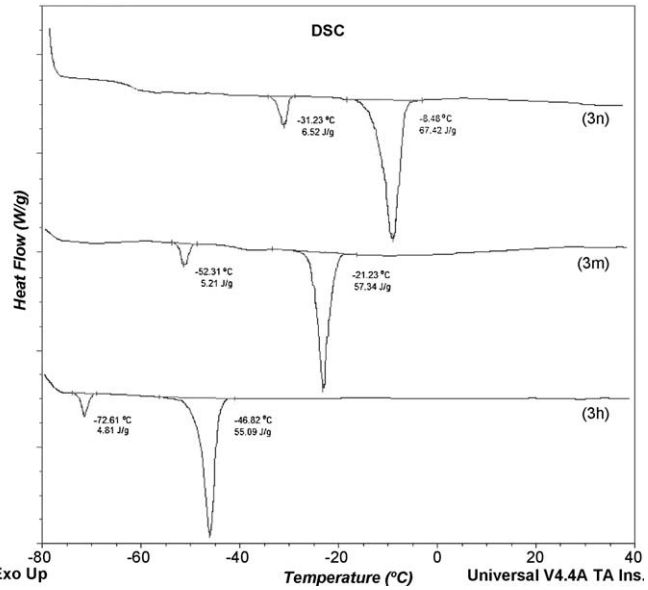


Fig. 1. DSC thermograms of PFE-*6,5* (**3h**), PFE-*6,8* (**3m**) and PFE-*8,8* (**3n**).

Similarly to semifluorinated *n*-alkanes FH-*m*,*n*, the endothermic effects observed in PFE-*m*,*n* could be attributed to transitions between highly organized solid phases. Thermograms for compounds **3l**, **3n**–**3z** did not show any secondary endothermic peak probably indicating that for values of the ratio *m*/*n* different to one or nearly one a disordering effect is introduced and the molecular symmetry is lost. This behavior is in good agreement with that of semifluorinated *n*-alkanes FH-*m*,*n* [24] indicating a little effect of the ethereal linkage on structural organization in solid state.

Semifluorinated *n*-alkanes FH-*m*,*n* have marked surface activity in organic solvents. They are able to stabilize perfluorocarbon emulsions [25] producing both micelles in hydrocarbons [26] and reversed micelles in fluorocarbons [27] at very low concentrations. In addition, they form gel phases in binary mixtures with hydrocarbon liquids. In order to compare the properties of PFE-*m*,*n* with FH-*m*,*n* the surface active properties of PFE-*m*,*n* were assessed by the following tests: (1) foaming tendency in different organic solvents [28,29]; (2) maximum surface tension reduction in different organic solvents regardless of the concentration of the PFE-*m*,*n* (defined as *surfactant effectiveness*); (3) characterizing micelles in *n*-dodecane via dynamic light scattering and detecting gel-phase formation in binary mixtures with hydrocarbons.

10-ml of a 10 mM solution of PFE-*m*,*n* in organic solvent was shaken for 10 s and set to the bench. If any foam was noted the sample was considered foaming and marked with a F and the time for the breakdown of the foam was recorded. Non-foaming PFE-*m*,*n* solutions were marked with a n.f.o. All PFE-*m*,*n* have only limited surface activity being completely soluble and showing no foaming ability in the organic solvents tested, as reported in Table 2. Tensiometric measurements showed the inability of PFE-*m*,*n* to lower significantly the surface tension even up to 200 mM concentration (Table 2). It is noteworthy that an increase in *n* has virtually no effect on surface tension reduction of solutions. PFE-*8,3* lowers the surface tension of *n*-dodecane from 25.4 mN m^{-1} down to 23.1 mN m^{-1}; PFE-*8,21* performs similarly lowering the surface tension to 22.8 mN m^{-1}. The increase in *m* from 4 to 8 results in a mild surface tension reduction: while PFE-*4,3* virtually does not affect the surface tension of *n*-dodecane, PFE-*8,3* reduces it from 26.5 down to 23.1 mN m^{-1}.

In order to measure critical micelle concentration, dynamic light scattering tests were performed on *n*-dodecane solutions with progressively higher concentration of PFEs. Dynamic light scattering showed that these compounds are completely unable to form micelles even at concentrations higher than 200 mM, regardless of the fluorocarbon–hydrocarbon ratio (*m*/*n*).

Table 3
Comparison between the solubility in silicon oil of PFE-*m*,*n* and FH-*m*,*n* having the same values for *m* and *n*.

Compound	Symbol	*m*	*n*	Silicon oil solubility[a] (wt/wt) %
3g	PFE-*4,5*	4	5	93
3h	PFE-*6,5*	6	5	43
3i	PFE-*8,5*	8	5	31
3l	PFE-*4,8*	4	8	91
3m	PFE-*6,8*	6	8	40
3n	PFE-*8,8*	8	8	28
–	HF-*4,5*	4	5	41
–	HF-*6,5*	6	5	28
–	HF-*8,5*	8	5	16
–	HF-*4,8*	4	8	51
–	HF-*6,8*	6	8	28
–	HF-*8,8*	8	8	15

[a] The values refers to the percentages of PFE-*m*,*n* in RS-OIL 5000 at which the onset of turbidity a (@ 25 °C) is observed.

As reported by Twieg et al. [30] heating a mixture of a semifluorinated *n*-alkane FH-*m*,*n* in hydrocarbon solvents above its melting point and allowing it to cool a gel phase forms. The temperature T_c at which the gel phase begins to form (gel point) strongly depends on the molecular structure of FH-*m*,*n*, and on process variables such as concentration and the heating/cooling rate [31]. In order to investigate whether PFE-*m*,*n* **3o**–**3z**, which are solids at room temeprature, have the ability to form gel phases, gel point tests were performed by cooling mixtures of PFE-*m*,*n* in different organic solvents at a fixed concentration (10 ml of solvent per gram of PFE-*m*,*n*). The temperature of the mixture was measured and plotted as a function of time. If gelation occurred the temperature of the mixture was expected to remain nearly constant for a period [32]. As reported in Table 2, under the conditions examined, mixtures of PFE-*m*,*n* **3o**–**3z** in non-polar, polar and fluorinated organic solvents are isotropic solutions failing to exhibit any transition to gel-like phases.

The *m*/*n* ratio plays an important role in determining the refractive index (n_D^{20}) and the solubility of PFE-*m*,*n* in silicone oils such as RS-OIL 5000 (with a kinematic viscosity of 5000 cS). Data reported in Tables 1 and 2 show that an increase in *n* implies an increase of the refractive index and the solubility in silicone oil while *m* has the opposite effect. Table 3 shows a comparison between the solubility of FH-*m*,*n* and PFE-*m*,*n* in silicone OIL RS 5000. This comparison points out that PFE-*m*,*n* have a solubility in silicon oils from 30% to 56% higher than that of FH-*m*,*n* with the same ratio *m*/*n*. The introduction of a flexible ethereal bond between the rigid fluorinated moiety and the hydrocarbon chain probably increases the molecule's solubility leading to a higher affinity for silicon based solvents.

3. Conclusion

The availability of a simple and efficient procedure to synthesize PFE-*m*,*n* with varying the hydrocarbon-fluorocarbon ratio *m*/*n* enabled to control important physical parameters such as solubility in organic solvents, in particular silicone oils, refractive index (n_D^{20}) and density.

PFE-*m*,*n* synthesized in the present work show virtually no surface activity in solution with common organic solvents unlike semifluorinated *n*-alkanes FH-*m*,*n*. Further, they do not yield to

micellar aggregates or gel-like structures. Compounds **3h**, **3m** and **3n** having a hydrocarbon–fluorocarbon ratio of nearly 1 show a solid–solid transition below the melting point revealing a thermotropic behavior similarly to FH-*m*,*n*. The lengthening of the hydrocarbon chain induces the disappearance of this solid–solid transition. This is probably due to a progressive loss of molecular symmetry which appears to be a prerequisite for the formation of supramolecular aggregates.

Thanks to their physico-chemical properties PFE-*m*,*n* have been recentely tested as long-term postoperative tamponade agents to aid retinal reattachement after surgery to repair retinal tears or detachements. The high solubility of PFE-*m*,*n* in silicone oils and their refractive indexes similar to those of silicone oils enable the design of soluble mixtures that can be used as long-term postoperative tamponade agents having specific gravity of 1.12–1.58 such that the probability of retinal damage due to weight is reduced. In addition the low surface tension of PFE-*m*,*n* helps the uniform wetting of retina allowing its complete relaxation and proper positioning.

4. Experimental

4.1. General experimental procedures

1H,1H,2H,2H-perfluoro-*1*-hexanol, 1H,1H,2H,2H-perfluoro-*1*-octanol and 1H,1H,2H,2H-perfluoro-*1*-decanol were commercial grade reagents supplied by Elf Atochem S.A.; 1-bromoethane, 1-bromopropane, 1-bromopentane, 1-bromohexane, 1-bromooctane, 1-bromotetradecane, 1-bromoocatdecane, 1-bromodocosane were purchased from Aldrich Chemical Co. Silicone oil with a kinematic viscosity of 5000 cS (OIL-RES 5000) was purchased from AL.CHI.M.I.A. S.R.L. Other reagents employed were common laboratory materials. All the chemical reagents were used as received. GLC analyses of the reaction mixtures were performed using a Carlo Erba GC6000 Vega Serie 2 instrument (15 m × 0.25 mm silica fused capillary column, PS264 stationary phase). Typical operative conditions were: temperature program 60 °C, 15 °C min^{-1} to 250 °C; He gas carrier 1 mL min^{-1}. GC/MS spectra were measured on a Carlo Erba Instrument MFC 500/QMD1000 using a silica fused capillary PS264 column (30 m × 0.25 mm) on a Finnigan Mat TSQ7000 (capillary column 30 m × 0.32 mm). Typical conditions were: temperature program 60 °C for 2 min, 10 °C min^{-1} to 280 °C; He as gas carrier 1 mL min^{-1}). Mass spectra of the solids were obtained on a AUTOSPEC Macromass Manchester (UK) double focusing instrument operating in electron impact (EI) mode (70 eV, 200 μA). FTIR spectra were measured using a Nicolet Avatar 330 FTIR spectrophotometer. Scan band width: 4000–400 cm^{-1}.^{1}H and ^{19}F NMR spectra were recorded on a Bruker 200 AC spectrometer operating at 200.13 and 50.32 MHz, respectively. Peak positions are relative to Me_4Si and were calibrated against the residual solvent resonance (^{1}H). ^{19}F NMR measurements were recorded on a Varian FT 80 spectrometer operating at 74.844 MHz. Peak positions are reported relative to $CFCl_3$.

Indexes identifying the various carbon atoms are assigned as follows:

$CF_3(a)CF_2(b)CF_2(c)CF_2(d)CF_2(e)CF_2(f)CF_2(g)CF_2(h)$
$CH_2(y)CH_2(x)OCH_2(\zeta)CH_2()CH_2(\chi/\upsilon)CH_2(\beta)CH_3(\alpha)$

Differential scanning calorimetry (DSC) was performed using a TA Instrument model DSC 2920 operating with sealed stainless steel caps. Measurements were carried out in the range −80/80 °C and at a heating rate of 10 °C min^{-1}. Elemental analyses were performed with a CHNS Fisons instrument, mod. EA 1108. Surface free energy for liquids was determined using a Kruss Tensiometer K8 equipped with a DuNoy platinum ring. Surface free energy for solids was determined using a Kruss G10/DSA10 goniometer interfaced to image-capture software. Measurements were made using de-ionized water and diiodomethane as testing liquids and with drops having an average volume of 10–15 μl. Dynamic light scattering experiments were performed preparing PFE-*m*,*n* solutions in *n*-dodecane at different concentrations from 5 up to 210 mM and injecting them through a 0.45-μm PTFE filter. Light scattering experiments were performed on a 90 Plus particle size analyzer at 25 °C with a laser wavelenght of 635 nm. High molecular weight reaction products were separated and purified by flash chromatography. Separations were performed with a VersaFlash® HTPF system equipped with Versapak® silica cartridges purchased from SUPELCO. Silica cartridges caracteristics: inner diameter: 40 mm–length: 75 mm–silica weight: 51 g; mobile phase: dichloromethane (5%)–hexane (95%). The mobile phase was fed at the top of the column with a flow rate of 15 mL min^{-1} by means of a VersaFash volumetric piston pump with variable speed.

4.2. General procedures

4.2.1. Preparation of partially fluorinated ethers PFE-m,n: general procedure

A mixture comprising 100 mmol of 1H,1H,2H,2,-perfluoroalkanol $F(CF_2)_mCH_2CH_2OH$ (*m* = 4, 6, 8), 60 ml of N-methyl-2-pyrrolidone, 200 mmol of 1-bromoalkane $Br(CH_2)_nH$ (*n* = 2, 3, 5, 8, 14, 21) and 60 ml of a 45% aqueous solution of potassium hydroxide was heated under stirring for 5 h at 50 °C, then at 70 °C for 2 h so as to complete the reaction. The raw reaction mixture was filtered and then diluted in 20 ml of water. Compounds **3a**–**3n** were recovered by distillation under reduced pressure. Compounds **3m**–**3z** were purified via flash cromatography. Reaction yields are reported in Table 1.

*4.2.1.1. 1,1,1,2,2,3,3,4,4-Nonafluoro-7-oxanonane, PFE-4,2 (**3a**).* Colourless liquid; spectral data: MS *m*/*z* (rel. ab. %): 292 ($[M]^+$, 10%); 277 ($[M-CH_3]^+$, 30%), 263 ($[M-CH_3CH_2]^+$, 5%), 73 ($[M-CF_3(CF_2)_3]^+$, 10%), 59 ($[M-CF_3(CF_2)_3$, $-CH_2]^+$, 100%), 29 ($[M-CF_3(CF_2)_3CH_2CH_2O]^+$, 100%); FTIR: ν_{C-F} 1122–1321 cm^{-1}, ν_{C-H} 2851–2923 cm^{-1}. ^{1}H NMR: δ = 0.90 (t, $CH_3(\alpha)$, 3H); 3.35 (t, $CH_2(\beta)$, 2H); 3.73 (t, CH_2(x), 2H); 2.49 (ttt, CH_2(y), 2H); ^{19}F NMR: δ = −84.2 (t, CF_3(a), 3F); −128.9 (m, CF_2(b), 2F); −127.3 (m, CF_2(c), 2F); −116.2 (m, CF_2(d), 2F). Anal. calcd for $C_8H_9F_9O$: C, 32.9%; F, 58.6%; H, 3.1%. Found: C, 32.1%; F, 58.1%; H, 2.9%.

*4.2.1.2. 1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-9-oxaundecane, (PFE-6,2), (**3b**).* Colourless liquid; spectral data: MS *m*/*z* (rel. ab. %): 392 ($[M]^+$, 5%); 277 ($[M-CH_3]^+$, 30%), 363 ($[M-CH_3CH_2]^+$, 5%), 73 ($[M-CF_3(CF_2)_5]^+$, 5%), 59 ($[M-CF_3(CF_2)_5$, $-CH_2]^+$, 100%), 29 ($[M-CF_3(CF_2)_5CH_2CH_2O]^+$, 100%); FTIR: ν_{C-F} 1120–1325 cm^{-1}, ν_{C-H} 2860–2900 cm^{-1}. ^{1}H NMR: δ = 0.90 (t, $CH_3(\alpha)$, 3H); 3.36 (t, $CH_2(\beta)$, 2H); 3.74 (t, CH_2(x), 2H); 2.50 (ttt, CH_2(y), 2H); ^{19}F NMR: δ = −83.9 (t, CF_3(a), 3F); −129.1 (m, CF_2(b), 2F); −126.3 (m, CF_2(c), 2F); −125.6 (m, CF_2(d), 2F); −124.6 (m, CF_2(e), 2F); −116.0 (m, CF_2(f), 2F). Anal. calcd for $C_{10}H_9F_{13}O$: C, 30.6%; F, 63.0%; H, 2.3%. Found: C, 30.9%; F, 62.6%; H, 2.1%.

*4.2.1.3. 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluoro-11-oxatridecane, (PFE-8,2), (**3c**).* Colourless liquid; spectral data: MS *m*/*z* (rel. ab. %): 492 ($[M]^+$, 5%); 377 ($[M-CH_3]^+$, 20%), 463 ($[M-CH_3CH_2]^+$, 10%), 73 ($[M-CF_3(CF_2)_7]^+$, 10%), 59 ($[M-CF_3(CF_2)_7$, $-CH_2]^+$, 100%), 29 ($[M-CF_3(CF_2)_8CH_2CH_2O]^+$, 100%); FTIR: ν_{C-F} 1125–1320 cm^{-1}, ν_{C-H} 2870–2910 cm^{-1}. ^{1}H NMR: δ = 0.90 (t, $CH_3(\alpha)$, 3H); 3.38 (t, $CH_2(\beta)$, 2H); 3.73 (t, CH_2(x), 2H); 2.48 (ttt, CH_2(y), 2H); ^{19}F NMR: δ = −83.6 (t, CF_3(a), 3F); −128.5 (m, CF_2(b), 2F); −126.4 (m, CF_2(c), 2F); −125.4 (m, CF_2(d), 2F); −124.6 (m, CF_2(e), 2F); −123.1 (m,

CF_2(f), 2F); −122.5 (m, CF_2(g), 2F); −115.4 (m, CF_2(h), 2F). Anal. calcd for $C_{12}H_9F_{17}O$: C, 29.3%; F, 65.6%; H, 1.8%. Found: C, 29.8%; F, 66.4%; H, 1.9%.

*4.2.1.4. 1,1,1,2,2,3,3,4,4-Nonafluoro-7-oxadecane, (PFE-4,3), (**3d**).* Colourless liquid; spectral data: MS *m/z* (rel. ab. %): 306 ($[M]^+$, 10%), 291 ($[M-CH_3]^+$, 30%), 277 ($[M-CH_2CH_3]^+$, 30%), 263 ($[M-CH_3CH_2CH_2]^+$, 10%), 87 ($[M-CF_3(CF_2)_3]^+$, 5%), 73 ([$M-CF_3(CF_2)_3$, $-CH_2]^+$, 90%), 43 ($[M-CF_3(CF_2)_3CH_2CH_2O]^+$, 100%); FTIR: ν_{C-F} 1118–1305 cm^{-1}, ν_{C-H} 2880–2930 cm^{-1}. ^1H NMR: δ = 0.90 (t, $CH_3(\alpha)$, 3H); 1.56 (t, $CH_2(\beta)$, 2H); 3.41 (t, $CH_2(\chi)$, 2H); 3.73 (t, CH_2(x), 2H); 2.49 (ttt, CH_2(y), 2H); ^{19}F NMR: δ = −84.2 (t, CF_3(a), 3F); −128.8 (m, CF_2(b), 2F); −127.4 (m, CF_2(c), 2F); −116.1 (m, CF_2(d), 2F). Anal. calcd for $C_9H_{11}F_9O$: C, 35.3%; F, 55.6%; H, 3.6%. Found: C, 35.9%; F, 55.0%; H, 3.3%.

*4.2.1.5. 1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-9-oxadodecane, (PFE-6,3), (**3e**).* Colourless liquid; spectral data: MS *m/z* (rel. ab. %): 406 ($[M]^+$, 5%), 391 ($[M-CH_3]^+$, 25%), 377 ($[M-CH_2CH_3]^+$, 20%), 363 ($[M-CH_3CH_2CH_2]^+$, 15%), 87 ($[M-CF_3(CF_2)_5]^+$, 10%), 73 ([$M-CF_3(CF_2)_5$, $-CH_2]^+$, 100%), 43 ($[M-CF_3(CF_2)_5CH_2CH_2O]^+$, 100%); FTIR: ν_{C-F} 1125–1310 cm^{-1}, ν_{C-H} 2890–2910 cm^{-1}. ^1H NMR: δ = 0.90 (t, $CH_3(\alpha)$, 3H); 1.55 (t, $CH_2(\beta)$, 2H); 3.42 (t, $CH_2(\chi)$, 2H); 3.74 (t, CH_2(x), 2H); 2.50 (ttt, CH_2(y), 2H); ^{19}F NMR: δ = −83.9 (t, CF_3(a), 3F); −129.1 (m, CF_2(b), 2F); −126.3 (m, CF_2(c), 2F); −125.6 (m, CF_2(d), 2F); −124.6 (m, CF_2(e), 2F); −116.0 (m, CF_2(f), 2F). Anal. calcd for $C_{11}H_{11}F_{13}O$: C, 32.5%; F, 60.8%; H, 2.7%. Found: C, 31.9%; F, 61.2%; H, 2.5%.

*4.2.1.6. 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluoro-11-oxatetradecane, (PFE-8,3), (**3f**).* Colourless liquid; spectral data: MS *m/z* (rel. ab. %): 506 ($[M]^+$, 5%); 491 ($[M-CH_3]^+$, 20%), 377 ($[M-CH_3CH_2]^+$, 15%), 463 ($[M-CH_3CH_2CH_2]^+$, 10%), 87 ($[M-CF_3(CF_2)_7]^+$, 10%), 73 ($[M-CF_3(CF_2)_7$, $-CH_2]^+$, 100%), 43 ($[M-CF_3(CF_2)_8CH_2CH_2O]^+$, 100%); FTIR: ν_{C-F} 1120–1320 cm^{-1}, ν_{C-H} 2890–2920 cm^{-1}. ^1H NMR: δ = 0.90 (t, $CH_3(\alpha)$, 3H); 1.54 (t, $CH_2(\beta)$, 2H); 3.41 (t, $CH_2(\chi)$, 2H); 3.73 (t, CH_2(x), 2H); 2.51 (ttt, CH_2(y), 2H); ^{19}F NMR: δ = −83.7 (t, CF_3(a), 3F); −128.4 (m, CF_2(b), 2F); −126.2 (m, CF_2(c), 2F); −125.6 (m, CF_2(d), 2F); −124.8 (m, CF_2(e), 2F); −123.3 (m, CF_2(f), 2F); −122.7 (m, CF_2(g), 2F); −115.2 (m, CF_2(h), 2F). Anal. calcd for $C_{13}H_{11}F_{17}O$: C, 30.8%; F, 63.8%; H, 2.2%. Found: C, 30.2%; F, 63.4%; H, 2.3%.

*4.2.1.7. 1,1,1,2,2,3,3,4,4-Nonafluoro-7-oxadodecane, (PFE-4,5), (**3g**).* Colourless liquid; spectral data: MS *m/z* (rel. ab. %): 334 ($[M]^+$, 10%), 319 ($[M-CH_3]^+$, 20%), 305 ($[M-CH_2CH_3]^+$, 20%), 291 ($[M-CH_3CH_2CH_2]^+$, 10%), 277 ($[M-CH_3CH_2CH_2CH_2]^+$, 10%); 115 ($[M-CF_3(CF_2)_3]^+$, 5%), 101 ([$M-CF_3(CF_2)_3$, $-CH_2]^+$, 70%), 71 ($[M-CF_3(CF_2)_3CH_2CH_2O]^+$, 100%); FTIR: ν_{C-F} 1110–1290 cm^{-1}, ν_{C-H} 2870–2920 cm^{-1}. ^1H NMR: δ = 0.89 (t, $CH_3(\alpha)$, 3H); 1.32 (m, $CH_2(\beta)$–$CH_2(\chi)$, 4H); 1.56 (m, $CH_2(\delta)$, 2H); 3.45 (t, $CH_2(\varepsilon)$, 2H); 3.73 (t, CH_2(x), 2H); 2.49 (ttt, CH_2(y), 2H); ^{19}F NMR: δ = −84.2 (t, CF_3(a), 3F); -128.9 (m, CF_2(b), 2F); −127.4 (m, CF_2(c), 2F); −116.3 (m, CF_2(d), 2F). Anal. calcd for $C_{11}H_{15}F_9O$: C, 39.5%; F, 51.2%; H, 4.5%. Found: C, 39.2%; F, 50.5%; H, 4.2%.

*4.2.1.8. 1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-9-oxatetradecane, (PFE-6,5), (**3h**).* Colourless liquid; spectral data: MS *m/z* (rel. ab. %): 434 ($[M]^+$, 5%), 419 ($[M-CH_3]^+$, 15%), 405 ($[M-CH_2CH_3]^+$, 10%), 391 ($[M-CH_3CH_2CH_2]^+$, 10%), 377 ($[M-CH_3CH_2CH_2CH_2]^+$, 10%); 115 ($[M-CF_3(CF_2)_5]^+$, 10%), 101 ([$M-CF_3(CF_2)_5$, $-CH_2]^+$, 50%), 71 ($[M-CF_3(CF_2)_5CH_2CH_2O]^+$, 100%); FTIR: ν_{C-F} 1125–1310 cm^{-1}, ν_{C-H} 2810–2930 cm^{-1}. ^1H NMR: δ = 0.88 (t, $CH_3(\alpha)$, 3H); 1.33 (m, $CH_2(\beta)$–$CH_2(\chi)$, 4H); 1.56 (m, $CH_2(\delta)$, 2H); 3.45 (t, $CH_2(\varepsilon)$, 2H); 3.73 (t, CH_2(x), 2H); 2.49 (ttt, CH_2(y), 2H); ^{19}F NMR: δ = −83.8 (t, CF_3(a), 3F); −129.2 (m, CF_2(b), 2F); −126.2 (m, CF_2(c), 2F); −125.7 (m, CF_2(d), 2F); −124.5 (m, CF_2(e), 2F); −116.1 (m, CF_2(f), 2F). Anal. calcd for $C_{13}H_{15}F_{13}O$: C, 36.0%; F, 57.0%; H, 3.4%. Found: C, 35.5%; F, 56.4%; H, 3.8%.

*4.2.1.9. 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluoro-11-oxahexdecane, (PFE-8,5), (**3i**).* Colourless liquid; spectral data: MS *m/z* (rel. ab. %): 534 ($[M]^+$, 10%), 519 ($[M-CH_3]^+$, 15%), 505 ($[M-CH_2CH_3]^+$, 20%), 491 ($[M-CH_3CH_2CH_2]^+$, 10%), 477 ($[M-CH_3CH_2CH_2CH_2]^+$, 10%); 115 ($[M-CF_3(CF_2)_7]^+$, 5%), 101 ([$M-CF_3(CF_2)_7$, $-CH_2]^+$, 70%), 71 ($[M-CF_3(CF_2)_7CH_2CH_2O]^+$, 100%); FTIR: ν_{C-F} 1120–1300 cm^{-1}, ν_{C-H} 2810–2930 cm^{-1}. ^1H NMR: δ = 0.88 (t, $CH_3(\alpha)$, 3H); 1.33 (m, $CH_2(\beta)$–$CH_2(\chi)$, 4H); 1.56 (m, $CH_2(\delta)$, 2H); 3.45 (t, $CH_2(\varepsilon)$, 2H); 3.73 (t, CH_2(x), 2H); 2.49 (ttt, CH_2(y), 2H); ^{19}F NMR: δ = −83.5 (t, CF_3(a), 3F); −128.2 (m, CF_2(b), 2F); −126.5 (m, CF_2(c), 2F); −125.2 (m, CF_2(d), 2F); −124.6 (m, CF_2(e), 2F); −123.1 (m, CF_2(f), 2F); −122.3 (m, CF_2(g), 2F); −115.1 (m, CF_2(h), 2F). Anal. calcd for $C_{15}H_{15}F_{17}O$: C, 33.7%; F, 60.5%; H, 2.8%. Found: C, 33.1%; F, 60.9%; H, 2.3%.

*4.2.1.10. 1,1,1,2,2,3,3,4,4-Nonafluoro-7-oxapentadecane, (PFE-4,8), (**3l**).* Colourless liquid; spectral data: MS *m/z* (rel. ab. %): 397 ($[M]^+$, 5%), 382 ($[M-CH_3]^+$, 15%), 368 ($[M-CH_2CH_3]^+$, 15%), 353 ($[M-CH_3CH_2CH_2]^+$, 5%), 339 ($[M-CH_3CH_2CH_2CH_2]^+$, 5%); 178 ($[M-CF_3(CF_2)_3]^+$, 10%), 164 ([$M-CF_3(CF_2)_3$, $-CH_2]^+$, 80%), 134 ($[M-CF_3(CF_2)_3CH_2CH_2O]^+$, 100%); FTIR: ν_{C-F} 1100–1260 cm^{-1}, ν_{C-H} 2850–2910 cm^{-1}. ^1H NMR: δ = 0.88 (t, $CH_3(\alpha)$, 3H); 1.33 (m, $CH_2(\beta)$–$CH_2(\phi)$, 8H); 1.58 (m, $CH_2(\gamma)$, 2H); 3.43 (t, $CH_2(\eta)$, 2H); 3.73 (t, CH_2(x), 2H); 2.49 (ttt, CH_2(y), 2H); ^{19}F NMR: δ = −84.1 (t, CF_3(a), 3F); −128.8 (m, CF_2(b), 2F); −127.5 (m, CF_2(c), 2F); −116.1 (m, CF_2(d), 2F). Anal. calcd for $C_{14}H_{21}F_9O$: C, 42.3%; F, 43.1%; H, 5.2%. Found: C, 41.8%; F, 42.1%; H, 5.5%.

*4.2.1.11. 1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-9-oxaheptadecane, (PFE-6,8), (**3m**).* Colourless liquid; spectral data: MS *m/z* (rel. ab. %): 497 ($[M]^+$, 5%), 482 ($[M-CH_3]^+$, 10%), 468 ($[M-CH_2CH_3]^+$, 20%), 453 ($[M-CH_3CH_2CH_2]^+$, 10%), 439 ($[M-CH_3CH_2CH_2CH_2]^+$, 10%); 178 ($[M-CF_3(CF_2)_5]^+$, 15%), 164 ([$M-CF_3(CF_2)_5$, $-CH_2]^+$, 70%), 134 ($[M-CF_3(CF_2)_5CH_2CH_2O]^+$, 100%); FTIR: ν_{C-F} 1120–1280 cm^{-1}, ν_{C-H} 2810–2920 cm^{-1}. ^1H NMR: δ = 0.89 (t, $CH_3(\alpha)$, 3H); 1.35 (m, $CH_2(\beta)$–$CH_2(\phi)$, 8H); 1.57 (m, $CH_2(\gamma)$, 2H); 3.42 (t, $CH_2(\eta)$, 2H); 3.74 (t, CH_2(x), 2H); 2.50 (ttt, CH_2(y), 2H); ^{19}F NMR: δ = −83.7 (t, CF_3(a), 3F); −129.3 (m, CF_2(b), 2F); −126.3 (m, CF_2(c), 2F); −125.9 (m, CF_2(d), 2F); −124.7 (m, CF_2(e), 2F); −116.2 (m, CF_2(f), 2F). Anal. calcd for $C_{16}H_{21}F_{13}O$: C, 38.6%; F, 34.4%; H, 4.2%. Found: C, 38.1%; F, 33.2%; H, 3.9%.

*4.2.1.12. 1,1,1,2,2,3,3,4,4,5,5,6,6,8,8-Heptadecafluoro-11-oxanonadecane, (PFE-8,8), (**3n**).* Colourless viscous liquid; spectral data: MS *m/z* (rel. ab. %): 597 ($[M]^+$, 10%), 582 ($[M-CH_3]^+$, 5%), 568 ($[M-CH_2CH_3]^+$, 10%), 553 ($[M-CH_3CH_2CH_2]^+$, 15%), 539 ($[M-CH_3CH_2CH_2CH_2]^+$, 5%); 178 ($[M-CF_3(CF_2)_7]^+$, 10%), 164 ([$M-CF_3(CF_2)_7$, $-CH_2]^+$, 90%), 134 ($[M-CF_3(CF_2)_7CH_2CH_2O]^+$, 100%); FTIR: ν_{C-F} 1110–1290 cm^{-1}, ν_{C-H} 2800–2900 cm^{-1}. ^1H NMR: δ = 0.88 (t, $CH_3(\alpha)$, 3H); 1.36 (m, $CH_2(\beta)$–$CH_2(\phi)$, 8H); 1.56 (m, $CH_2(\gamma)$, 2H); 3.45 (t, $CH_2(\eta)$, 2H); 3.75 (t, CH_2(x), 2H); 2.51 (ttt, CH_2(y), 2H); ^{19}F NMR: δ = −83.3 (t, CF_3(a), 3F); −128.1 (m, CF_2(b), 2F); −126.4 (m, CF_2(c), 2F); −125.3 (m, CF_2(d), 2F); −124.8 (m, CF_2(e), 2F); −123.0 (m, CF_2(f), 2F); −122.5 (m, CF_2(g), 2F); −115.0 (m, CF_2(h), 2F). Anal. calcd for $C_{18}H_{21}F_{17}O$: C, 36.2%; F, 28.6%; H, 3.5%. Found: C, 36.9%; F, 29.2%; H, 3.8%.

*4.2.1.13. 1,1,1,2,2,3,3,4,4-Nonafluoro-7-oxaheneicosane, (PFE-4,14), (**3o**).* White solid; spectral data: MS *m/z* (rel. ab. %): 536 ($[M]^+$, 10%), 521 ($[M-CH_3]^+$, 10%), 507 ($[M-CH_2CH_3]^+$, 15%), 493 ($[M-CH_3CH_2CH_2]^+$, 10%), 479 ($[M-CH_3CH_2CH_2CH_2]^+$, 10%); 317 ($[M-CF_3(CF_2)_3]^+$, 15%), 303 ([$M-CF_3(CF_2)_3$, $-CH_2]^+$, 100%), 273 ([M–

$CF_3(CF_2)_3CH_2CH_2O]^+$, 100%); FTIR: ν_{C-F} 1105–1270 cm^{-1}, ν_{C-H} 2840–2920 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.89 (t, $CH_3(\alpha)$, 3H); 1.30 (m, $CH_2(\beta)$–$CH_2(\nu)$, 22H); 1.55 (m, $CH_2(o)$, 2H); 3.41 (t, $CH_2(\pi)$, 2H); 3.72 (t, $CH_2(x)$, 2H); 2.50 (ttt, $CH_2(y)$, 2H); ^{19}F NMR ($CDCl_3$): δ = −84.2 (t, $CF_3(a)$, 3F); −128.9 (m, $CF_2(b)$, 2F); −127.1 (m, $CF_2(c)$, 2F); −116.8 (m, $CF_2(d)$, 2F). Anal. calcd for $C_{20}H_{33}F_9O$: C, 44.8%; F, 32.0%; H, 6.1%. Found: C, 44.2%; F, 31.5%; H, 5.9%.

*4.2.1.14. 1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-9-oxatricosane, (PFE-6,14), (**3p**).* White solid; spectral data: MS *m*/*z* (rel. ab. %): 636 ($[M]^+$, 5%), 621 ($[M-CH_3]^+$, 15%), 607 ($[M-CH_2CH_3]^+$, 15%), 593 ($[M-CH_3CH_2CH_2]^+$, 5%), 579 ($[M-CH_3CH_2CH_2CH_2]^+$, 15%); 317 ($[M-CF_3(CF_2)_5]^+$, 10%), 303 ($[M-CF_3(CF_2)_5, -CH_2]^+$, 100%), 273 ($[M-CF_3(CF_2)_5CH_2CH_2O]^+$, 100%); FTIR: ν_{C-F} 1100–1250 cm^{-1}, ν_{C-H} 2830–2930 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.90 (t, $CH_3(\alpha)$, 3H); 1.31 (m, $CH_2(\beta)$–$CH_2(\nu)$, 22H); 1.54 (m, $CH_2(o)$, 2H); 3.41 (t, $CH_2(\pi)$, 2H); 3.72 (t, $CH_2(x)$, 2H); 2.49 (ttt, $CH_2(y)$, 2H; ^{19}F NMR: δ = −83.5 (t, $CF_3(a)$, 3F); −129.1 (m, $CF_2(b)$, 2F); −126.4 (m, $CF_2(c)$, 2F); −125.8 (m, $CF_2(d)$, 2F); −124.5 (m, $CF_2(e)$, 2F); −116.3 (m, $CF_2(f)$, 2F). Anal. calcd for $C_{22}H_{33}F_{13}O$: C, 41.5%; F, 38.8%; H, 5.2%. Found: C, 40.8%; F, 38.1%; H, 5.4%.

*4.2.1.15. 1,1,1,2,2,3,3,4,4,5,5,6,6,8,8-Heptadecafluoro-11-oxapentacosane, (PFE-8,14), (**3q**).* White solid; spectral data: MS *m*/*z* (rel. ab. %): 736 ($[M]^+$, 5%), 721 ($[M-CH_3]^+$, 15%), 707 ($[M-CH_2CH_3]^+$, 10%), 693 ($[M-CH_3CH_2CH_2]^+$, 10%), 679 ($[M-CH_3CH_2CH_2CH_2]^+$, 10%); 317 ($[M-CF_3(CF_2)_7]^+$, 5%), 303 ($[M-CF_3(CF_2)_7, -CH_2]^+$, 100%), 273 ($[M-CF_3(CF_2)_7CH_2CH_2O]^+$, 90%); FTIR: ν_{C-F} 1150–1270 cm^{-1}, ν_{C-H} 2880–2910 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.88 (t, $CH_3(\alpha)$, 3H); 1.32 (m, $CH_2(\beta)$–$CH_2(\nu)$, 22H); 1.55 (m, $CH_2(o)$, 2H); 3.42 (t, $CH_2(\pi)$, 2H); 3.71 (t, $CH_2(x)$, 2H); 2.50 (ttt, $CH_2(y)$, 2H; ^{19}F NMR: δ = −83.2 (t, $CF_3(a)$, 3F); −128.4 (m, $CF_2(b)$, 2F); −126.1 (m, $CF_2(c)$, 2F); −125.6 (m, $CF_2(d)$, 2F); −124.3 (m, $CF_2(e)$, 2F); −123.5 (m, $CF_2(f)$, 2F); −122.1 (m, $CF_2(g)$, 2F); −115.5 (m, $CF_2(h)$, 2F). Anal. calcd for $C_{24}H_{33}F_{17}O$: C, 39.1%; F, 43.9%; H, 4.5%. Found: C, 38.5%; F, 42.9%; H, 4.2%.

*4.2.1.16. 1,1,1,2,2,3,3,4,4-Nonafluoro-7-oxapentacosane, (PFE-4,18), (**3r**).* White solid; spectral data: MS *m*/*z* (rel. ab. %): 516 ($[M]^+$, 10%), 501 ($[M-CH_3]^+$, 15%), 487 ($[M-CH_2CH_3]^+$, 10%), 473 ($[M-CH_3CH_2CH_2]^+$, 5%), 459 ($[M-CH_3CH_2CH_2CH_2]^+$, 5%); 297 ($[M-CF_3(CF_2)_3]^+$, 10%), 383 ($[M-CF_3(CF_2)_3, -CH_2]^+$, 100%), 253 ($[M-CF_3(CF_2)_3CH_2CH_2O]^+$, 90%); FTIR: ν_{C-F} 1100–1260 cm^{-1}, ν_{C-H} 2850–2910 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.88 (t, $CH_3(\alpha)$, 3H); 1.28 (m, $CH_2(\beta)$–$CH_2(\theta)$, 30H); 1.58 (m, $CH_2(\rho)$, 2H); 3.50 (t, $CH_2(\sigma)$, 2H); 3.80 (t, $CH_2(x)$, 2H); 2.52 (ttt, $CH_2(y)$, 2H); ^{19}F NMR ($CDCl_3$): δ = −84.2 (t, $CF_3(a)$, 3F); −128.5 (m, $CF_2(b)$, 2F); −127.8 (m, $CF_2(c)$, 2F); −116.2 (m, $CF_2(d)$, 2F). Anal. calcd for $C_{24}H_{41}F_9O$: C, 55.8%; F, 33.1%; H, 7.9%. Found: C, 55.4%; F, 33.9%; H, 7.4%.

*4.2.1.17. 1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-9-oxaheptacosane, (PFE-6,18), (**3s**).* White solid; spectral data: MS *m*/*z* (rel. ab. %): 616 ($[M]^+$, 10%), 601 ($[M-CH_3]^+$, 10%), 587 ($[M-CH_2CH_3]^+$, 5%), 573 ($[M-CH_3CH_2CH_2]^+$, 10%), 559 ($[M-CH_3CH_2CH_2CH_2]^+$, 10%); 297 ($[M-CF_3(CF_2)_5]^+$, 10%), 383 ($[M-CF_3(CF_2)_5, -CH_2]^+$, 100%), 253 ($[M-CF_3(CF_2)_5CH_2CH_2O]^+$, 80%); FTIR: ν_{C-F} 1080–1250 cm^{-1}, ν_{C-H} 2800–2880 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.90 (t, $CH_3(\alpha)$, 3H); 1.30 (m, $CH_2(\beta)$–$CH_2(\theta)$, 30H); 1.59 (m, $CH_2(\rho)$, 2H); 3.43 (t, $CH_2(\sigma)$, 2H); 3.77 (t, $CH_2(x)$, 2H); 2.49 (ttt, $CH_2(y)$, 2H); ^{19}F NMR: δ = −83.0 (t, $CF_3(a)$, 3F); −129.8 (m, $CF_2(b)$, 2F); −127.1 (m, $CF_2(c)$, 2F); −126.2 (m, $CF_2(d)$, 2F); −125.0 (m, $CF_2(e)$, 2F); −116.8 (m, $CF_2(f)$, 2F). Anal. calcd for $C_{26}H_{41}F_{13}O$: C, 50.6%; F, 40.0%; H, 6.6%. Found: C, 50.0%; F, 39.2%; H, 6.1%.

*4.2.1.18. 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluoro-11-oxanonacosane, (PFE-8,18), (**3t**).* White solid; spectral data: MS *m*/*z* (rel. ab. %): 716 ($[M]^+$, 10%), 701 ($[M-CH_3]^+$, 5%), 687 ($[M-CH_2CH_3]^+$, 10%), 673 ($[M-CH_3CH_2CH_2]^+$, 5%), 659 ($[M-CH_3CH_2CH_2CH_2]^+$, 15%); 297 ($[M-CF_3(CF_2)_7]^+$, 5%), 383 ($[M-CF_3(CF_2)_7, -CH_2]^+$, 90%), 253 ($[M-CF_3(CF_2)_7CH_2CH_2O]^+$, 100%); FTIR: ν_{C-F} 1120–1280 cm^{-1}, ν_{C-H} 2840–2920 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.91 (t, $CH_3(\alpha)$, 3H); 1.32 (m, $CH_2(\beta)$–$CH_2(\theta)$, 30H); 1.57 (m, $CH_2(\rho)$, 2H); 3.45 (t, $CH_2(\sigma)$, 2H); 3.81 (t, $CH_2(x)$, 2H); 2.53 (ttt, $CH_2(y)$, 2H); (b), 2F); −127.1 (m, $CF_2(c)$, 2F); −126.2 (m, $CF_2(d)$, 2F); −125.0 (m, $CF_2(e)$, 2F); −116.8 (m, $CF_2(f)$, 2F). ^{19}F NMR: δ = −83.9 (t, $CF_3(a)$, 3F); −128.9 (m, $CF_2(b)$, 2F); −126.6 (m, $CF_2(c)$, 2F); −125.9 (m, $CF_2(d)$, 2F); −125.0 (m, $CF_2(e)$, 2F); −124.0 (m, $CF_2(f)$, 2F); −122.0 (m, $CF_2(g)$, 2F); −115.8 (m, $CF_2(h)$, 2F). Anal. calcd for $C_{28}H_{41}F_{17}O$: C, 46.9%; F, 45.1%; H, 5.7%. Found: C, 46.0%; F, 44.4%; H, 6.1%.

*4.2.1.19. 1,1,1,2,2,3,3,4,4-Nonafluoro-7-oxaoctacosane, (PFE-4,21), (**3u**).* White solid; spectral data: MS *m*/*z* (rel. ab. %): 558 ($[M]^+$, 10%), 543 ($[M-CH_3]^+$, 10%), 529 ($[M-CH_2CH_3]^+$, 15%), 515 ($[M-CH_3CH_2CH_2]^+$, 10%), 501 ($[M-CH_3CH_2CH_2CH_2]^+$, 10%); 339 ($[M-CF_3(CF_2)_3]^+$, 15%), 325 ($[M-CF_3(CF_2)_3, -CH_2]^+$, 90%), 295 ($[M-CF_3(CF_2)_3CH_2CH_2O]^+$, 100%); FTIR: ν_{C-F} 1150–1250 cm^{-1}, ν_{C-H} 2820–2950 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.90 (t, $CH_3(\alpha)$, 3H); 1.30 (m, $CH_2(\beta)$–$CH_2(\upsilon)$, 38H); 1.60 (m, $CH_2(\omega)$, 2H); 3.55 (t, $CH_2(\zeta)$, 2H); 3.82 (t, $CH_2(x)$, 2H); 2.54 (ttt, $CH_2(y)$, 2H); ^{19}F NMR ($CDCl_3$): δ = −84.5 (t, $CF_3(a)$, 3F); −128.9 (m, $CF_2(b)$, 2F); −128.0 (m, $CF_2(c)$, 2F); −116.7 (m, $CF_2(d)$, 2F). Anal. calcd for $C_{27}H_{47}F_9O$: C, 58.1%; F, 30.6%; H, 8.4%. Found: C, 57.0%; F, 31.4%; H, 8.0%.

*4.2.1.20. 1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-9-oxatriacontane, (PFE-6,21), (**3v**).* White solid; spectral data: MS *m*/*z* (rel. ab. %): 658 ($[M]^+$, 10%), 643 ($[M-CH_3]^+$, 15%), 629 ($[M-CH_2CH_3]^+$, 10%), 615 ($[M-CH_3CH_2CH_2]^+$, 5%), 601 ($[M-CH_3CH_2CH_2CH_2]^+$, 15%); 339 ($[M-CF_3(CF_2)_5]^+$, 10%), 325 ($[M-CF_3(CF_2)_5, -CH_2]^+$, 95%), 295 ($[M-CF_3(CF_2)_5CH_2CH_2O]^+$, 100%); FTIR: ν_{C-F} 1160–1270 cm^{-1}, ν_{C-H} 2840–2930 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.91 (t, $CH_3(\alpha)$, 3H); 1.33 (m, $CH_2(\beta)$–$CH_2(\upsilon)$, 38H); 1.59 (m, $CH_2(\omega)$, 2H); 3.56 (t, $CH_2(\zeta)$, 2H); 3.81 (t, $CH_2(x)$, 2H); 2.52 (ttt, $CH_2(y)$, 2H); ^{19}F NMR: δ = −82.9 (t, $CF_3(a)$, 3F); −129.2 (m, $CF_2(b)$, 2F); −126.9 (m, $CF_2(c)$, 2F); −126.0 (m, $CF_2(d)$, 2F); −124.9 (m, $CF_2(e)$, 2F); −116.2 (m, $CF_2(f)$, 2F). Anal. calcd for $C_{29}H_{47}F_{13}O$: C, 52.9%; F, 37.5%; H, 7.1%. Found: C, 51.8%; F, 36.7%; H, 7.5%.

*4.2.1.21. 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluoro-11-oxadotriacontane, (PFE-8,21), (**3z**).* White solid; spectral data: MS *m*/*z* (rel. ab. %): 758 ($[M]^+$, 5%), 743 ($[M-CH_3]^+$, 10%), 729 ($[M-CH_2CH_3]^+$, 5%), 715 ($[M-CH_3CH_2CH_2]^+$, 10%), 701 ($[M-CH_3CH_2CH_2CH_2]^+$, 10%); 339 ($[M-CF_3(CF_2)_7]^+$, 15%), 325 ($[M-CF_3(CF_2)_7, -CH_2]^+$, 90%), 295 ($[M-CF_3(CF_2)_7CH_2CH_2O]^+$, 100%); FTIR: ν_{C-F} 1150–1210 cm^{-1}, ν_{C-H} 2820–2910 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.88 (t, $CH_3(\alpha)$, 3H); 1.33 (m, $CH_2(\beta)$–$CH_2(\upsilon)$, 38H); 1.61 (m, $CH_2(\omega)$, 2H); 3.51 (t, $CH_2(\zeta)$, 2H); 3.77 (t, $CH_2(x)$, 2H); 2.50 (ttt, $CH_2(y)$, 2H); ^{19}F NMR: δ = −83.4 (t, $CF_3(a)$, 3F); −128.3 (m, $CF_2(b)$, 2F); −126.2 (m, $CF_2(c)$, 2F); −125.1 (m, $CF_2(d)$, 2F); −124.5 (m, $CF_2(e)$, 2F); −123.8 (m, $CF_2(f)$, 2F); −122.1 (m, $CF_2(g)$, 2F); −115.1 (m, $CF_2(h)$, 2F). Anal. calcd for $C_{31}H_{47}F_{17}O$: C, 49.1%; F, 42.6%; H, 6.2%. Found: C, 48.4%; F, 41.2%; H, 5.8%.

References

[1] R.E. Banks, B.E. Smart, J.C. Tatlow, Organofluorine Chemistry, Principles and Commercial Applications, Plenum Press, New York, 1994, pp. 70–72.
[2] H. Meinert, A. Knoblich, Biomater. Artif. Cells Immobilization Biotechnol. 21 (1993) 583–595.
[3] S. Fuller, Y. Li, G.J.T. Tiddy, E. Wyn-Jones, R.D. Arnell, Langmuir 11 (1995) 1980–1983.
[4] E. Traverso, A. Rinaldi, US Patent 5202041 (1993).
[5] A. Karydas, US Patent 5914298 (1999).
[6] G.P. Gambaretto, US Patent 4724093 (1988).

[7] G.P. Gambaretto, L. Conte, G. Fornasieri, C. Zarantonello, D. Tonei, A. Sassi, R. Bertani, J. Fluorine Chem. 121 (2003) 57–63.
[8] A. Sekiya, S. Misaki, J. Fluorine Chem. 101 (2001) 215–221.
[9] R.J. Dams, Z.M. Qiu, R.R.L. Smolders, D.M. Coppens, M. Nagase, WO Patent 9916809 (1999).
[10] S. Chang, J. Sparrow, WO Patent 2005/117850 A1 (2005).
[11] L. Conte, A. Zaggia, M. Beccaro, E. Bettini, P. Signori, WO Patent 2009/133575 A1 (2009).
[12] S. Chang, J. Sparrow, T. Iwamoto, A. Gershbein, R. Ross, Retina 11 (1991) 367–374.
[13] R.D. Chambers, R.H. Mobbs, Adv. Fluorine Chem. 4 (1965) 50–112.
[14] J. Murata, M. Tamura, A. Sekiya, Green Chem. 4 (2002) 60–63.
[15] G.K.S. Prakash, J. Hu, A. Clah, Arkivoc (iii) (2003) 104–119.
[16] N.O. Brace, J. Fluorine Chem. 93 (1999) 1–25.
[17] Y. Fujii, E. Tamura, S. Yano, H. Furugaki, Kao Corp., US 6006026 (2000).
[18] W. Huang, C. Jin, D.K. Derzon, T.A. Huber, J.A. Last, P.P. Provencio, A.S. Gopalan, M. Dugger, D.Y. Sasaki, J. Colloid Interf. Sci. 272 (2004) 457–464.
[19] H. Mainert, U. Geister, J. Fluorine Chem. 68 (1994) 221–226.
[20] J.F. Rabolt, T.P. Russell, R.J. Twieg, Macromolecules 17 (1984) 2786–2794.
[21] C. Viney, T.P. Russel, L.E. Depero, R.J. Twieg, Cryst. Liq. Crystallogr. 168 (1989) 63–82.
[22] C. Pugh, J. Hopken, M. Moeller, Polym. Prep. (Am. Chem. Soc., Div. Polym. Chem.) 29 (1988) 460–461.
[23] T.P. Russel, J.F. Rabolt, R.J. Twieg, R.L. Siemens, B.L. Farmer, Macromolecules 19 (1986) 1135–1143.
[24] B. Ameduri, B. Boutevin, Well-Architectured Fluoropolymers: Synthesis, Properties and Applications, Elsevier, 2004,, p. 236.
[25] M.P. Krafft, A. Chittofrati, J.G. Riess, Curr. Opin. Colloid Interf. Sci. 8 (2003) 251–258.
[26] H. Kuwahara, M. Hamada, Y. Ishikawa, T. Kunitake, J. Am. Chem. Soc. 115 (1993) 3002–3003.
[27] M.P. Turberg, J.E. Brady, J. Am. Chem. Soc. 110 (1988) 7797–7801.
[28] J. Hopken, C. Pugh, W. Richtering, M. Moller, Makromol. Chem. 189 (1988) 911–925.
[29] G.L. Gaines, Langmuir 7 (1991) 3054–3056.
[30] R.J. Twieg, T.P. Russell, R. Siemens, J.F. Rabolt, Macromolecules 18 (1985) 1361–1362.
[31] M. Napoli, L. Conte, G.P. Gambaretto, J. Fluorine Chem. 85 (1997) 163–167.
[32] M. Napoli, L. Conte, A. Guerrato, J. Fluorine Chem. 110 (2001) 47–58.