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New hydrofluoropolyethers
I. Synthesis and reaction pathway evaluation

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Abstract

A novel family of hydrofluoropolyethers (HFPEs) was obtained with 60–80% selectivity by hydrogenation of perfluoropolyether acyl chlorides with Pt/CaF_2. These compounds are characterized by a macromeric fluorinated body end-capped, on one or both sides, by a (1,1-difluoro)ethoxy group. A reaction pathway for the reduction was proposed consistently with the observed yields and side products. The hemiacetal originated by reaction of the aldehyde (first product of reduction) with the corresponding alcohol was postulated to be the key precursor leading to the HFPE. The metal appears to play a fundamental role promoting the hydrogenolysis of this unexpected intermediate. Exhaustive reduction of the alcohol, generally recognized as the path affording hydrocarbons in the hydrogenation of acyl chlorides, was excluded by products analysis and by specific experiments.

Keywords: Hydrofluoropolyethers; Acyl chloride; Hydrogenolysis; Platinum; Aldehyde

1. Introduction

The phase-out of low molecular weight chlorofluorocarbons (CFCs), and more generally of chlorine containing molecules (HCFCs), has promoted a significant effort for environmentally safer alternatives. Products that can be used as CFCs and HCFCs substitutes in refrigeration, as blowing agents and cleaning fluids have been synthesised, positively evaluated, present for more than a decade. Among them HFCs have been promoted on a very wide scale, especially HFC-134a, as 'safe' alternative to the corresponding CFCs.

More recent studies have shown that a new possibility is represented by partially hydrogenated molecules containing ethereal linkages. These hydrofluoroethers (HFEs) have been described in several scientific contributions [1–3]. Different methods are available for their synthesis: (1) fluorination of ethers [4–9], (2) nucleophilic or radical addition to fluoroolefins [10–12], (3) electrophilic alkylation of appropriate fluorinated substrates [13–16], (4) decarboxylation of fluorinated substrates in presence of hydrogen donors [3], and, finally, (5) reaction of perfluoropolyether diacyl fluorides with methyl fluoroformate [17].

At the present HFEs represent a possible alternative to HFCs because they are characterized by a good compromise between performance in use and environment protection. They combine a good set of properties with physicochemical lability and reactivity. This latter characteristic guarantees a reduced lifetime in the troposphere so minimizing the undesired radical reactions in the stratosphere that represent the major drawback of CFCs and HCFCs molecules [18,19].

Among the new HFE candidates α,ω-(dihydro)fluoropolyethers (HFPEs) are an innovative class. They can be synthesised by a proprietary Solvay-Solexis technology [20–23] enabling the fine tuning of the main molecular parameters, like MW and MWD. As a consequence specific grades can be obtained characterized by tailored physicochemical properties. Moreover, these molecules offer a significantly reduced environmental impact, combined with non-toxicity [3].

In the present work this approach has been further explored with the aim of finding new reaction routes, starting from functionalised fluoropolyethers, for the synthesis of new HFPEs.

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Specifically, a new synthetic method will be presented, and discussed. It allows the achievement of new structures, otherwise not feasible with already established reactions. The synthesis of (1,1-difluoroethoxy)fluoropolyethers and α,ω-bis[(1,1-difluoroethoxy)fluoropolyethers] will be described, a reaction mechanism for their formation will be proposed consistent with the observed reaction pathways and products analysis. The proposed synthetic approach is of wide scope, in fact the conversion of $–OCF_2COCl$ to $–OCF_2CH_3$, described in the present work for perfluorinated or chlorofluorine containing molecules, is independent from the length and the nature of the chain bonded to the reactive centre.

The combination of a favourable synthetic approach with an expected interesting set of easily tuneable physicochemical properties, through modulation of the PFPE chain, makes this new catalytic reduction a powerful tool for the synthesis of interesting candidates as environmental friendly new chemicals.

The elucidation of the physicochemical properties of the molecules described in the present work will be the subject of further studies, with special focus on the contribution of the end-groups and molecular weight to each specific property.

2. Results and discussion

The (1,1-difluoroethoxy)fluoropolyethers and α,ω-bis[(1,1-difluoroethoxy)fluoropolyether] here described were obtained by an unconventional synthetic approach [24], e.g. the hydrogenation of perfluoropolyether acyl chlorides mediated by platinum (reaction (1)).

$$R_fOCF_2C(O)Cl \xrightarrow{H_2,\ Pt} R_fOCF_2CH_3 \qquad (1)$$

where $R_f = –CF_2CF_2OCF_2CF_2–$; $Cl(C_3F_6O)_{n-1}C_3F_6–$.

These reactions, as far as functional fluoropolyethers are concerned, seldom proceed with extended or even exhaustive homolytic cleavage of σ C–O bonds. Alcohols are usually obtained from carboxylic acids in very good yields, even if high temperature and hydrogen pressure, in presence of very efficient catalysts, are necessary. Milder conditions make it possible, in some cases, to isolate the corresponding aldehydes [25].

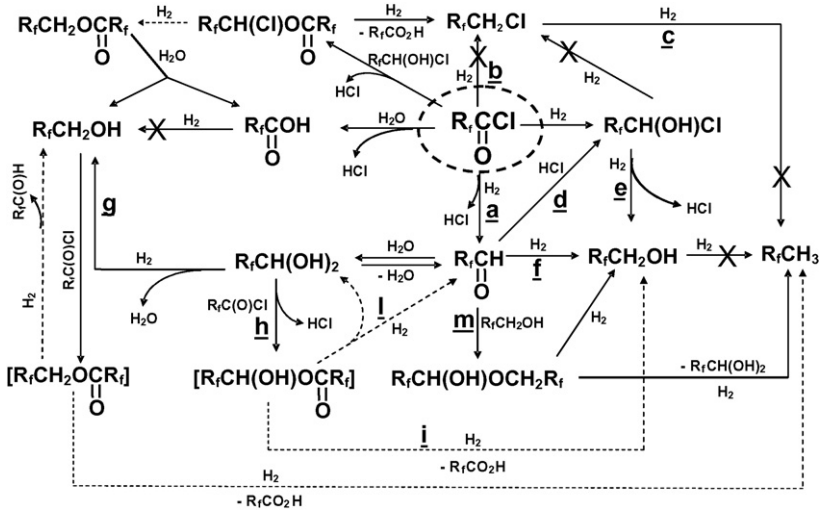
The acyl chlorides were prepared, as described in the experimental section, from the corresponding acyl fluorides. PFPE acyl fluorides are in turn obtained by well established processes developed by Solvay Solexis, e.g. photopolymerisation of perfluoroolefins and oxygen [26–30].

Independently from the number of functional groups present in the starting molecules and from their molecular weight, conversion of the starting acyl chloride was always quantitative and selectivity to corresponding HFPE high, ranging from 60% to 81%.

The main product was the HFPE, however, formation of the alcohol $RfCH_2OH$ always occurred. The second by-product, when present, was the carboxylic acid deriving from hydrolysis of the starting acyl chloride RfC(O)Cl. However, its formation is strongly limited by the adopted experimental conditions that guarantee a very low steady concentration of acyl chloride and water.

The formation of these new HFPEs is peculiar to platinum metal. In fact, when Pd was used, the expected hydrogenation to aldehyde or alcohol, depending on temperature and catalyst surface area [25], was obtained. The well known ability of Platinum to promote hydrogenolysis reactions [31] suggested that homolytic cleavages of C–O σ bonds should be involved in the process. Moreover, the analysis of products distribution appeared consistent with a reaction pathway resulting from consecutive rather than independent processes. Based on these considerations we hypothesised that the HFPEs of the present study are obtained by a multi-step reduction process combining hydrogenation of carbonyl bonds and homolytic cleavage, Pt assisted, of C–O bonds (see Scheme 1).

The first step involves formation of the aldehyde by fast hydrogenolysis of the C–Cl bond of RfC(O)Cl (reaction a).



Scheme 1. General reaction scheme for the hydrogenation of RfC(O)Cl.

Exhaustive carbonyl hydrogenation was excluded because the chloro-derivative $RfCH_2Cl$ was never observed (reaction b). Moreover, the possibility that this intermediate, if formed, immediately converts by a further hydrogenolysis step to the corresponding HFPE ($RfCH_3$), contradicted the evidence that, when synthesised on-purpose, it proved completely unreactive in the same experimental conditions (reaction c).

A partial hydrogenation of the starting RfC(O)Cl is very unlikely and, in any case, the corresponding α-chloro-alcohol [RfCH(OH)Cl] was never detected (reaction d), so it must be considered, if present, a highly reactive species quickly reduced to the corresponding alcohol (reaction e).

Several other reactions, consistently with the proposed mechanism and the observed product distribution, can justify the presence of the alcohol ($RfCH_2OH$) as the main side product.

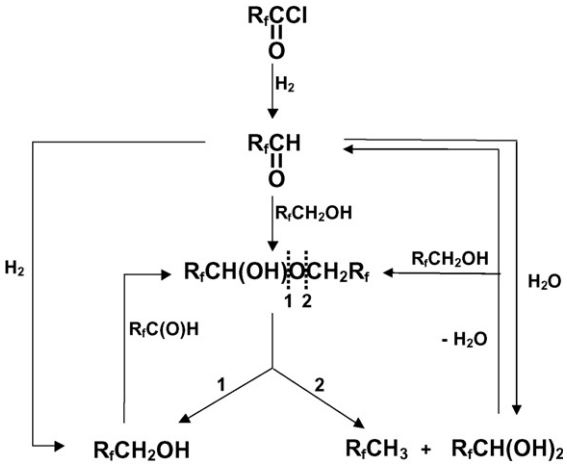
First of all, the aldehyde can be further reduced to alcohol by a one step process (reaction f), or by two subsequent steps, consisting of hydration and reduction, respectively (reaction g). Water can be present as impurity (humidity) or generated by some of the described reaction pathways. The hydrated intermediate [$RfCH(OH)_2$], analogously to other OH containing intermediates reported in the reaction scheme, could react with the starting acyl chloride forming the corresponding esters (reaction h), which in principle could undergo hydrogenolysis to alcohol (carboxylic acid as side product), or to aldehyde and its hydrated form (reactions i and l, respectively) [32]. However, the strong hydrolysis sensitivity of these fluorinated esters makes these reactions highly improbable and for this reason they have been shown as dotted lines. The hydrolysis reactions have not been reported in the simplified reaction scheme.

Taking into consideration the above analysis of experimental results, it is evident that the key intermediate for the synthesis of target HFPE is the corresponding aldehyde.

The typical product composition is 60–81% HFPE + 40–19% (alcohol + carboxylic acid), the carboxylic acid, always present as minor impurity, being strongly dependent on the water present in the system.

Surprisingly, the alcohol, easily generated by aldehyde reduction, is stable to hydrogenation and does not further convert to HFPE, as confirmed by specific experiments carried out on pure product. Consequently, the aldehyde must form HFPE by a different pathway not involving two direct reduction steps, unlike the well-known exhaustive reduction of hydrogenated acyl chlorides [33].

This aldehyde, like other fluorinated carbonyl containing species, is highly reactive with respect to nucleophilic attack to the C atom of the carbonyl group. Therefore, a hemiacetal is easily formed by reaction with alcohol (reaction m). Moreover, this addition could be speeded up by the presence of an acid catalyst (HCl is a by-product of the hydrogenation process). The proposed mechanism considers this acetal easily convertible by hydrogenolysis to further reduced species. The structure and composition of these species essentially depend on the regioselectivity of this hydrogenolysis (see Scheme 2). Reaction 1 generates two alcoholic molecules, whereas through reaction 2 the target HFPE and aldehyde (as hydrated form) are obtained.



Scheme 2. Reaction mechanism for hydrofluoropolyethers formation.

Due to the high temperature selected for the reduction process (100 °C) the equilibrium between hydrated and anhydrous aldehyde should be shifted toward the anhydrous form. As a consequence, a new aldehyde molecule is available, so activating a cyclic catalytic process. However, the cycle could also be sustained by the hydrated aldehyde that could give directly the hemiacetal by reaction with the alcohol.

Interestingly, while the cleavage in position 1 is ineffective for the direct synthesis of HFPE, this pathway affording only alcoholic species, the cleavage in position 2 gives formally 50% yield of the desired HFPE. However, the evaluation of the whole reaction Scheme 2 justifies the observed higher yield (60–80%), because the hydrated aldehyde (or its anhydrous form) reacts with the alcohol generating a new active and effective intermediate (hemiacetal).

A cleavage in position 2 with a regioselectivity of 65–70% would give a HFPE yield close to 100% because equivalent amount of side products (alcohol and hydrated aldehyde) are formed.

Considering the observed yield (excluding any further contribution of different reaction pathways to HFPE formation), the actual regioselectivity is ca. 60% for the cleavage in position 2.

According to the above discussion, that considers the aldehyde as the key intermediate, its use as starting reagent should assure a yield in HFPE comparable to the one obtained

Table 1
Structures and molecular weights of Ac-n1-5 series and Ac-Z

Product	Structure	Molecular weight
Ac-n1	$Cl–CF_2CF(CF_3)OCF_2COCl$	312
Ac-n2	$Cl(C_3F_6O)_2CF_2COCl$[a]	478
Ac-n3	$Cl(C_3F_6O)_3CF_2COCl$[a]	644
Ac-n4	$Cl(C_3F_6O)_4CF_2COCl$[a]	810
Ac-n5	$Cl(C_3F_6O)_4CF(CF_3)OCF_2COCl$[a,b]	846
Ac-Z	$ClOCCF_2O(CF_2CF_2O)_2CF_2COCl$	459

[a] Two isomers: $ClCF_2CF(CF_3)–$ = 30%; $CF_3CF(Cl)CF_2–$ = 70% (molar base).
[b] The unit $–CF(CF_3)O–$ is randomly distributed along the oligomeric chain.

Table 2
^{19}F NMR data related to Ac-n1-5 series and Ac-Z

Product		δ (ppm)
Ac-n1	**a b c d** $ClCF_2CF(CF_3)OCF_2C(O)Cl$	−67.0 (**a**); −140.0 (**b**); −77.0 (**c**); −69.0 (**d**)
Ac-n2-4	**a b c e f g d** $ClCF_2CF(CF_3)O[CF_2CF(CF_3)O]_{1\text{-}3}CF_2C(O)Cl$ + **h i l e f g d** $CF_3CF(Cl)CF_2O[CF_2CF(CF_3)O]_{1\text{-}3}CF_2C(O)Cl$	−68.0 (**a**); −139.6 (**b**); −79.0 (**c**); −69.0 (**d**); −80.6 (**e**); −145.0 (**f**); −80.6 (**g**); −79.0 (**h**); −140.0 (**i**); −81.0 (**l**)
Ac-n5	**a b c e f g m n d** $ClCF_2CF(CF_3)O[CF_2CF(CF_3)O]_3CF(CF_3)OCF_2C(O)Cl$ + **h i l e f g m n d** $CF_3CF(Cl)CF_2O[CF_2CF(CF_3)O]_3CF(CF_3)OCF_2C(O)Cl$	−68.0 (**a**); −140.0 (**b**); −79.0 (**c**); −69.0 (**d**); −80.6 (**e**); −145.0 (**f**); −80.6 (**g**); −79.0 (**h**); −140.0 (**i**); −81.0 (**l**); −95.0 (**m**); −86.8 (**n**)
Ac-Z	**o p q** $ClC(O)CF_2OCF_2CF_2OCF_2CF_2OCF_2C(O)Cl$	−77.4 (**o**); −88.9 (**p**); −89.0 (**q**)

from the acyl chloride. Specifically carried out experiments only partially confirmed this hypothesis. The aldehyde, in fact, converts to HFPE with a lower yield. Therefore, a contribution of some activated species on the metal catalyst cannot be totally excluded, for instance a just formed activated alcohol that immediately converts on the catalytic site to HFPE. Distinctive kinetic rates, due to reaction conditions not exactly equivalent, that can strongly affect the stationary concentrations of the species involved in the process, cannot be excluded as well. Typically the presence of HCl, well-known poisoning agents in catalytic reduction reactions, could influence the aldehyde/alcohol ratio, key parameter in the proposed mechanism.

3. Conclusions

The aim of this work was to describe a new approach towards the synthesis of novel hydrofluoroethers (HFEs), here indicated as HFPEs due to the presence of a perfluoropolyether chain in the structure. This goal was achieved through an apparently conventional hydrogenation of PFPE precursors end-capped by reducible acyl chloride groups. However, the detailed analysis of both yield and by-products structures, together with specific experiments devoted to the elucidation of the reactivity of possible intermediates, strongly support the hypothesis that an unconventional and unexpected reaction pathway is effective. In fact, unlike the conventional step by step reduction mechanism, moving from oxidized to progressively reduced species, in the present case the target HFPE is obtained by hydrogenolysis of the addition product between two key intermediates: aldehyde and alcohol. These intermediates alone do not give the target HFPE at all, as in the case of alcohol, or forms the HFPE with lower yield. Therefore, this reduction represents a nice example where side products, ''per se'' stable in the adopted reaction conditions (as alcoholic species in the present case), form a new effective intermediate, by reacting each other, so increasing the total yield.

The fundamental physical characterization of these new molecules will be the subject of further studies, in order to elucidate the influence of molecular weight and structure on properties.

Among the wide spectrum of different structures achievable thanks to this original approach, chlorine-free molecules can be selected. Thanks to the favourable reaction pathway and an expected good combination of physical properties, these molecules could be considered as interesting candidates for a new friendly generation of fluorinated fluids. However, further work is needed to complete their physical and chemical evaluation, with special emphasis on their atmospheric lifetime and global warming potential.

4. Experimental

4.1. Materials and physicochemical characterizations

The PFPE starting materials, e.g. PFPE acylfluorides, were all from Solvay Solexis. Thionyl chloride, hexachloroplatinic (IV) acid hydrate, methanol, silica gel 60 (all from Aldrich Co.) and calcium fluoride (Carlo Erba Reagents) were used as received. Galden® D100 [1/1 volume mixture of (*per*fluorobutyl)tetrahydrofurane and (*per*fluoropropyl)tetrahydropyrane, by Solvay Solexis] was distilled immediately prior to use. IR spectra at room temperature (20 °C) have been recorded with a Nicolet 20SX FT-IR spectrometer. Acquisition parameters: resolution = 2 cm^{-1}, scans = 512. ^{19}F and ^{1}H NMR spectra were recorded on neat samples using a Varian Mercury instrument operating at 288 and 300 MHz, respectively. ^{19}F chemical shift values (ppm) were referenced to those of $CFCl_3$

Table 3
Selectivity for the synthesis of mono- and bis-(1,1-difluoroethoxy)fluoropolyethers

Reagent[a]	Product	Selectivity[b]
Ac-n1	$ClCF_2CF(CF_3)OCF_2CH_3$	72
Ac-n2	$Cl(C_3F_6O)_2CF_2CH_3$[c]	81
Ac-n3	$Cl(C_3F_6O)_3CF_2CH_3$[c]	73
Ac-n4	$Cl(C_3F_6O)_4CF_2CH_3$[c]	75
Ac-n5	$Cl(C_3F_6O)_4CF(CF_3)OCF_2CH_3$[c]	60
Ac-Z	$CH_3CF_2O(CF_2CF_2O)_2CF_2CH_3$	80

[a] Conversion was always >99%.
[b] % molar base.
[c] $ClCF_2CF(CF_3)$– = 30%; $CF_3CF(Cl)CF_2$– = 70% (molar base).

Table 4
^{19}F NMR data related to H-n1-5 series and H-Z

Product		δ (ppm)
H-n1	**a b c d** $ClCF_2CF(CF_3)OCF_2CH_3$	−67.0 (**a**); −140.0 (**b**); −77.0 (**c**); −60.6 (**d**)
H-n2-4	**a b c e f g d** $ClCF_2CF(CF_3)O[CF_2CF(CF_3)O]_{1\text{-}3}CF_2CH_3$ +	−68.0 (**a**); −139.6 (b); −79.0 (**c**); −61.4 (**d**); −80.6 (**e**); −145.0 (**f**); −80.6 (**g**); −79.0 (**h**); −140.0 (**i**); −81.0 (**l**)
	h i l e f g d $CF_3CF(Cl)CF_2O[CF_2CF(CF_3)O]_{1\text{-}3}CF_2CH_3$	
H-n5	**a b c e f g m n d** $ClCF_2CF(CF_3)O[CF_2CF(CF_3)O]_3CF(CF_3)OCF_2CH_3$ +	−68.0 (**a**); −140.0 (**b**); −79.0 (**c**); −61.4 (**d**); −80.6 (**e**); −145.0 (**f**); −80.6 (**g**); −79.0 (**h**); −140.0 (**i**); −81.0 (**l**); −95.0 (**m**); −86.8 (**n**)
	h i l e f g m n d $CF_3CF(Cl)CF_2O[CF_2CF(CF_3)O]_3CF(CF_3)OCF_2CH_3$	
H-Z	**o p q** $CH_3CF_2OCF_2CF_2OCF_2CF_2OCF_2CH_3$	−63.6 (**o**); −88.9 (**p**); −89.0 (**q**)

(trichlorofluoromethane), determined in separate experiments. Tetramethylsilane (TMS) was used as the internal standard (0.5%, w/w) for the ^1H chemical shifts. GC/MS analyses were performed on a HP 5890 gas chromatograph equipped with Porabond Q column (diameter 0.32 mm, length 25 m) coupled with a HP 5989 mass spectrometer. The Pt content in the catalyst was determined using a Philips (model PW 2400) X-ray fluorescence (XRF) spectrometer monitoring the Pt Lα line referred to a specific calibration curve.

4.2. PFPE acyl chlorides: Ac-n1-5, Ac-Z

The structures and molecular weights of the starting acyl chlorides are shown in Table 1. The monofunctional structures were named Ac-n1-5 depending on the number of repeating perfluoroisopropoxy units. The difunctional compound was named Ac-Z.

The PFPE acyl fluorides were firstly hydrolysed to the corresponding acids and then converted to acyl chlorides by reaction with thionyl chloride, which is the best reagent, since the by-products are gases and the acyl halide is easily isolated [34]. The acyl chlorides can also be prepared by an exchange reaction with inorganic chlorides [25].

The following procedure, described for Ac-n1 was used for all the compounds.

To 250 ml (408 g, 3.40 mol) of $SOCl_2$ and 10 ml of pyridine under N_2 atmosphere was added dropwise the PFPE carboxylic acid of formula $Cl–C_3F_6OCF_2COOH$ (257 g, 1.04 mol) obtained by hydrolysis of the corresponding acyl fluoride. The reaction mixture was stirred at 60 °C until complete evolution of gaseous by-products and then cooled to room temperature. The lower organic phase was separated and the product isolated by distillation as a low viscous, colourless liquid (293 g, yield 99%). IR: 1800 cm^{-1} ν(CO). ^{19}F NMR: Table 2.

4.3. Pt/CaF_2

2.74 g of H_2PtCl_6 were dissolved at room temperature in 250 ml of methanol. 69.2 g of CaF_2 were then added and the alcohol evaporated under vacuum. The resulting powder was dispersed in 500 g of Galden D® 100 and hydrogenated for 1 h at 100 °C (8 l h^{-1}, atmospheric pressure). After removal of the solvent 70 g of Pt/CaF_2 were obtained as a grey powder. The surface area was measured by the Brunauer, Emmett and Teller (BET) method, and resulted to be 14 m^2 g^{-1}. The XRF analysis of the catalyst showed a Pt content of 1.7% (w/w), close to the theoretical value (1.8%, w/w).

4.4. (1,1-Difluoroethoxy)fluoropolyethers: H-n1-5, H-Z

The following procedure, here described for Ac-n_3, was applied to the whole series.

32.5 g of Pt/CaF_2 (Pt 1.7%, w/w) were suspended in 400 ml of Galden® D100 and heated to 100 °C. 38.9 g of Ac-n3 (60 mmol) were introduced over 30 min together with hydrogen (20 l h^{-1}, atmospheric pressure). After additional 15 min under hydrogen stream the reaction mass was cooled to room temperature and Pt/CaF_2 filtered off. The crude mixture was purified by chromatography on silica, in order to remove the alcohol by-product (9.8 g, 16 mmol), characterized by the following structure: $Cl(C_3F_6O)_3CF_2CH_2OH$. The target product $Cl(C_3F_6O)_3CF_2CH_3$ was finally isolated through multiple fractional distillation on a Spaltrohr-Fischer HMS 500-HV/C column (90 theoretical plates) with purity higher than 98% (26.4 g, 73% yield) as confirmed by GC–MS analysis. The selectivity obtained for each product is shown in Table 3. Products were named H-n1-5 (depending on the number of repeating units in the structure), and H-Z, for mono- and difunctional derivatives, respectively. ^{19}F NMR: Table 4; ^1H NMR (neat) δ: 2.57 (*t*, 3H, $J_{F–H}$ = 14 Hz $ClCF_2CF(CF_3)OCF_2\mathbf{CH_3}$).

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