

Review

## An Environmentally Friendly Class of Fluoropolyether: $\alpha,\omega$ -Dialkoxyfluoropolyethers

Menghua Wu <sup>1</sup>, Walter Navarrini <sup>1,2,\*</sup>, Gianfranco Spataro <sup>3</sup>, Francesco Venturini <sup>1</sup> and Maurizio Sansotera <sup>1</sup>

<sup>1</sup> Dipartimento di Chimica, Politecnico di Milano, 7, via Mancinelli, I-20131 Milano, Italy; E-Mails: menghua.wu@mail.polimi.it (M.W.); francesco.venturini@chem.polimi.it (F.V.); maurizio.sansotera@polimi.it (M.S.)

<sup>2</sup> Consorzio INSTM, Via G. Giusti 9, I-50121, Firenze, Italy

<sup>3</sup> C.R.S. Solvay Specialty Polymer, viale Lombardia 20, I-20021 Bollate (MI), Italy; E-Mail: gianfranco.spataro@solvay.com

\* Author to whom correspondence should be addressed; E-Mail: walter.navarrini@polimi.it; Tel.: +39-02-2399-3029; Fax: +39-02-2399-3180.

Received: 21 February 2012; in revised form: 27 March 2012 / Accepted: 27 March 2012 / Published: 11 April 2012

---

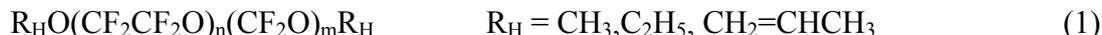
**Abstract:** The  $\alpha,\omega$ -dialkoxyfluoropolyethers (DA-FPEs) characterized by the structure  $R_HO(CF_2CF_2O)_n(CF_2O)_mR_H$  have been developed as a new class of environmentally friendly hydrofluoroethers (HFES) suitable as solvents, long-term refrigerants, cleaning fluids, and heat transfer fluids. Synthetic methodologies for DA-FPEs described here consist of radical-initiated oxypolymerization of olefin, peroxy-elimination reaction in peroxidic perfluoropolyethers (P-PFPEs) and further chemical modification of  $\alpha,\omega$ -diacylfluoride PFPE. The physical properties of selected  $\alpha,\omega$ -dimethoxyfluoropolyethers (DM-FPEs) have been evaluated and compared with analogous hydrofluoropolyethers (HFPEs) having  $-OCF_2H$  as end-groups. Atmospheric implications and global warming potentials (GWPs) of selected DA-FPEs are also considered.

**Keywords:**  $\alpha,\omega$ -dimethoxyfluoropolyethers; hydrofluoropolyethers; physical properties

---

## 1. Introduction

$\alpha,\omega$ -Dialkoxyfluoropolyethers (DA-FPEs) are partially fluorinated polyethers not containing chlorine atoms. Hence, they do not contribute to ozone depletion [1].



The incorporation of two alkoxy-groups provides reactive sites, which limit their atmospheric lifetime [1–3]; therefore, when compared with perfluoropolyethers (PFPEs), they have a lower environmental impact in terms of global warming potential (GWP) [1]. Furthermore, perfluorinated ether units from polymeric backbones also makes them well characterized by typical properties of PFPEs, like high thermal and chemical stability, no acute toxicity and excellent heat exchange properties [4]. Lastly, due to the presence of the above-mentioned alkoxy-groups as ending groups, they show good solvent properties with several organic liquids, such as ketones and alcohols [5]. All these appealing properties of DA-FPEs make them excellent candidates as CFC, perfluocarbons and halons substitutes in a number of applications, like foaming and fire extinguishing agents, cleaning agents for sophisticated electronic devices and heat transfer fluids [6–8].

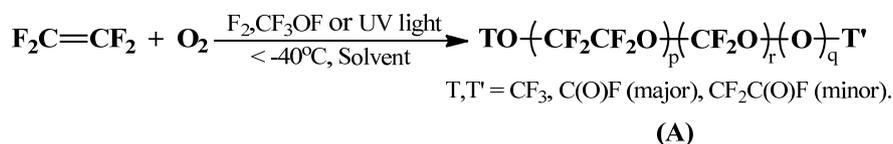
## 2. Syntheses of $\alpha,\omega$ -Dialkoxyfluoropolyethers

The synthesis of DA-FPEs described here involves a combination of a few innovative and conventional synthetic technologies. The whole process includes the following steps: (1) The oxidative polymerization of perfluoroolefinic monomers into peroxidic perfluoropolyethers (P-PFPEs) as a precursor; (2) the subsequent reduction of P-PFPEs to produce diacyl fluorides perfluoropolyether (DAF-PFPE); (3) and the further chemical modification of  $\alpha,\omega$ -diacyl functional groups of DAF-PFPE to yield the final products  $\alpha,\omega$ -dialkoxyfluoropolyethers.

### 2.1. Oxypolymerization of Perfluoroolefin

Oxidative polymerization of perfluoroolefinic monomers like tetrafluoroethylene (TFE) by molecular oxygen into P-PFPEs (A) described in Figure 1, is a well-known reaction [9].

**Figure 1.** Oxidative polymerization of tetrafluoroethylene.



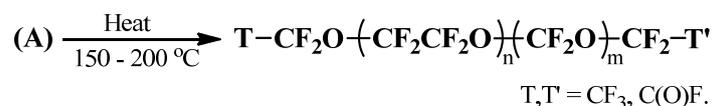
The forming peroxidic polymer has the following general structure: TO-(CF<sub>2</sub>CF<sub>2</sub>O)<sub>p</sub>-(CF<sub>2</sub>O)<sub>r</sub>-(O)<sub>q</sub>-T', comprising fluoroether repeating units (-CF<sub>2</sub>CF<sub>2</sub>O- and -CF<sub>2</sub>O-), interspersed peroxy units (-CF<sub>2</sub>CF<sub>2</sub>OO- and -CF<sub>2</sub>OO-) and perfluorinated alkyl groups, acyl fluoride or fluoroformate as chain end-groups (T, T'). Practically, this oxypolymerization can be activated either by high energy UV light or by employing elemental fluorine or perfluoroalkyl hypofluorites, especially CF<sub>3</sub>OF, as chemical initiators [9]. The peroxidic polymer is the result of a complex free radical oxidation reaction dominated by the chemistry of perfluoro oxyradicals [10]. The composition and the reaction yields of

forming PFPE polymers depend on irradiation condition, TFE concentration, fluid dynamics of the system and other classical physical parameters like temperature and pressure. Commonly, the average molecular weight of formed P-PFPEs (A) is more than  $10^4$  amu [11]. Carbonyl fluoride and tetrafluoroethylene oxide are the main by-products.

## 2.2. Deperoxidation of P-PFPEs

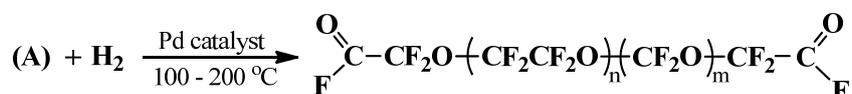
$\alpha,\omega$ -Diacyl PFPE can be obtained by thermal treatment or chemical reduction of peroxide bonds present in the above mentioned peroxidic precursor. Under the appropriate thermal treatment, homolysis of fragile peroxide bonds in P-PFPEs (A) produces PFPE alkoxy radicals; subsequently, the cleavage of the bond in  $\beta$ -position to the oxygen-centered radicals leads to the formation of reactive carbon-centered PFPE radicals [12,13]. The fast cage-combination reaction of these radicals takes place and leads to a PFPE material in which acyl fluoride and fluoroformyl moieties are nearly 50% of the end groups (Figure 2). Generally, above 150 °C those fluoroformate groups can also be converted into acyl fluorides. After the thermal treatment of the peroxidic PFPE, the reduced PFPE products can be distinguished into two fractions: The major one includes PFPE with monoacid end-groups, while the minor one comprises completely neutral (perfluoroalkyl end-groups) and diacyl fluoride PFPEs.

**Figure 2.** Deperoxidation of P-PFPEs by thermal treatment.



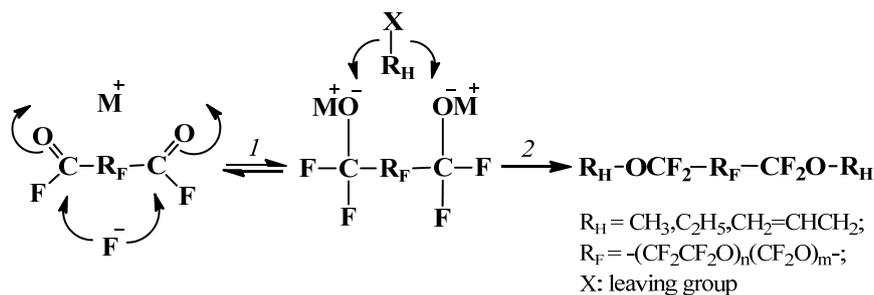
P-PFPEs (A) can also be converted directly to diacyl fluoride PFPEs,  $\text{F}(\text{O})\text{CCF}_2\text{O}(\text{CF}_2\text{CF}_2)_n(\text{CF}_2\text{O})_m\text{CF}_2\text{C}(\text{O})\text{F}$ , by chemically induced reduction of the peroxide units with better yield compared with thermal treatment (Figure 3). The chemical reduction is performed with reducing agents, such as hydrogen iodide or with molecular hydrogen in the presence of a noble metal catalyst (e.g., Palladium) [14].

**Figure 3.** Deperoxidation of P-PFPEs by chemical reduction.



## 2.3. Preparation of DA-FPEs by DAF-PFPE Alkylation

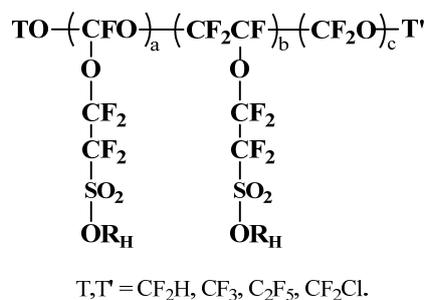
Finally, hydrofluoropolyethers DA-FPEs are prepared through the reaction of diacyl fluoride PFPEs (DAF-PFPEs) with electrophiles in the presence of a source of fluorine ions, generally, metal fluorides. This process actually comprises two steps (Figure 4): Firstly, in aprotic polar solvent, DAF-PFPEs react with fluoride ions released from metal fluorides to form metal perfluoroalkoxides  $\text{M}^+\text{OCF}_2\text{R}(\text{CF}_2)_n\text{OCF}_2\text{O}^-\text{M}^+$  as intermediates; secondly, metal perfluoroalkoxide is alkylated by a suitable alkylating agent  $\text{X}-\text{R}_\text{H}$  leading to the introduction of alkoxy groups at the end of the perfluoropolyether chain.

**Figure 4.** General two step reaction for synthesis DA-FPEs.

Metal perfluoroalkoxides are known as compounds characterized by low nucleophilicity [15] and they decompose into acylfluorides and metal fluorides, generally around room temperature. In order to increase the stability and the nucleophilic strength of these species, polar aprotic solvents (e.g., diglyme, tetraglyme) are generally required. The stability of these species depends on the nature of metal fluoride [16], temperature, and the solvent [17]. Metal perfluoroalkoxides are also important industrial intermediates in the synthesis of hypofluorites like  $\text{CF}_3\text{CF}_2\text{OF}$  [18] and fluorinated vinyl ethers [19,20]. Completely anhydrous reaction conditions are required, because in presence of water the hydrolysis of acyl fluoride groups generates hydrofluoric acid, HF, which can be absorbed by the solid metal fluoride giving  $\text{MHF}_2$  [16]. Because of the low nucleophilicity of perfluoroalkoxides, strong alkylating agents with high electrophilicity are needed to effectively react with metal perfluoroalkoxides and form DA-FPEs.

### 2.3.1. Alkylation of PFPE Dialkoxides

In the past years, there have been many disclosures reported on finding effective alkylating agents suitable for perfluoroalkoxides. Dialkylsulfate was one of the first specific reagents used [21], because of its strong alkylating ability. In fact, it has been used to alkylate almost every nucleophile [22,23], but the alkylating temperature of dialkylsulfate needs to be lower than 20 °C and undesired viscose gels can be formed at this temperature and remarkably reduce the alkylation rate and yield. Moreover, dialkyl sulfates are highly toxic and their carcinogenic activity makes them inapplicable for large-scale industrial production.

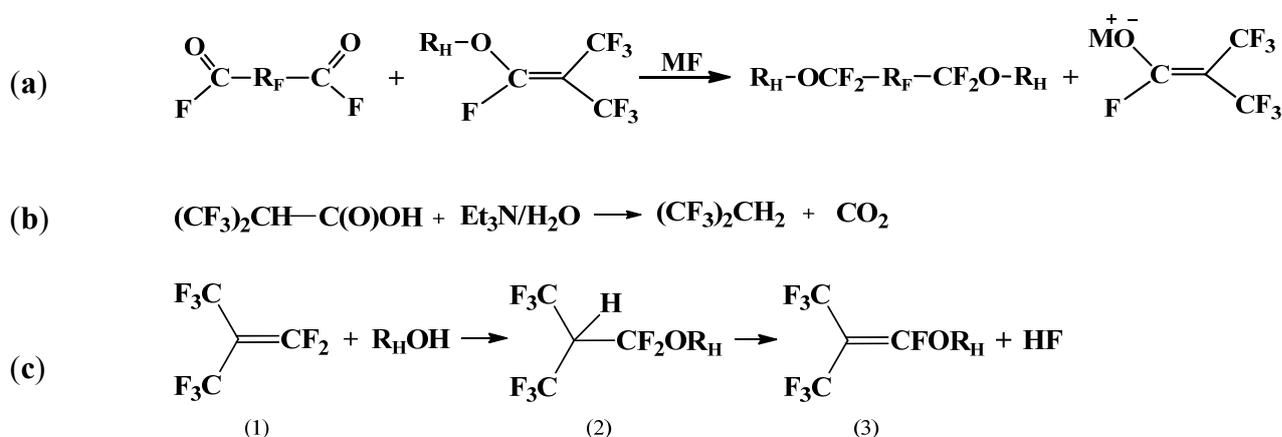
**Figure 5.** Alkyl ester of the polysulphonic PFPE.

Dialkyl sulfites and the alkyl ester of polysulphonic PFPE (Figure 5) were also proposed and applied as alkylating agents in reactions with acylfluorides to synthesize hydrofluoroethers (HFE) [6,24]. Compared with dialkyl sulfate, dialkyl sulphite and the alkyl ester of polysulphonic PFPE are

considered non-carcinogenic, and their alkylating temperature over 100 °C avoids the formation of undesired gels. However, the molar yield of the product resulting from the use of these two alkylating agents is low (below 20%), in addition, the preparation of alkyl ester polysulphonic PFPE is particularly difficult.

Fluorovinyl alkyl ethers,  $(CF_3)_2C=CFO-R_H$ , were also considered as one of the most efficient but expensive class of alkylating agent for metal perfluoroalkoxides [25]. A high molar yield of HFEs was achieved by using heptafluoro-*iso*-butenyl methyl ether [26] in the reaction with metal perfluoroalkoxides, shown in Figure 6(a). A nonvolatile conjugated base  $(CF_3)_2C=CO^-FK^+$  was formed as by-product after the reaction that can be hydrolyzed into its carboxylic acid  $(CF_3)_2CHC(O)OH$ . Lastly, the carboxylic acid was decarboxylated with an aqueous base to form hexafluoropropane as another valuable product; this reaction is shown in Figure 6(b). Fluorovinyl alkyl ethers are commercially available products and they can also be prepared following the synthetic route described in Figure 6(c): The reaction between perfluoro-*iso*-butene (1) and a proper alcohol produces an octafluoro-*iso*-butyl alkyl ether (2) and by its subsequent dehydrofluorination the alkylating agent (3) and HF are synthesized.

**Figure 6.** (a) Reaction between DAF-PFPEs and fluorovinyl alkyl ethers; (b) Byproduct converted into hexafluoropropane; (c) Synthetic route for alkylating agent -fluorovinyl alkyl ethers.



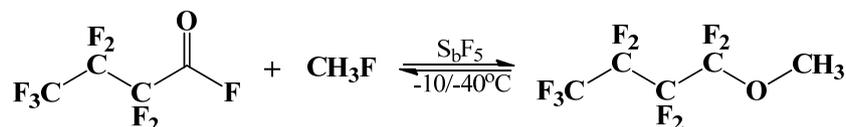
Newly developed alkylating agents which have strong a alkylating ability and less toxicity have been emerging in the past years, but these kinds of alkylating methods have an unavoidable common drawback: A stoichiometric amount of metal fluoride is usually needed to provide metal perfluoroalkoxides, and large amounts of partially reacted solid metal fluoride is left over after the reaction.

### 2.3.2. Catalytic Alkylation of Perfluoro(mono)acyl Fluorides and DAF-PFPE

A classical example of catalytic alkylation is the alkylation of perfluoroacyl fluorides performed by employing  $SbF_5$  as acid catalyst in anhydrous medium that reacts with alkyl fluoride to produce HFE (Figure 7). The first step in this pathway is the reaction of  $SbF_5$  with alkyl fluoride forming high valence metal  $SbF_6^-$ . The extra F ion from  $SbF_6^-$  attacks the carbonyl group of acyl fluorides forming

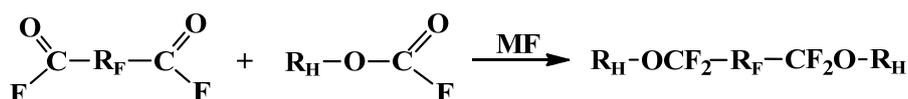
alkoxides. Subsequently, the nucleophilic addition to *in situ* generated alkoxides produces the PFPE with alkoxy-group endings. In this reaction, work-up with a large amount of partially reacted metal fluoride is avoided; however, the drawback of this method is that the active acid catalyst may promote undesired isomerization or decomposition reactions and consequently deliver low or erratic yields [27].

**Figure 7.** Alkylation of acylfluorides with  $\text{SbF}_5$  as acid catalyst.



DA-PFPEs can be also successfully obtained via a novel synthetic route that consists in the reaction of DAF-PFPEs with alkyl fluoroformate (Figure 8) in the presence of a source of fluorine ions, generally metal fluoride (MF); the reaction can be regarded as catalytic alkylation of *in situ* generated PFPE dialkoxides.

**Figure 8.** Reaction between DAF-PFPEs and alkyl fluoroformate with metal fluoride as source fluorine ions.



**Table 1.** Preparation of selected DA-PFPEs through perfluoropolyether acylfluorides alkylation.

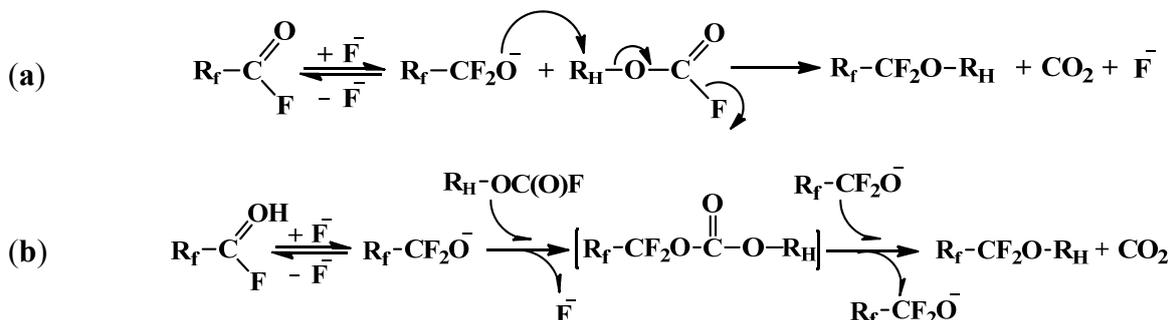
Acylfluoride	Fluoroformate	HFE	Conv.%	Sel.%
z-DAF <sup>a</sup>	$\text{CH}_3\text{OC}(\text{O})\text{F}$	$\text{CH}_3\text{O}-(\text{Z-PFPE})-\text{OCH}_3$	90	100
z-DAF <sup>a</sup>	$\text{CH}_3\text{CH}_2\text{OC}(\text{O})\text{F}$	$\text{CH}_3\text{CH}_2\text{O}-(\text{Z-PFPE})-\text{OCH}_2\text{CH}_3$	96	100
z-DAF <sup>a</sup>	$\text{CH}_2=\text{CHCH}_2\text{O}(\text{O})\text{F}$	$\text{CH}_2=\text{CHCH}_2\text{O}-(\text{Z-PFPE})-\text{OCH}_2\text{CH}=\text{CH}_2$	90	100

<sup>a</sup> linear DAF-PFPE:  $\text{FC}(\text{O})\text{CF}_2\text{O}-(\text{CF}_2\text{CF}_2\text{O})_n(\text{CF}_2\text{O})_m-\text{CF}_2\text{C}(\text{O})\text{F}$  (AMW 620 amu).

This fluoride-catalyzed fluoroformates alkylating reaction gives DA-PFPEs in good yield and  $\text{CO}_2$  is the only by-product. Due to the big differences of boiling points among alkyl fluoroformates, DAF-PFPE and DA-PFPEs, un-reacted alkylating reagents can be easily restored through a standard distillation. Alkyl fluoroformate can be methyl, ethyl as well as allyl fluoroformates. The great variety of fluoroformate alkylating reagents improves the utility of this straightforward alkylating reaction. Examples of several successfully employed fluoroformates, which reacted with high boiling point linear DAF-PFPE with good selectivity and yield are reported in Table 1 [28,29].

This catalytic alkoxides alkylation followed two supposed pathways (Figure 9): (a) A nucleophilic addition of the perfluoroalkoxide to alkyl fluoroformate directly forming the DA-PFPE and  $\text{CO}_2$ ; or (b) through the carbonate intermediate,  $\text{R}_\text{F}\text{CFOC}(\text{O})\text{OR}_\text{H}$ , followed by a second nucleophilic substitution to generate the corresponding products [28]. According to both pathways, the rearrangement of the fluoroformate group can release fluorides and replenish the perfluoro-alkoxy-anions formation by reacting with a new acylfluoride. Therefore, alkyl fluoroformates can be applied not only as alkylating agents but also as an alternative fluorine ion source for the alkoxide formation.

**Figure 9.** Reaction mechanism for the synthesis of DM-FPEs. For clarity, here using  $R_f-C(O)F$  to represent DAF-PFPEs.



The alkyl fluoroformates are not commercially available and their synthesis comprises the reaction of carbonyl difluoride with alcohols at a low temperature in the presence of anhydrous sodium fluoride. The main by-products of their synthesis are alkyl carbonate,  $R_HOC(O)OR_H$ , and hydrogen fluoride. Alkyl carbonate is formed by further reaction of the forming methyl fluoroformate with alcohol. Hydrogen fluoride can be rapidly scavenged by sodium fluoride [30].

### 3. Chemical Physical Properties of $\alpha,\omega$ -Dialkoxyperfluoropolyethers

One of the most representative classes of DA-FPEs is that of  $\alpha,\omega$ -dimethoxyfluoropolyethers (DM-FPEs) with the structure  $CH_3O(CF_2CF_2O)_n(CF_2O)_mCH_3$  (where the indices  $n$  and  $m$  define the random distribution of the related moieties content). In Table 2, the structures and molecular weights of four DM-FPEs samples are reported. The chemical structure is also identified by two digit numbers (*i.e.*, 01, 02, 03 and 13): The first digit indicates the number of  $-CF_2O-$  units and the second digit indicates the number of  $-CF_2CF_2O-$  units in the molecule.

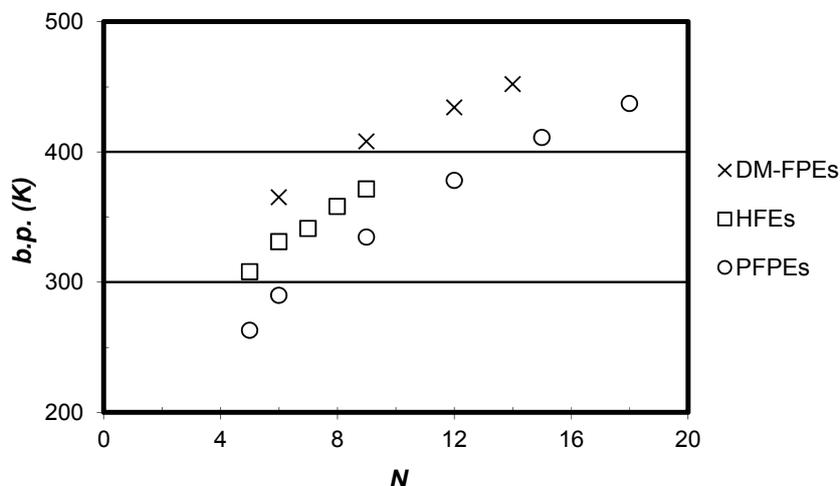
**Table 2.** Structure, molecular weight (MW) and purity of DM-FPEs samples.

Sample	Structure	MS	Purity (% by GC)
DM01	$CH_3OCF_2CF_2OCH_3$	162	99.8
DM02	$CH_3OCF_2CF_2OCF_2CF_2OCH_3$	278	99.9
DM03	$CH_3OCF_2CF_2OCF_2CF_2OCF_2CF_2OCH_3$	394	99.0
DM13	$CH_3OCF_2CF_2OCF_2OCF_2CF_2OCF_2CF_2OCH_3$	460	96.8

#### 3.1. Boiling Point

The boiling points (*b.p.*) of DM-FPEs are reported in Figure 10 as a function of the number of backbone chain atoms ( $N$ ), *i.e.*, carbon plus oxygen atoms. They increase regularly with  $N$ . In Figure 10, DM-FPEs boiling points are also compared with those of  $\alpha,\omega$ -dihydrofluoroethers (HFES) [31] and perfluoropolyethers (PFPEs) [32].

**Figure 10.** Boiling points as a function of the number of chain atoms,  $N$ , for DM-FPEs ( $\times$ ), HFES ( $\square$ ) and PFPEs ( $\circ$ ).



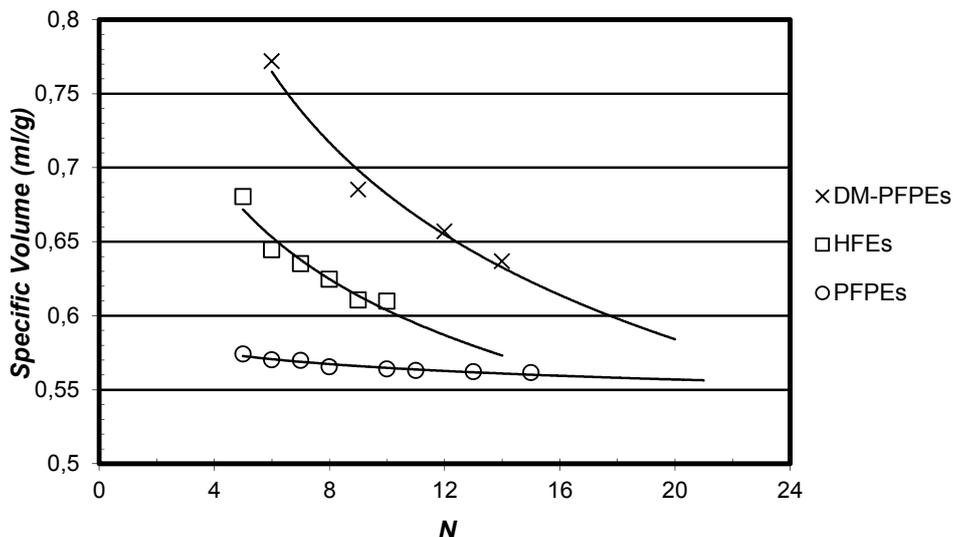
The highest boiling points are those of DM-FPEs, the intermediates are HFES and the lowest ones are PFPEs. The above-mentioned result reflects the typical low intermolecular interactions of perfluorinated compounds. Partially fluorinated ethers, like HFES and DM-FPEs, display higher boiling temperatures and this is indicative of greater intermolecular polar interactions [11].

Considering three similar fluoromethylethers,  $\text{CF}_3\text{OCF}_3$  (b.p. 214 K;  $\mu = 0.49$  D),  $\text{CF}_2\text{HO CF}_3$  (b.p. 238 K,  $\mu = 1.18$  D) and  $\text{CH}_3\text{OCF}_3$  (b.p. 250 K,  $\mu = 2.56$  D), the boiling points and the dipole moments have analogous tendencies [33]. The progressive substitution of fluorine atoms with hydrogen in the methoxy end caps leads to a stronger dipole and consequently, to an increase of the boiling point, as shown in Figure 10. The boiling point differences between PFPEs and HFES and between PFPEs and DM-FPEs are not constant but decrease continuously with the chain length. Since the attractive forces are due to polar terminal groups, their relative intensity decreases as  $N$  increases and, as a result, the boiling points of HFES, DM-FPEs and PFPE tend to an asymptote at higher  $N$  values.

### 3.2. Density

A comparison of the specific volume ( $V_{sp}$ ) at 298 K of DM-FPEs, HFES and PFPEs series is shown in Figure 11. The DM-FPEs sequence shows the highest specific volume and the PFPEs the lowest at identical number of chain atoms,  $N$ . The  $V_{sp}$  of PFPEs is almost constant and independent of  $N$ . The specific volumes of DM-FPEs and HFES decrease continuously to a plateau that approximately coincides with the constant  $V_{sp}$  of PFPEs. This behavior can also be explained on the basis of the differences between terminal groups. Moving from  $-\text{CF}_3$  to  $-\text{CF}_2\text{H}$  and to  $-\text{CH}_3$ , the molecular weight of the groups diminishes; on the contrary, the variation of volume is less noticeable because the Van der Waals radii of fluorine and hydrogen are similar [34]: 0.147 and 0.12 nm, respectively. Consequently, the difference in specific volume between the three series is mainly due to the variation of molecular weight, explaining the tendencies of  $V_{sp}$  observed in Figure 11. Furthermore, as the weight fraction of the chain ends decreases with  $N$ , it is logical that the specific volume of HFES and DM-FPEs tends to the  $V_{sp}$  values of PFPEs when the chain is sufficiently long.

**Figure 11.** Specific volume at 298 K as a function of the number of chain atoms,  $N$ , for DM-FPEs ( $\times$ ), HFEs ( $\square$ ) and PFPEs ( $\circ$ ).

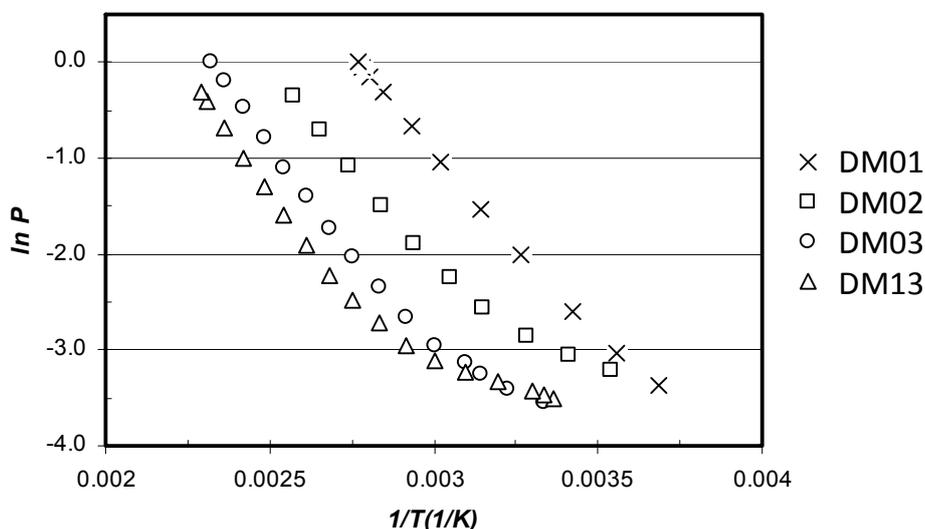


### 3.3. Vapor Pressure and Vaporization Enthalpy

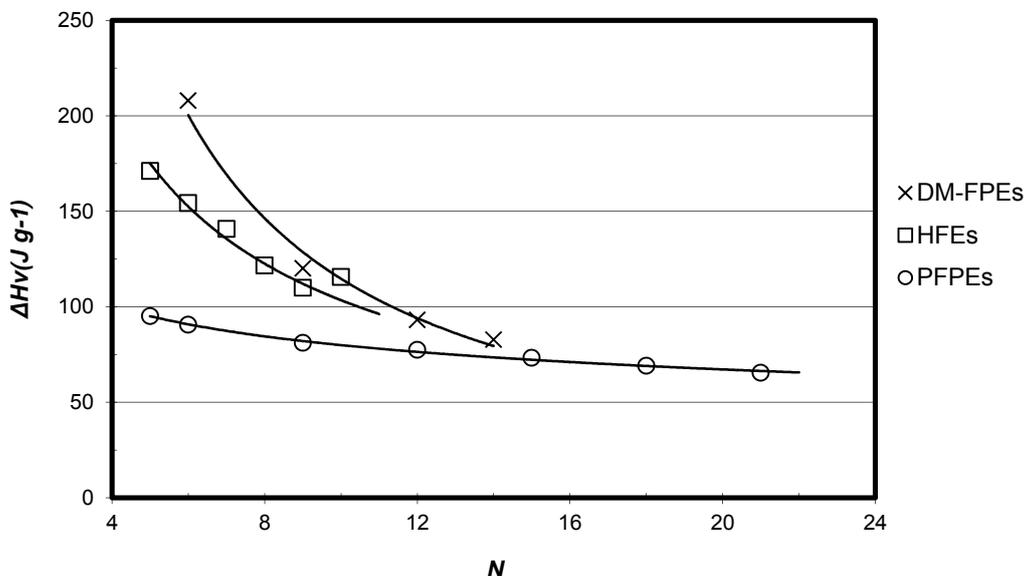
The vapor pressure data, plotted as Clausius-Clapeyron equation in Figure 12, show a deviation from linearity at low temperatures, which is common for many oligomeric substances. Vaporization enthalpies ( $\Delta H_v$ ) are also derived from the Clausius-Clapeyron plot in the range of temperatures in which the function is linear.

The  $\Delta H_v$  data of DM-FPEs, reported as a function of number of chain atoms,  $N$ , are compared with those of HFEs and PFPEs in Figure 13. These data indicate the highest values for DM-FPEs, intermediate for HFEs and the lowest for PFPEs. As the effect of the polar terminal groups ( $-\text{OCF}_2\text{H}$  and  $-\text{OCH}_3$ ) diminishes with the length of the chain,  $\Delta H_v$  also decreases and tends to the values of PFPEs when  $N$  is above 15 [4].

**Figure 12.** Clausius-Clapeyron plot for DM-FPEs: DM01 ( $\times$ ), DM02 ( $\square$ ), DM03 ( $\circ$ ) and DM13 ( $\Delta$ ). (See also Table 2 for detailed composition of these DM-FPEs samples.)



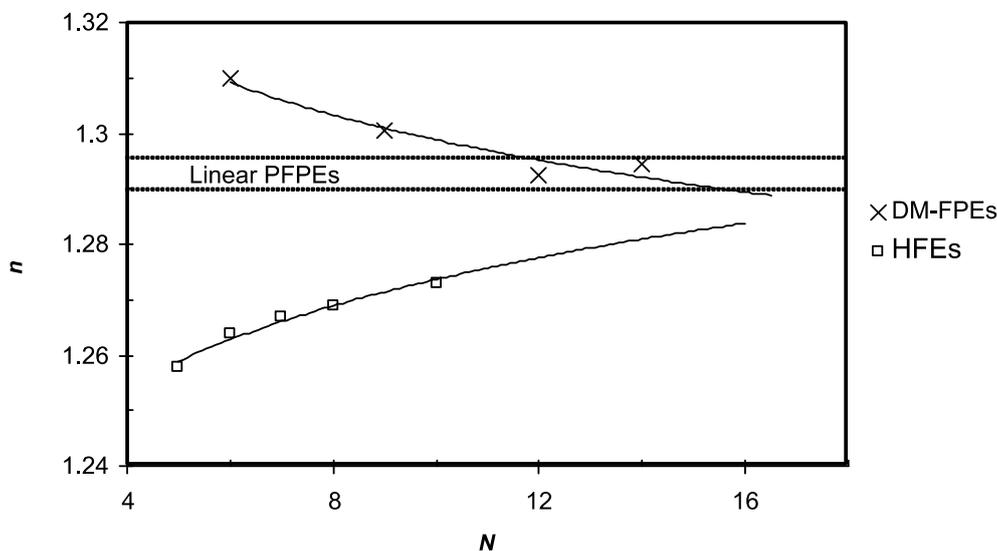
**Figure 13.** Vaporization enthalpy,  $\Delta H_v$ , as a function of the number of chain atoms,  $N$ , for DM-FPEs ( $\times$ ), HFEs ( $\square$ ) and PFPEs ( $\circ$ ).



### 3.4. Refractive Index

The refractive indices of the series DM-FPEs and HFEs plotted as a function of the number of chain atoms,  $N$ , indicate two opposed behaviors (Figure 14). In particular the refractive index  $n$  increases for DM-FPEs and decreases for HFEs. In both cases, increasing the chain length, the refractive indices tend to a plateau value, close to the characteristic refractive index of linear PFPEs (1.290–1.295) [11]. The tendencies of DM-FPEs and HFEs refractive indices are mainly due to the terminal groups that contribute to  $n$  in an opposite way. As reported in the literature, the group influence of  $-\text{OCH}_3$  is higher than that of  $-\text{OCF}_3$ , while that of  $-\text{OCF}_2\text{H}$  is lower [35].

**Figure 14.** Refractive index ( $n$ ) at 293 K as a function of the number of chain atoms,  $N$ , for DM-FPEs ( $\times$ ) and HFEs ( $\square$ ), and the range of refractive index of linear PFPEs.



#### 4. Atmospheric Chemistry of DA-FPEs

The absence of chlorine atoms in HFEs makes them possess a negligible ozone depleting potential (ODP), but the presence of C-F and C-O bonds may absorb in the terrestrial infrared radiation region (800–1200  $\text{cm}^{-1}$ ), and could play a significant role as a greenhouse gas. Therefore, considerable attention has been paid in recent years to perform both experimental and theoretical studies on atmospheric chemistry of HFEs. However, surprisingly, only relatively little information about DA-FPEs has been reported [36,37]. Since the only available data on DA-FPEs compounds are related to DM-FPEs with structure  $\text{CH}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_n\text{CH}_3$  that only contain the  $-(\text{CF}_2\text{CF}_2\text{O})-$  units, the discussion has been focused prevalently on the atmospheric chemistry of these compounds.

##### 4.1. Atmospheric Lifetimes and Decomposition Mechanism of $\alpha,\omega$ -Dialkoxyperfluoropolyethers

In 2004, the first understanding of the atmospheric chemistry for DM-FPEs was achieved by studying the kinetics and mechanism of  $\text{CH}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_n\text{CH}_3$  ( $n = 1-3$ ) oxidation which is initiated by Cl atoms and OH radicals in the atmosphere; the impact of their degradation products on the climate were also discussed [1]. Like most organic compounds, the primary tropospheric degradation of  $\text{CH}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_n\text{CH}_3$  is mainly dominated by the attack of OH radicals [38]. Understanding of reaction kinetics is essential for the evaluation of the atmospheric lifetime of these molecules. In addition to the reaction with hydroxyl radicals (OH), organic compounds can also be removed from the atmosphere via photolysis, wet deposition, and reaction with  $\text{NO}_3$  radicals, Cl atoms, and  $\text{O}_3$  [38–40]. For saturated compounds such as  $\text{CH}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_n\text{CH}_3$ , reactions with  $\text{NO}_3$  radicals and  $\text{O}_3$  are typically too slow to be of importance [1]. The average concentration of Cl atoms in the troposphere is orders of magnitude less than that of OH radicals [41]. Reaction with Cl atoms will be a less significant atmospheric loss mechanism. Since ethers do not absorb at UV wavelengths  $> 200$  nm, photolytic sink will be not be an important degradation pathway [42] either. Highly fluorinated molecules, such as  $\text{CH}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_n\text{CH}_3$ , are hydrophobic and wet deposition is unlikely to be of importance. In conclusion, the atmospheric lifetime of  $\text{CH}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_n\text{CH}_3$  is determined by its reaction with OH.

Smog chambers equipped with FTIR spectrometers were used to study the Cl atom and OH radical initiated oxidation of  $\text{CH}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_n\text{CH}_3$  in 720 Torr of air at 296.3 K. Relative rate methods were used to measure  $k(\text{Cl}+\text{CH}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_n\text{CH}_3) = 3.7 (\pm 0.7) \times 10^{-13}$  and  $k(\text{OH}+\text{CH}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_n\text{CH}_3) = 2.9 (\pm 0.5) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \cdot \text{s}^{-1}$ . The relative rate method is widely used to measure the reactivity of OH radicals with organic compounds [43]. The hydrogen abstraction reaction from the terminal groups has been assumed, according to established literature data, as the rate-determining step for the decomposition of the entire molecule [44]. It is well known that  $-\text{CF}_2\text{CF}_2-$  units are unreactive toward Cl and OH radicals. Thus, the reactivity of  $\text{CH}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_n\text{CH}_3$  is confined to the C–H bonds on either end-groups of the molecule. Indeed, appropriate studies showed that the reactivity of the methyl group did not change noticeably by increasing the number  $n$  of  $-(\text{CF}_2\text{CF}_2\text{O})-$  units from 1 to 3 [45]. Nevertheless, the average concentration of Cl atoms in the troposphere is orders of magnitude less than that of OH radicals [41]. Thus, knowing the  $k(\text{OH}+\text{CH}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_n\text{CH}_3)_s$  rate constant, the DM-FPEs atmospheric lifetime has been evaluated to be two years [1].

Tuazon *et al.* claimed that in air the oxidation of HFEs with difluoromethoxy ending groups,  $\text{OCF}_2\text{H}$ , like  $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H}$ ,  $\text{HCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H}$ , and  $\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$ , gives  $\text{C}(\text{O})\text{F}_2$  as the only carbon-containing product [46]. For DM-PFEs which end with methoxy-groups, fluoroformates  $\text{CH}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_n\text{C}(\text{O})\text{H}$  were recognized as the only oxidation decomposition products with a 100% yield; the formed fluoroformates can be further oxidized to di-formates  $\text{H}(\text{O})\text{CO}(\text{CF}_2\text{CF}_2\text{O})_n\text{C}(\text{O})\text{H}$  [1]. Concerning the impacts of fluoroformates on the climate, since fluorinated esters are known to be easily hydrolyzed [46,47], it is usually assumed that they can be easily removed through wet deposition; therefore Andersen *et al.* [1] deduced that formate  $\text{CH}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_n\text{C}(\text{O})\text{H}$  is not expected to be persistent or pose any significant environmental hazard. However, Bravo *et al.* [48] assumed that the highly fluorinated nature of fluoroformates may decrease their solubility in water and could contribute a significant indirect GWP. Up to now, due to the lack of experimental data like gas-to-water equilibrium and solubility test of fluoroformates, it is still unclear how rapidly fluoroformates will be removed via uptake and hydrolysis in rain/cloud/seawater [49]. Further experimental examinations are needed for the determination of the atmospheric implication of fluoroformates.

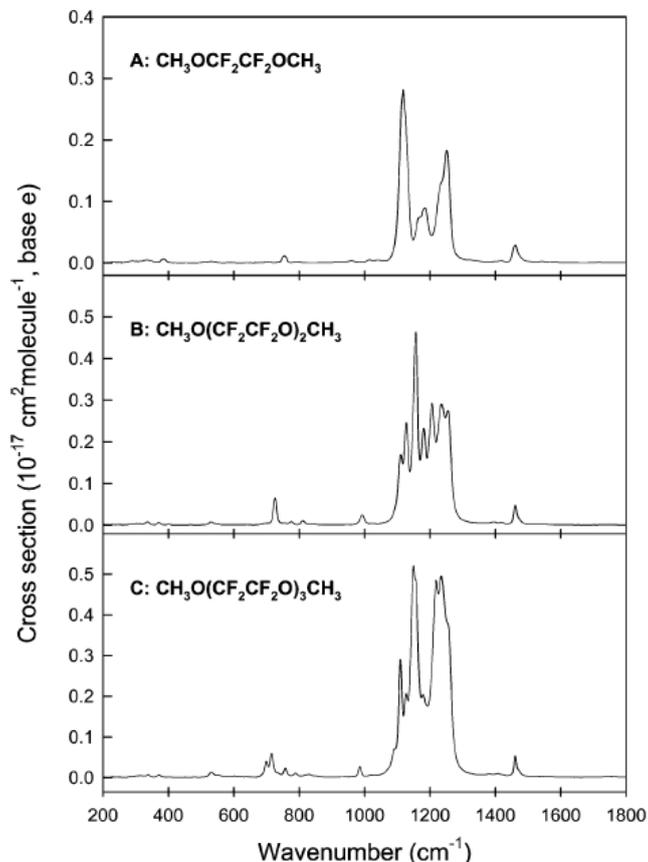
#### 4.2. Global Warming Potential

In 1995, Pinnock *et al.* outlined a method to determine the instantaneous forcings (IF) from the IR absorption spectra such as those reported in Figure 14. As the values of GWP can be estimated on the basis of the IF, in Table 3 GWP relative to carbon dioxide of DM-FPEs at 100 year time horizons has been reported, and the comparison with other greenhouse gases, such as  $\text{CF}_3\text{Cl}$  (CFC-11),  $\text{CF}_2\text{HO}(\text{CF}_3)$  (HFE125),  $\text{CH}_3\text{OCF}_3$  (HFE143a) and other HFEs, is reported in Table 3.

**Table 3.** Atmospheric lifetimes and global warming potential (GWP relative to carbon dioxide) of DM-FPEs, CFC and HFE.

	IF ( $\text{W}\cdot\text{m}^{-2}\cdot\text{ppb}^{-1}$ )	Lifetime (y)	GWP 100 years Time horizon	Reference
$\text{CFCl}_3$ (CFC11)	0.25	45	4750	IPCC/TEAP
$\text{CF}_2\text{HO}(\text{CF}_3)$ (HFE125)	0.44	136	14900	IPCC/TEAP
$\text{CH}_3\text{OCF}_3$ (HFE143a)	0.27	4.3	756	IPCC/TEAP
$\text{C}_4\text{F}_9\text{OCH}_3$ (HFE-7100)	0.31	5	390	[50]
$\text{HCF}_2\text{OCF}_2\text{H}$	0.40	11.3	3699	[8,9]
$\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{H}$	0.66	12.1	2700	[50]
$\text{HCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H}$	0.87	6.2	1500	[50]
$\text{HCF}_2\text{OCF}_2\text{OCF}_2\text{CF}_2\text{OCF}_2\text{H}$	1.37	6.3	1840	[8,9]
$\text{CH}_3\text{OCH}_3$	0.020	0.015	0.3	[41,42]
DM01	0.32	2	230	[1]
DM02	0.61	2	270	[1]
DM03	0.83	2	250	[1]

**Figure 15.** Infrared spectra of  $\text{CH}_3\text{OCF}_2\text{CF}_2\text{OCH}_3$  (A),  $\text{CH}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_2\text{CH}_3$  (B), and  $\text{CH}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_3\text{CH}_3$  (C).



It is evident from Table 3 that DM-FPEs have relatively high instantaneous forcing (IF) but much lower GWPs, if compared with CFC11 and HFE compounds. In addition, the higher the number of  $-(\text{CF}_2\text{CF}_2\text{O})-$  units, the higher the absorption in the  $800\text{--}1200\text{ cm}^{-1}$  range, that is responsible for the high IF. Thus the reason of the mitigation of DM-FPEs GWP is mostly due to their short atmospheric lifetimes and the emission of DM-FPEs into the atmosphere should not contribute significantly to the climate change.

On the basis of the data of DM-FPEs which contain only  $-(\text{CF}_2\text{CF}_2\text{O})-$  units and the studies on series of HFPE with  $-\text{CF}_2\text{H}$  end-groups [51], it seems reasonable to expect that the reactivity of C–H bonds is independent from the number of  $-\text{CF}_2\text{O}-$  units in the DM-FPE molecule. However, there are no available kinetic data for DM-FPEs with structure  $\text{CH}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_n(\text{CF}_2\text{O})_m\text{CH}_3$  to confirm this assumption.

In addition, DM-FPE commercial products are mixtures of homologous copolymers with similar lengths but different unites, *i.e.*, different  $n$  and  $m$ ; further experimental studies are most likely necessary for a better understanding of the effects of the  $(\text{CF}_2\text{CF}_2\text{O})_n/(\text{CF}_2\text{O})_m$  ratio on atmospheric chemistry of DM-FPEs.

## Acknowledgements

The authors wish to acknowledge the generous support from Solvay-Solexis Fluorine Chemistry Chair contributed to this study.

## References

1. Andersen, M.P.S.; Hurley, M.D.; Wallington, T.J.; Blandini, F.N.; Jensen, R.; Librando, V.; Hjorth, J.; Marchionni, G.; Avataneo, M.; Visca, M.; *et al.* Atmospheric chemistry of  $\text{CH}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_n\text{CH}_3$  ( $n = 1-3$ ): Kinetics and mechanism of oxidation initiated by Cl atoms and OH radicals, IR spectra, and global warming potentials. *Phys. Chem. A* **2004**, *108*, 1964–1972.
2. WMO (World Meteorological Organization). Scientific Assessment of Ozone Depletion: 2002, Global Ozone Research and Monitoring Project; Report No. 47, Geneva, Switzerland, 2003.
3. Wallington, T.J.; Schneider, W.F.; Sehested, J.; Bilde, M.; Platz, J.; Nielsen, O.J.; Molina, M.J. Atmospheric chemistry of HFE-7100 ( $\text{C}_4\text{F}_9\text{OCH}_3$ ): Kinetics of its reaction with OH radicals, UV spectra and kinetic data for  $\text{C}_4\text{F}_9\text{OCH}_2\cdot$  and  $\text{C}_4\text{F}_9\text{OCH}_2\text{O}_2\cdot$  radicals, and the atmospheric fate of  $\text{C}_4\text{F}_9\text{OCH}_2\text{O}\cdot$  radicals. *J. Phys. Chem. A* **1997**, *101*, 8264–8274.
4. Marchionni, G.; Avataneo, M.; de Patta, U.; Maccone, P.; Pezzin, G. Physical properties of four alpha-omega-dimethoxyfluoropolyethers. *J. Fluor. Chem.* **2005**, *126*, 465–473.
5. Marchionni, G.; de Patta, U.; Avataneo, M. Liquid-liquid extraction of polar organic substances from their aqueous solutions with fluorinated extracting liquids. European Patent Application, EP 1346757 A, 24 September 2003.
6. Marchionni, G.; Visca, M. Perfluoropolyethers (PFPEs) having at least an alkylether end group and respective preparation process. *European Patent Application*. EP 1275678, 23 April 2003.
7. Marchionni, G.; Petricci, S.; Guarda, P.A.; Spataro, G.; Pezzin, G. The comparison of thermal stability of some hydrofluoroethers and hydrofluoropolyethers. *J. Fluor. Chem.* **2004**, *125*, 1081–1086.
8. Marchionni, G.; Maccone, P.; Pezzin, G. Thermodynamic and other physical properties of several hydrofluoro-compounds. *J. Fluor. Chem.* **2002**, *118*, 149–155.
9. Malavasi, M.; Sianesi, D. Novelties and prospects in the synthesis of perfluoropolyethers by oxidative polymerization of fluoroolefins. *J. Fluor. Chem.* **1999**, *95*, 19–25.
10. Guarda, P.A.; Barchiesi, E.; Fontana, G.; Petricci, S.; Pianca, M.; Marchionni, G. Peroxidic perfluoropolyether from tetrafluoroethylene oxidation: Micro structural analysis by NMR spectroscopy and mechanistic considerations. *J. Fluor. Chem.* **2005**, *126*, 141–153.
11. Sianesi, D.; Marchionni, G.; de Pasquale, R.J. Perfluoropolyethers (PFPEs) from perfluoroolefin photooxidation: Fomblin<sup>®</sup> and Galden<sup>®</sup> fluids. In *Organofluorine Chemistry Principles and Commercial Applications*; Bank, R.E., Smart, R.E., Tatlow, J.C., Eds.; Plenum Publishing Corporation: New York, NY, USA, 1994; pp. 431–457.
12. Sansotera, M.; Navarrini, W.; Gola, M.; Bianchi, L.C.; Wormald, P.; Famulari, A.; Avataneo, M. Peroxidic perfluoropolyether for the covalent binding of perfluoropolyether chains on carbon black surface. *J. Fluor. Chem.* **2011**, *132*, 1254–1261.
13. Navarrini, W.; Venturini, F.; Sansotera, M.; Ursini, M.; Metrangolo, P.; Resnati, G.; Galimberti, E.; Barchiesi, E.; Dardani, P. The use of perfluoroalkyl hypofluorites for an efficient synthesis of perfluorinated ethers characterized by low Ostwald coefficient. *J. Fluor. Chem.* **2008**, *129*, 680–685.

14. Sianesi, D.; Caporiccio, G. Sulphonic derivatives having the structure of polyoxapoly fluoroalkanes. U.S. Patent, 3,847,978, 23 December 1974.
15. Prakash, G.K.S.; Hu, J.; Olah, G.A. Alkylation of in situ generated fluorinated alkoxides: Novel synthesis of partially fluorinated ethers. *Arkivoc SD-369C* **2003**, 104–119.
16. Evans, F.W.; Litt, M.H.; Weidler-Kubanee, A.M.; Avonda, F.P. Formation of adducts between fluorinated ketones and metal fluorides. *J. Org. Chem.* **1968**, *33*, 1837–1839.
17. Parker, A.J. The effects of solvation on the properties of anions in dipolar aprotic solvents. *Q. Rev. Chem. Soc.* **1962**, *16*, 163–187.
18. Lerman, O.; Rozen, S. Novel method for introduction of the perfluoroethoxy group using elemental fluorine. Synthesis and chemistry of fluoroxypentafluoroethane. *J. Org. Chem.* **1980**, *45*, 4122–4125.
19. Navarrini, W.; Tortelli, V.; Russo, A.; Corti, S. Organic hypofluorites and their new role in industrial fluorine chemistry. *J. Fluor. Chem.* **1999**, *95*, 27–39.
20. Feiring, E.A.; Wonchoba, R.E.; Rozen, S. Synthesis of partially fluorinated monomers and polymers for ion-exchange resins. *J. Fluor. Chem.* **1999**, *93*, 93–101
21. Croix, L.S.; Szur, A.J. Ether compounds as inhalant anesthetics. U.S. Patent, 3,962,460, 8 June 1976.
22. Paquette, L.A. *Encyclopedia of Reagents for Organic Synthesis*; John Wiley & Sons: Hoboken, NJ, USA, 1995; pp. 2132–2135.
23. Suter, C.M. *The Organic Chemistry of Sulfur*; Wiley & Sons: Hoboken, NJ, USA, 1944; pp. 48–74.
24. Marchionni, G.; Mario, V. PFPEs having at least an alkylether end group and respective preparation process. U.S. Patent, 7,488,852, 10 February 2009.
25. Lamanna, W.M.; Flynn, R.M.; Vitcak, D.R.; Qiu, Z.-M. Catalytic process for making hydrofluoroethers. PCT WO 9947480, 23 September 1999.
26. Behr, F.E.; Cheburkov, Y. Process for preparing hydrofluoroethers. U.S. Patent, 6,023,002, 8 February 2000.
27. Lamanna, W.M.; Flynn, R.M.; Vitcak, D.R.; Qiu, Z.-M. Catalytic process for making hydrofluoroethers. U.S. Patent, 6,046,368, 4 April 2000.
28. Galimberti, M.; Fontana, G.; Resnati, G.; Navarrini, W. New catalytic alkylation of in situ generated perfluoro-alkyloxy-anions and perfluoro-carbanions. *J. Fluor. Chem.* **2005**, *126*, 1578–1586.
29. Navarrini, W.; Galimberti, M.; Fontana, G. Process for preparing hydrofluoroethers. European patent application EP 1462434A, 16 March 2004.
30. Klauke, E. Braden, R. Fluoroformates. GB 1216639, 23 December 1970.
31. Marchionni, G.; Bassi, M.; Fontana, G.; Maccone, P. Ajroldi, J. Some physical chemical properties of alpha-omega dihydroperfluoropolyethers. *J. Fluor. Chem.* **1999**, *98*, 41–54.
32. Marchionni, G.; Ajroldi, G.; Righetti, M.C.; Pezzin, G. Molecular interactions in perfluorinated and hydrogenated compounds: Linear paraffins and ethers. *Macromolecules* **1993**, *26*, 1751–1757.
33. Marchionni, G.; Avataneo, M.; de Patto, U.; Maccone, P.; Pezzin, G. Physical properties of four alpha-omega dimethoxyfluoropolyethers. *J. Fluor. Chem.* **2005**, *126*, 465–473.

34. Bondi, A. Van der waals volumes and radii. *J. Phys. Chem.* **1964**, *68*, 441–451.
35. Le, T.D.; Weers, J.G. Group contribution-additivity and quantum mechanical models for predicting the molar refractions, indexes of refraction, and boiling points of fluorochemicals. *J. Phys. Chem.* **1995**, *99*, 13909–13916.
36. Blowers, P.; Moline, D.M.; Tetrault, K.F.; Wheeler, R.R.; Tuchawena, S.L. Prediction of radiative forcing values for hydrofluoroethers using density functional theory methods. *J. Geophys. Res.* **2007**, *112*, doi: 10.1029/2006JD008098.
37. Blowers, P.; Moline, D.M.; Tetrault, K.F.; Wheeler, R.R.; Tuchawena, S.L. Global warming potentials of hydrofluoroethers. *Environ. Sci. Technol.* **2008**, *42*, 1301–1307.
38. Blanco, M.B.; Teruel, M.A. Atmospheric degradation of fluoroesters (FESs): Gas-phase reactivity study towards OH radicals at 298 K. *Atmos. Environ.* **2007**, *41*, 7330–7338.
39. Blanco, M.B.; Bejan, I.; Barnes, I.; Wiesen, P.; Teruel, M.A. Kinetics of the reactions of chlorine atoms with selected fluoroacetates at atmospheric pressure and 298 K. *Chem. Phys. Lett.* **2008**, *453*, 18–23.
40. Hudlicky, M. *Chemistry of Organic Fluorine Compounds*, 2nd ed.; Ellis Horwood: Chichester, UK, 1976; pp. 255–257.
41. Finlayson-Pitts, B.J.; Pitts, J.N., Jr. *Atmospheric Chemistry: Fundamentals and Experimental Techniques*; John Wiley and Sons: New York, NY, USA, 1986.
42. Calvert, J.G.; Pitts, J.N., Jr. *Photochemistry*; John Wiley: New York, NY, USA, 1966.
43. Atkinson, R.; Baulch, D.L.; Cox, R.A.; Crowley, J.N.; Hampson, R.F.; Hynes, R.G.; Jenkin, M.E.; Rossi, M.J.; Troe, J.; Wallington, T.J. Evaluated kinetic and photochemical data for atmospheric chemistry: Volume IV—Gas phase reactions of organic halogen species. *Atmos. Chem. Phys.* **2008**, *8*, 4141–4496.
44. AFEAS Workshop. *Kinetics and Mechanisms for the Reaction of Halogenated Organic Compounds in the Troposphere*; AFEAS Workshop: Dublin, Ireland, 1993.
45. Pinnock, S.; Hurley, M.D.; Shine, K.P.; Wallington, T.J.; Smyth, T.J. Radiative forcing of climate by hydrochlorofluorocarbons and hydrofluorocarbons. *J. Geophys. Res. Atmos.* **1995**, *100*, 23227–23238.
46. Bunyard, W.C.; Kadla, J.F.; de Simone, M.S. Viscosity effects on the thermal decomposition of bis(perfluoro-2-N-propoxypropionyl) peroxide in dense carbon dioxide and fluorinated solvents. *J. Am. Chem.* **2001**, *123*, 7199–7206.
47. Sansotera, M.; Bianchi, C.L.; Lecardi, G.; Marchionni, G.; Metrangolo, P. Resnati, G.; Navarrini, W. Highly hydrophobic carbon black obtained by covalent linkage of perfluorocarbon and perfluoropolyether chains on the carbon surface. *Chem. Mater.* **2009**, *21*, 4498–4504.
48. Bravo, I.; Diaz-de-mera, Y.; Aranda, A.; Moreno, E.; Nutt, D.R.; Marston, G. Radiative efficiencies for fluorinated esters: Indirect global warming potentials of hydrofluoroethers. *Phys. Chem. Chem. Phys.* **2011**, *13*, 17185–17193.
49. Javadiando, S.M.; Nielsen, J.; Wallington, J.T.; Hurley, D.A.; Owens, G.J. Atmospheric chemistry of n-butanol: kinetics, mechanisms, and products of Cl atom and OH radical initiated oxidation in the presence and absence of NO(x). *Environ. Sci. Technol.* **2007**, *41*, 7389–7395.

50. IPCC. *Climate Change 2001: The Scientific Basis*; IPCC: Geneva, Switzerland, 2001.
51. Wallington, T.J.; Hurley, M.D.; Nielsen, O.J. The radiative efficiency of HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H (Galden<sup>®</sup> PFPEs) revisited. *Int. J. Chem. Kinet.* **2008**, *40*, 819–825.

© 2012 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).