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# Hydrofluoropolyethers

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## Abstract

α,ω-Dihydrofluoropolyethers (HFPEs) have been synthesized by a novel process consisting of radical-initiated oxypolymerization of tetrafluoroethylene, chemical cleavage of peroxy groups, and chemical modification of the resulting difunctional fluoropolyethers. The physicochemical properties of the HFPEs depend upon the molecular weight, and are influenced by their hydrogen atoms. The effect of terminal hydrogens is however reduced with increasing molecular weight. The HFPE molecules show a certain degree of polarity, which allows miscibility with polar solvents. The hydrogen abstraction reaction is a limiting factor in the atmospheric lifetime of this class of products, thus reducing their environmental impact.

The preliminary toxicological tests indicate the products to be substantially nontoxic.

*Keywords:* Hydrofluoropolyethers; Fluorinated fluids; Physicochemical properties; Environmental impact

## 1. Introduction

Fluorinated fluids have covered for several years the high performance end of a number of applications in the most advanced industrial sectors, like semiconductor and electronic industry, aerospace and avionics, transportation in general. The ability of these fluids to withstand the most severe working conditions, their durability and their compatibility with most materials have been the driving force for their development [1].

The major drawback of perfluorinated fluids is strictly connected with one of their most important properties, i.e. the physicochemical inertness and lack of reactivity. As a result, being the reaction with atmospheric radicals, the major sink of foreign molecules in the troposphere, when a perfluorocarbon (PFC) is emitted into the atmosphere, its lifetime will be exceedingly long: values in the order of several thousand years have been published [2,3].

The recently increased attention on the environment and on the effect of anthropogenic emissions on the global climatic changes, as expressed by the Kyoto Protocol, has stated the need for the regulation of the production, use and emission of several classes of products having a high global warming impact. In view of this, the need has risen to design new fluids capable of satisfying the needs of high demanding applications without significant loss in performance but with far reduced global environmental impact. As a further driving force for performing such a task, there exist a number of applications, like precision and electronic cleaning, fire suppression, foaming, where previously used CFCs and halons have not yet found acceptable substitutes.

In the present work, we will describe the synthesis and properties of a novel class of fluids, the α,ω-dihydro-fluoropolyethers (HFPEs):

$$HCF_2O(CF_2CF_2O)_m(CF_2O)_nCF_2H \qquad (1)$$

which could be effective substitutes of CFCs, perfluorocarbons and halons without major drawbacks: we will further present their toxicological properties and will discuss their environmental impact.

## 2. Synthesis of α,ω-dihydrofluoropolyethers

HFPEs are obtained by the combination of a number of technologies, both original [4–6] and already established in the industrial practice or published in scientific papers [7].

These technologies include the oxidative polymerization of fluorinated monomers, the chemical or catalytical cleavage of the peroxy groups in the polyether–polyperoxide precursor to yield substantially difunctional fluoropolyethers, the chemical modification of the terminal groups to yield the final product (1), characterized by the presence of only $OCF_2H$ terminal groups at both end of the molecular chain.

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The most innovative and original step is the controlled oxidative polymerization of tetrafluoroethylene (TFE). This reaction is carried out in the presence of oxygen at a high pressure [5], at a very low temperature (−40°C/−90°C) in a hydrofluorocarbon (HFC) or fluorocarbon (FC) solvent. Elemental fluorine or hypofluorites are used as radical initiators [4]. A peroxide polymeric precursor (2) is formed as a result of the polymerization reaction

$$CF_2{=}CF_2 + O_2 \xrightarrow{F_2} T\text{–}O\text{–}(CF_2CF_2O)_p\text{–}(CF_2O)_q\text{–}(O)_v\text{–}T' \tag{2}$$

whose constituents are fluoroether repeating units ($-CF_2CF_2O-$ and $-CF_2O-$) and interspersed peroxy units ($-CF_2CF_2OO-$ and $-CF_2OO-$). The end groups T and T′ are perfluorinated ($-CF_3$ and $-CF_2CF_3$). Composition of the polymer and reaction yield (>90 mol%) depends on temperature and TFE concentration. Carbonyl fluoride and tetrafluoroethylene oxide are the main by-products. The process and reaction kinetic model are also briefly described in a paper by Malavasi and Sianesi in the same issue of this journal.

The main reaction steps leading to the formation of a specific molecular structure are described below.

The sum of a fluorine atoms to TFE initiates the polymerization reaction. The subsequent addition of oxygen to the fluorinated carbon radicals (3–5) and the addition of tetrafluoroethylene to the alkoxy or peroxy radicals (6–9) are responsible for the chain growth and for the formation of ether and peroxy linkages in the polymer molecule.

(a) *Addition of oxygen*:

$$R_fOCF_2CF_2^{\circ} + O_2 \rightarrow R_fOCF_2CF_2OO^{\circ} \tag{3}$$

$$R_fO_2CF_2CF_2^{\circ} + O_2 \rightarrow R_fO_2CF_2CF_2OO^{\circ} \tag{4}$$

$$R_fOCF_2^{\circ} + O_2 \rightarrow R_fCF_2OO^{\circ} \tag{5}$$

(b) *Addition of alkoxy and peroxy radicals to tetrafluoroethylene*:

$$R_fOCF_2O^{\circ} + CF_2{=}CF_2 \rightarrow R_fOCF_2OCF_2CF_2^{\circ} \tag{6}$$

$$R_fOCF_2CF_2O^{\circ} + CF_2{=}CF_2 \rightarrow R_fOCF_2CF_2OCF_2CF_2^{\circ} \tag{7}$$

$$R_fOCF_2OO^{\circ} + CF_2{=}CF_2 \rightarrow R_fOCF_2O_2CF_2CF_2^{\circ} \tag{8}$$

$$R_fOCF_2CF_2OO^{\circ} + CF_2{=}CF_2 \rightarrow R_fOCF_2CF_2O_2CF_2CF_2^{\circ} \tag{9}$$

The main reactions which are responsible for the overall chain structure are:

(a) *Coupling of peroxy radicals to yield alkoxy radicals and molecular oxygen*:

$$2R_fOCF_2O_2^{\circ} \rightarrow 2R_fOCF_2O^{\circ} + O_2 \tag{10}$$

$$2R_fOCF_2CF_2O_2^{\circ} \rightarrow 2R_fOCF_2CF_2O^{\circ} + O_2 \tag{11}$$

$$R_fOCF_2O_2^{\circ} + R_fOCF_2CF_2O_2^{\circ} \rightarrow R_fOCF_2O^{\circ} + R_fOCF_2CF_2O^{\circ} + O_2 \tag{12}$$

(b) β-*Scission of alkoxy radicals*:

$$R_fOCF_2CF_2O^{\circ} \rightarrow R_fOCF_2^{\circ} + COF_2 \tag{13}$$

The control of the distribution of the ether and peroxide bonds in the polyether–polyperoxide chain is of paramount importance, in that it determines the properties of the final product. In the "classic" PFPE photochemical synthesis, UV irradiation contributes to the increase in the concentration of the ether bonds by cleavage of the peroxides. In the absence of light, control of peroxide just depends on the coupling reaction whose occurrence is mainly controlled by the concentrations of both the monomer and the growing radicals. Of course, final composition is also related to the usual physical parameters, namely temperature, pressure, solvent, and fluidodynamics of the system.

The molecular weight of the precursor polymer is controlled by the termination reaction. In our system, the only significant termination occurs by coupling of peroxy radicals yielding a peroxidic bridge between the reacting molecules

$$2R_fOCF_2O_2^{\circ} \rightarrow R_fOCF_2OOCF_2OR_f + O_2 \tag{14}$$

$$2R_fOCF_2CF_2O_2^{\circ} \rightarrow R_fOCF_2CF_2OOCF_2CF_2OR_f + O_2 \tag{15}$$

$$R_fOCF_2O_2^{\circ} + R_fOCF_2CF_2O_2^{\circ} \rightarrow R_fOCF_2OOCF_2CF_2OR_f + O_2 \tag{16}$$

The control of the molecular weight could be obtained by acting on the same parameters described above; actually, even a strong effect of the nature of the solvent was recorded on the polymer structure [8]. This has been interpreted as the influence of two fundamental parameters: the solvation of the growing polymer chain and the rheology of the concentrated polymer solution at the low temperature.

Subsequent synthetic steps rely on more conventional technologies. The nature of the substrate and the effect of perfluorination on the reactivity of functional groups need, however, nontrivial modifications of the apparently simple chemical reactions involved. The peroxidic linkaged can be cleaved and transformed into functional groups either by the combination of reducing agents and alcohol to yield carboxylic acid esters, or by reaction with hydrogen over a suitable catalyst to substantially bifunctional acyl fluorides.

The acyl fluoride group can then be converted, by decarboxylation in the presence of hydrogen donors, into hydrogen-containing end groups

$$R_fOCF_2COF + OH^- \rightarrow R_fOCF_2H + CO_2 + F^- \tag{17}$$

The chemical structure of the precursor, which does not contain monomer sequences, and the intrinsic instability of fluoroformates ensure the presence of only end groups having structure (17). This is an obvious advantage in terms of reactivity, stability and homogeneous physicochemical, toxicological and environmental behavior of the material throughout its molecular weight distribution.

## 3. Physicochemical properties

### 3.1. Experimental

### 3.1.1. Fractionation and molecular properties

A relatively large polymer sample was separated into fractions having narrow boiling point range by fractional distillation. The composition and purity of the different fractions was characterized by $^{19}$F-NMR, infrared absorption, gas chromatographic analysis and gas chromatographic–mass spectroscopic analysis.

Pure samples of the lower boiling members of the series have also been isolated by distillation, and have been used as calibration samples and to perform some of the more critical characterizations, like the determination of the tropospheric lifetime (see below).

Molecular weight distributions were obtained by GC analysis, using for calibration the monodispersed fractions.

### 3.1.2. NMR and IR spectroscopy

The chemical structure of the fractions and of the crude product were studied by $^{19}$F nuclear magnetic resonance (NMR) measurements, and by infrared spectroscopy. The NMR data were generated using a Varian XL 200 spectrometer. The infrared spectra were obtained from a Nicolet 20S XB spectrometer.

### 3.1.3. Physical properties

The density ($\rho$) of the samples was determined by a picnometer at temperatures in the range −70°C to +100°C.

The pour point temperatures $T_f$ were measured according to the ASTM D97/57 method.

Kinematic viscosity ($\eta$) values were measured at various temperatures with Cannon–Fenske capillary viscometers, according to the ASTM D 445 standard method.

The vapor pressures were measured from −40°C up to the corresponding boiling point of each sample with the temperature controlled within ±0.1°C using a Druck pressure transducer (PDCR 922) combined with a digital pressure indicator (Druck DPI 260).

### 3.1.4. Dielectric constant

Dielectric studies have been performed at room temperature in a frequency range 100 Hz–100 kHz using a Polymer Laboratories DETA analyzer.

### 3.2. Results and discussion

The molecular weight distribution of a crude product and of the four fractions obtained by distillation are reported in Table 1.

In Table 2 the characteristic NMR bands of an HFPE sample are reported, together with the attributions. As an example, the spectrum of fraction B is reported in Fig. 1.

From the integrated band intensities it is possible to determine the structural abundance of different units, the average functionality and the structure of the end groups. From these data it is apparent that the high ratio between $CF_2CF_2O$ ($C_2$) and $CF_2O$ ($C_1$) units in the polymer chain ($C_2/C_1$ typically>4) are indicative of the little importance of the relatively slow β-scission reaction in the polymer growth. As a comparison, a conventional PFPE oil produced by the photochemical route has a $C_2/C_1$ from 0.5 to 1.5. The end groups are practically only $OCF_2H$, the perfluorinated groups accounting for less than 5% of the total.

Table 1
Molecular weight distribution of the different HFPE fractions isolated by distillation from the crude product

$HCF_2O(CF_2O)_n(CF_2CF_2O)_mCF_2H$

| MW | Boiling point (°C) | $n$ | $m$ | Crude | Fraction A | Fraction B | Fraction C | Fraction D |
|---|---|---|---|---|---|---|---|---|
| | | | | | Composition by GC analysis (wt%) | | | |
| 184 | 35 | 1 | 0 | 2.5 | 11.8 | | | |
| 234 | 58 | 0 | 1 | 21 | 88.1 | 0.6 | | |
| 250 | 68 | 2 | 0 | 0 | 0 | 0 | | |
| 300 | 85 | 1 | 1 | 5 | 0.1 | 20.4 | | |
| 350 | 98 | 0 | 2 | 19 | | 75.9 | 0.2 | |
| 366 | 109 | 2 | 1 | 0.5 | | 2 | 0.5 | |
| 416 | 123 | 1 | 2 | 4.5 | | 1 | 17.9 | |
| 466 | 133 | 0 | 3 | 10 | | | 38.8 | |
| 482 | 142 | 2 | 2 | 0.5 | | | 0.7 | |
| 532 | 151 | 1 | 3 | 4.5 | | | 18.1 | |
| 582 | 160 | 0 | 4 | 9 | | | 21.9 | 12 |
| 593 | 169 | 2 | 3 | 5 | | | 1 | 18 |
| 648 | 175 | 1 | 4 | 7.5 | | | 1 | 28 |
| 698 | 183 | 0 | 5 | 8 | | | | 30 |
| 714 | 190 | 2 | 4 | 2 | | | | 8 |
| 764 | 196 | 1 | 5 | 1 | | | | 4 |

Table 2
Assignment of the NMR $^{19}$F peaks of a HFPE fluid

| Structure | Chemical shift (ppm)[a] |
|---|---|
| $\mathrm{-OCF_2CF_2OC\underline{F}_2OCF_2CF_2O-}$ | −51.7 |
| $\mathrm{-OCF_2OC\underline{F}_2OCF_2CF_2O-}$ | −53.4 |
| $\mathrm{-OCF_2CF_2OC\underline{F}_2OCF_2H}$ | −54.2 |
| $\mathrm{-OCF_2OC\underline{F}_2OCF_2O-}$ | −55.1 |
| $\mathrm{-OCF_2OC\underline{F}_2OCF_2H}$ | −55.8 |
| $\mathrm{-OCF_2CF_2OC\underline{F}_3}$ | −56.1 |
| $\mathrm{-OCF_2OC\underline{F}_3}$ | −57.7 |
| $\mathrm{-OCF_2CF_2OC\underline{F}_2H}$ | −85.1 to −85.5 |
| $\mathrm{-OCF_2OC\underline{F}_2H}$ | −86.1 to −86.5 |
| $\mathrm{-OCF_2C\underline{F}_2OCF_2H}$ | −88.6 |
| $\mathrm{-OC\underline{F}_2CF_2OCF_2H}$ | −89.5 |
| $\mathrm{-OCF_2OC\underline{F}_2CF_2O-}$ | −90.3 |
| $\mathrm{-OCF_2C\underline{F}_2C\underline{F}_2CF_2O-}$ | −126 |
| $\mathrm{-OCF_2C\underline{F}_2CF_2O-}$ | −130 |

[a] With reference to $CFCl_3$.

The absence of other structures is confirmed also by the further information obtained by FTIR. The IR spectrum of HFPE fraction B is shown in Fig. 2. The IR spectra have been discussed and interpreted with the help of quantum chemical calculations in a recent paper by Radice et al. [9].

A summary of the physicochemical properties of HFPE fractions is reported in Table 3. In the following, these properties are briefly discussed; a much more detailed review of HFPE properties and an indepth analysis of their relationships with the actual molecular structure is going to be reported in a forthcoming specific paper.

The density $\rho$ data are plotted, for all the samples, in Fig. 3 as a function of temperature. For any given sample, and in a temperature range of practical interest, the density is a linearly decreasing function of the temperature. The thermal expansion coefficient is a function of the reciprocal molecular weight $M_n$: the values for all the samples are around $10^{-3}$°$C^{-1}$. The molecular weight $M_n$ also influences the density, which increases in a rather regular way with $M_n$.

Fig. 4 shows the kinematic viscosity–temperature relationship of the different fractions. The HFPE fluids, like their perfluorinated analogs, are Newtonian, i.e. their viscosity is independent of shear rate. The temperature dependence of the Newtonian viscosity of polymeric melts can be described by the simple Arrhenius equation

$$\ln \eta = A + E_a/RT, \qquad (18)$$

where $E_a$, the so-called flow activation energy, has the physical meaning of a temperature coefficient of viscosity. It has been found that $E_a$ increases slowly with the chain length and is of the order of 12 kJ/mol.

It is interesting to observe that HFPEs have good viscostatic properties. The high flexibility of the polymeric chain of HFPEs originating from the ether bonds provides a large

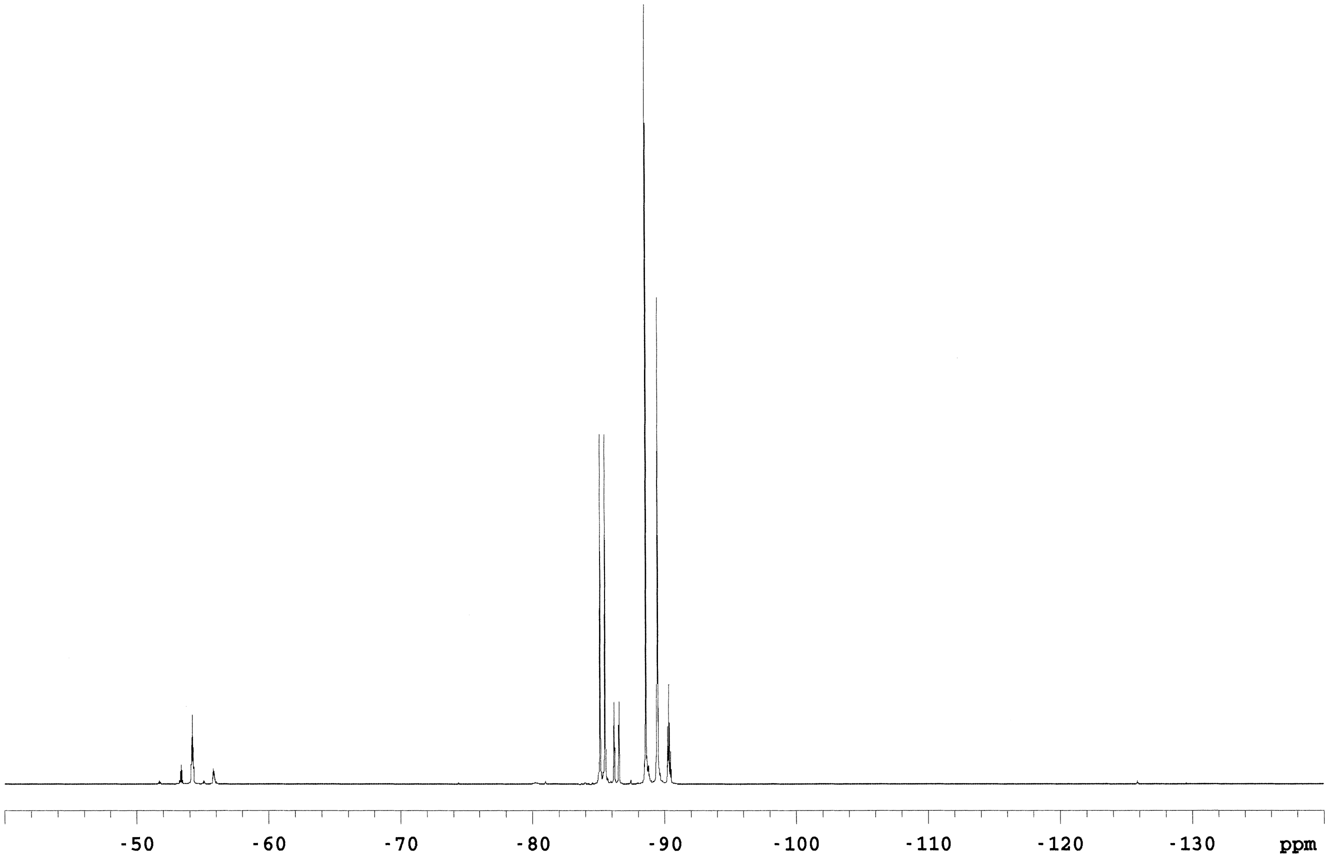

Fig. 1. $^{19}$F-NMR spectrum of hydrofluoropolyether, fraction B.

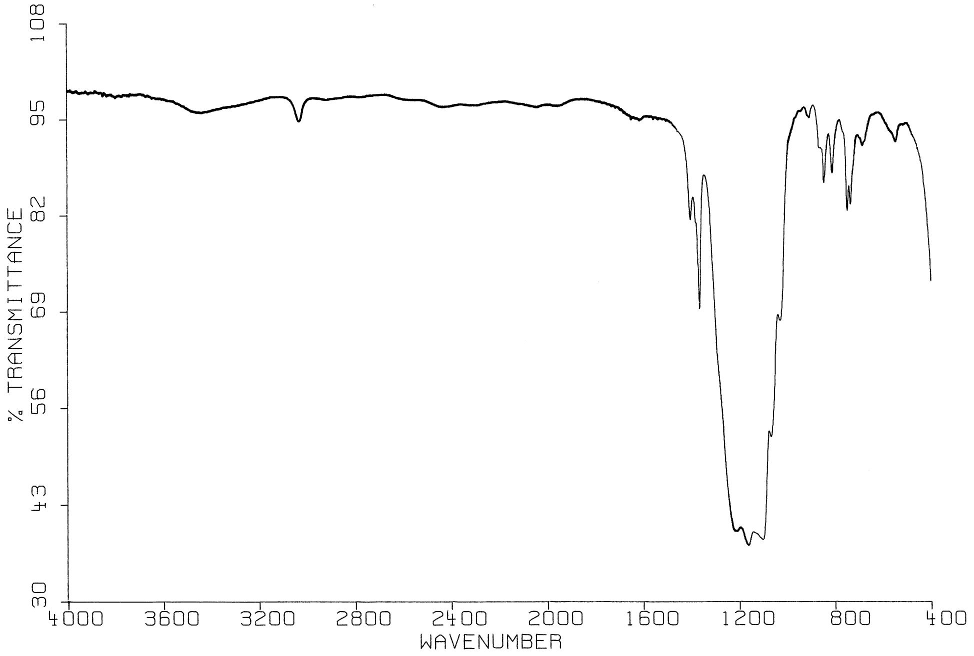

Fig. 2. Infrared spectrum of hydrofluoropolyether, fraction B.

temperature range of liquid state with a good viscosity index. The high flexibility prevents crystallization and explains the low freeze temperatures (pour points). The freeze temperatures have been measured for a series of HFPE fractions. These values, shown in Fig. 5, are related to the molecular weight of the fractions and this relationship can be somewhat rationalized by the equation

$$T_f = A - K/M_n, \tag{19}$$

where a fit could be obtained for a $K$ value of around $5\times10^3$ in a range of molecular weight 200–700.

Fig. 6 shows the vapor pressure of the different HFPE fractions as a function of temperature. The vapor pressure is related to the molecular weight. Within the temperature region of interest, this dependence can be reasonably described by the simplified Clausius–Clayperon equation

$$\log p = A - B/T, \tag{20}$$

where coefficients $A$ and $B$ are constant for each fluid, $T$ the absolute temperature, and $p$ is the vapor pressure. The values of the $\Delta H$ of vaporization of the HFPE fractions are calculated at the boiling point and range between 22 and 29 cal/g. The higher value is shown by the lowest boiling fraction, where the polarity of the molecule and the hydrogen bonding component provide a more significant contribution to the $\Delta H$ of vaporization (Table 3).

In Table 3, the dielectric constant and the volume resistivity are reported as a function of the molecular weight of HFPE. The dielectric constant and resistivity are a distinct function of the molecular weight, and reflect the polarity of

Table 3
Physicochemical properties of hydrofluoropolyether fractions with different boiling point ranges

| Properties | Units | Fraction A | Fraction B | Fraction C | Fraction D |
|---|---|---|---|---|---|
| Molecular weight | | 228 | 342 | 479 | 655 |
| Boiling point | °C | 51.5 | 94.4 | 125.1 | 177.8 |
| Pour point | °C | <−125 | −123 | −115 | −110 |
| Kinematic viscosity | | | | | |
| At −20°C | cSt | 0.71 | 1.25 | 2.61 | 4.74 |
| At 0°C | | 0.52 | 0.86 | 1.61 | 2.58 |
| At 25°C | | 0.37 | 0.59 | 0.89 | 1.50 |
| Density at 25°C | g/cm$^3$ | 1.56 | 1.62 | 1.68 | 1.72 |
| Vapor Pressure at 25°C | torr | 276.3 | 62.4 | 7.9 | 1.8 |
| Heat of vaporization at boiling point | cal/g | 28.9 | 21.8 | 24.1 | – |
| Specific heat | kcal/kg°C | 0.26 | 0.26 | 0.26 | – |
| Dielectric constant | | 5.2 | 4.4 | 3.55 | – |
| Volume resistivity at 1 kHz | ohm cm | $6.8\times10^8$ | $1.5\times10^9$ | $1.5\times10^{10}$ | – |
| Surface tension at 25°C | dyne/cm | 12.9 | 13.7 | 14.6 | 14.6 |
| Water content | ppm | 30 | 30 | 45 | 50 |

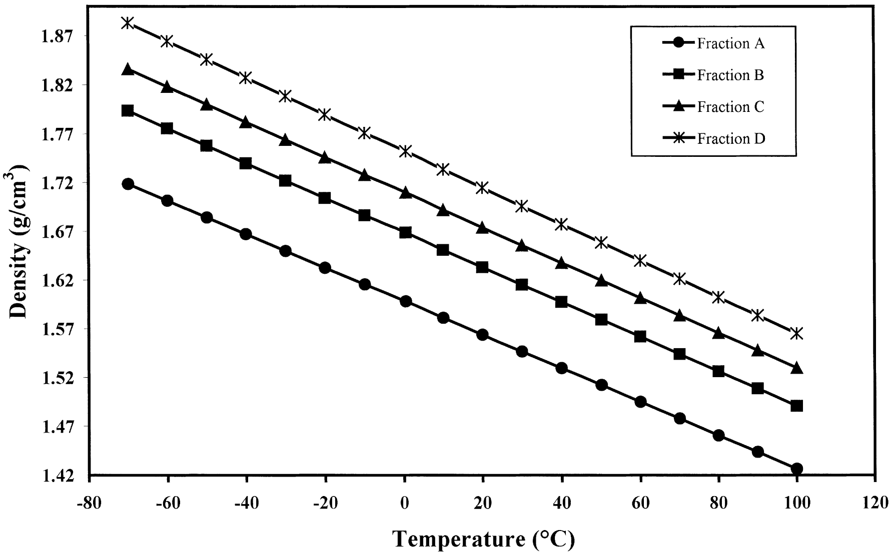

Fig. 3. Dependence of density on temperature for hydrofluoropolyethers.

the molecule. The shorter HFPE molecules behave indeed as quite polar fluids. This was already detected in an earlier work [7], where the miscibility of HFPE with several solvents has been reported. In general, lower boiling fractions show greater miscibility with polar fluids: monophasic regions in ternary diagrams comprising water, alcohols and HFPE have also been reported [10].

In view of their unique structure, and particularly of the presence of hydrogen atoms only in fixed positions, HFPEs show an exceedingly good chemical and thermal stability.

Prolonged contact up to 150°C with highly acidic (concentrated sulfuric, hydrochloric and nitric acids) and alkaline (40% KOH in water) media did not generate any structural degradation in the fluid structure. The fluid also showed high thermal and thermoxidative resistance being unaffected by heating in air at 250°C for 24 h.

## 4. Environmental impact

In evaluating the environmental impact of HFPE fluids, several aspects have been investigated. The toxicological part of the study included specific toxicity effects (acute), and the more general aspects of bioaccumulation and ecotoxicology, mainly related to aquatic environment.

The atmospheric fate of HFPE molecules has been experimentally studied by determining their reactivity with

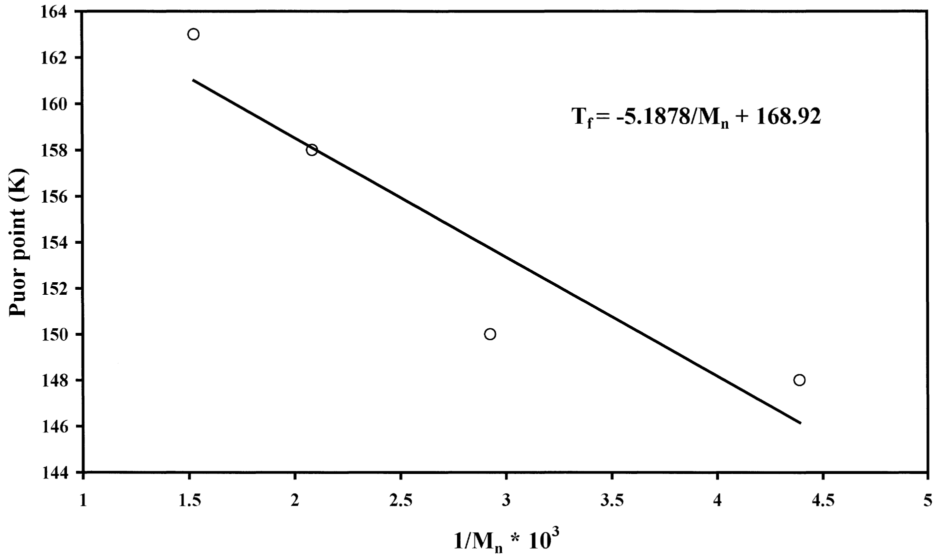

Fig. 4. Dependence of $T_f$ on molecular weight for hydrofluoropolyethers.

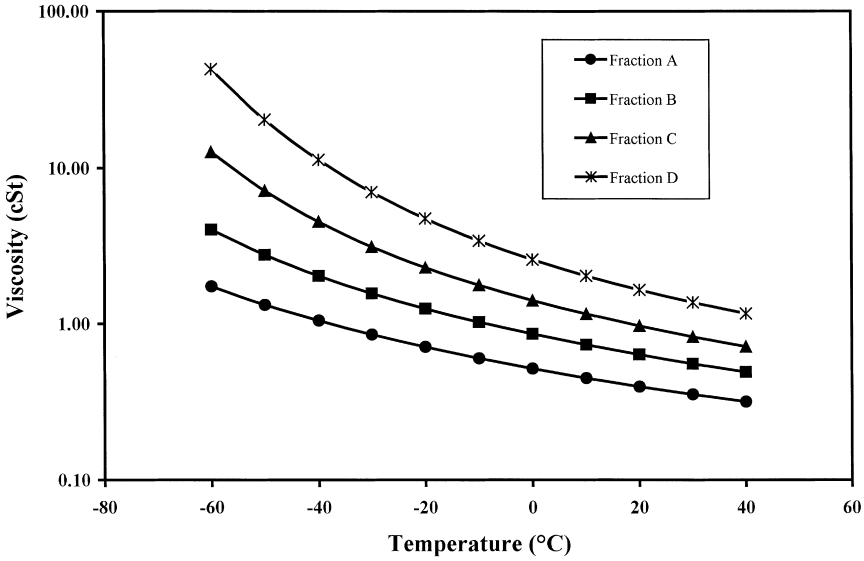

Fig. 5. Viscosity–temperature relationship for hydrofluoropolyethers.

atmospheric radicals, and by evaluating the decomposition mechanism and byproducts formation.

### 4.1. Toxicology

Toxicology of hydrofluoropolyethers has been studied on a polydispersed sample representative of the composition of the crude low boiling product. It comprised the members of the series having boiling temperatures between 40°C and 90°C.

The results are reported in Table 4. The toxicity of the product by oral (acute toxicity is in excess of 5 g/kg), inhalation (no deaths up to the maximum attained vapor concentration of ca. 3% by volume) and dermal ($LD_{50}$>2 g/kg), resulted to be very low. HFPE was non-irritant to the rabbit skin and eye and was devoid of skin sensitization potential in guinea pigs. Anesthetic-like effect has been recorded by inhalation upon exposure to concentrations above 1–1.4% by volume. This fact per se is not indicative of a toxic effect: indeed no tissue alterations have been found even at the highest concentrations following histopathological examination of the lungs as target organs by inhalation route. Very little data is presently available on these structures. However, in an earlier paper [11], weak anesthetic effect at high concentrations was reported for the fluorinated ether

$$HCF_2OCF_2H \quad (21)$$

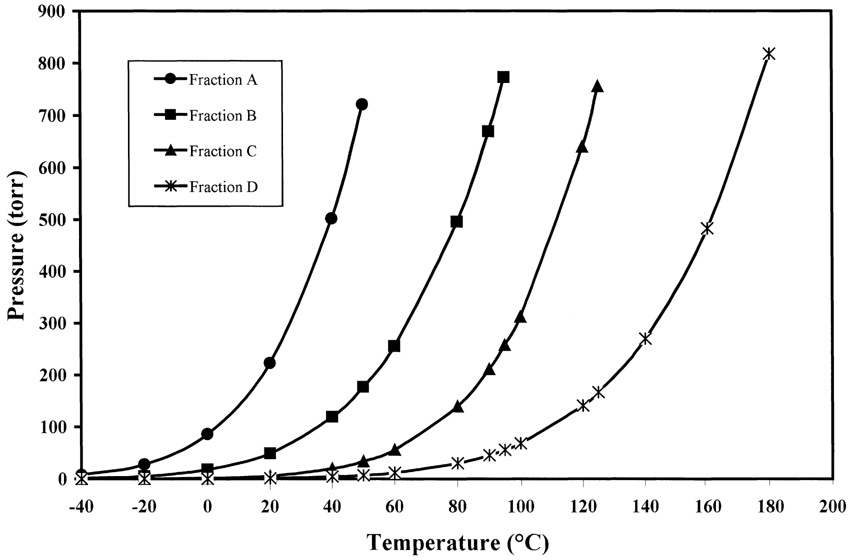

Fig. 6. Temperature dependence of vapor pressure for hydrofluoropolyethers.

Table 4
Acute toxicological tests performed to-date on hydrofluoropolyethers (HFPE fraction MW 320)

| Test | Results |
|---|---|
| Acute oral toxicity | $LD_{50}$>5000 mg/kg |
| 4 h Acute inhalation toxicity | LC50>26 400 ppmv (maximum attainable vapor concentration) |
| | NOEL for anesthetic-like effects between 9500 and 13 802 ppmv |
| | No deaths and no lung damage at all concentrations |
| Acute dermal toxicity | $LD_{50}$>2000 mg/kg |
| Skin sensitization (guinea pigs) | Not a sensitizer |
| Actue dermal irritation (albino rabbit) | Non-irritant |
| Acute eye irritation (rabbit) | Non-irritant |

which is the first representative of the HFPE series ($m=n=0$ in the general formula (1)), while another paper [12] on the same molecule simply reports its low toxicity (no effect up to 1% by volume).

The anesthetic-like effect, which we made evident by testing the product at very high concentrations in air, is rather surprising if compared with the data obtained on other fluids, all of them having perfluoropolyether structure. The results on these fluids, a perfluorinated Galden® HT70 (commercial low boiling fluid of Ausimont SpA), and a fluid having the same structure, but containing a single hydrogen atom on ca. 30% of the terminal groups, showed no effect up to 7–8% by volume concentrations [13]. The effect of the lower boiling components (boiling points 5°C and 35°C), the regular structure, and the strong dipole moment at both ends of the molecule could be assumed as a possible source of the weak anesthetic-like effects detected.

Further investigation is in progress, including repeated dose toxicity studies in rats (28 and 90 days), developmental toxicity studies in pregnant rats, cardiac sensitization in dogs and mutagenesis in vitro and in vivo.

Bioaccumulation potential has been studied by prolonged exposure of fish to a saturated aqueous solution of a HFPE having the same molecular weight distribution as the one used to carry out the toxicological studies. The bioaccumulation factor determined at the end of the experiment was less than 100, indicating a low potential of bioaccumulation in living organisms.

Acute toxicity was also studied in fish (*cyprinus carpio*) under flow-through conditions. The 96 h $LC_{50}$ was observed to be >21.1 mg/l, the highest attainable concentration in water.

Further studies on different aquatic organisms (*daphnia and algae*) are foreseen.

### *4.2. Atmospheric lifetime and decomposition mechanism*

The presence of carbon–hydrogen bonds in the HFPE molecule allows the abstraction of hydrogen by the atmospheric OH radicals. This reaction has been determined to be the fundamental mechanism limiting the atmospheric lifetime of most of the molecules emitted in the troposphere, and reducing their transport into the stratosphere [14].

The first experimental studies have been devoted to determine the decomposition mechanism and the decomposition products of HFPEs, in order to assess the environmental fate of these products, and to identify the possible formation of long-lived or potentially dangerous byproducts. The quantitative experimental study has been carried out upon reaction of three different compounds, having boiling points 35°C, 58°C and 85°C, with chlorine radicals in the gas phase [15]. Highly monodispersed samples obtained by fractionation of the crude HFPE have been used in these experiments.The quantitative determination of the decomposition products has shown that no long-lived or high environmental impact by-products are formed: indeed, the only decomposition product detected was $COF_2$, with measured yields up to 95% for all the compounds. $COF_2$ is a hydrolyzable molecule, which can be effectively removed from the atmosphere by humidity and raindrops. The mechanism accounting for the tropospheric degradation of HFPEs is depicted in Fig. 7 [15].

In order to assess the lifetime of HFPEs in the troposphere, the reaction constants with OH radical have been determined for several elements of the series. The same samples used to determine the decomposition mechanism have been used in the experimental work [16]. 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.

The experimental rate constants at 298 K and the calculated lifetimes are reported in Table 5, together with the other available data in the literature [7,17–22], relative to independently synthesized samples [17,18] and to preliminary work done on products supplied by Ausimont [19–21].

Reaction constants around $2.3\times10^{-15}$–$2.9\times10^{-15}$ are found for the first two elements of the series (Table 5, rows 1, 2, 4), with good agreement between data coming from different labs. Higher molecular weight samples show somewhat higher reactivity, with reaction constants around $4.6\times10^{-15}$–$5\times10^{-15}$ (Table 5, rows 5–7). The relative positioning of the reaction constants of the two groups of molecules are in quite good agreement with the results of ab initio calculations recently published [9] on the C–H bond dissociation energy in HFPEs, showing a distinct reduction in the bond strength with increasing molecular weight.

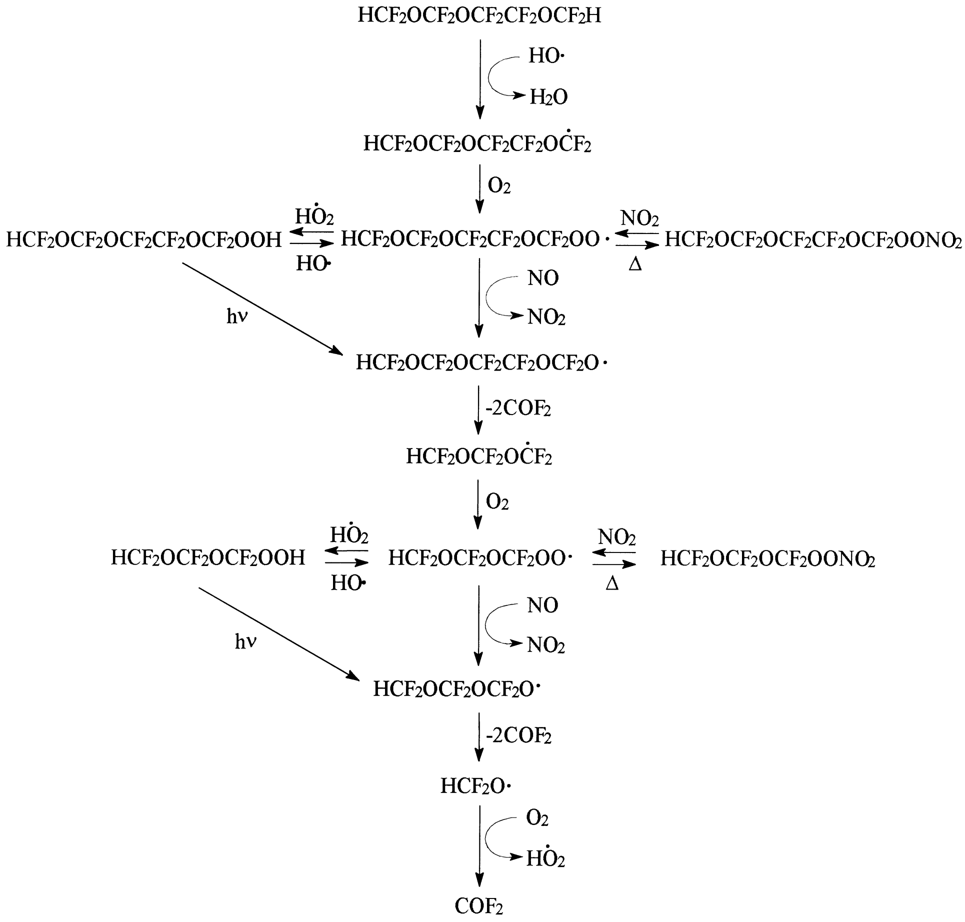

Fig. 7. Tropospheric decomposition mechanism of HFPE molecules.

Only the two extreme $k$ values (Table 5, rows 3, 8) fall quite out of range. The possible presence in the samples of impurities more readily oxidized than HFPE could be assumed to be the reason for the deviation of the results in both cases: indeed, the data on polydispersed sample have been obtained through determination of the concentration change of the OH radicals, while the lower constant was determined by monitoring the concentration change of the HFPE molecule, relative to a reference one (in the specific case, $CF_3CF_2H$, i.e. HFC 125).

The values of the lifetime of HFPEs seem to level off after the first two terms. This could be attributed to the leveling of the β- and γ-effects on the terminal $CF_2H$ groups, also evident in the ab initio calculations [9]. We intend to perform further measurements on higher boiling elements of the family, although this will result in increasing experimental difficulties due to the lower vapor pressure. However, by extrapolation from the data already available, the values of lifetime and global warming potential (GWP) are not expected to show significant changes.

As a conclusion, the lifetime of the lower boiling elements of the HFPE series are in the range 12–14 years: with increasing molecular weight this value is reduced to about seven years. No significant modification

Table 5
Reaction constants at 298 K of HFPEs with OH radicals and calculated atmospheric lifetime

| No. | Product | MW | Boiling point (°C) | $k$ ($cm^3$ $molec^{-1}$ $s^{-1}$) | Lifetime ($y$) | Reference |
|---|---|---|---|---|---|---|
| 1 | $HCF_2OCF_2H$ | 118 | 5 | $2.3\times10^{-15}$ | 11 | [17] |
| 2 | $HCF_2OCF_2H$ | 118 | 5 | $2.9\times10^{-15}$ | 14 | [18] |
| 3 | $HCF_2OCF_2OCF_2H$ | 184 | 35 | $1.3\times10^{-15}$ | 45 | [19,20] |
| 4 | $HCF_2OCF_2OCF_2H$ | 184 | 35 | $2.4\times10^{-15}$ | 13.6 | [16] |
| 5 | $HCF_2OCF_2CF_2OCF_2H$ | 234 | 58 | $4.7\times10^{-15}$ | 7 | [16] |
| 6 | $HCF_2OCF_2OCF_2CF_2OCF_2H$ | 300 | 85 | $3\times10^{-15}$ to $5\times10^{-15}$ | 5 to 9 | [21] |
| 7 | $HCF_2OCF_2OCF_2CF_2OCF_2H$ | 300 | 85 | $4.6\times10^{-15}$ | 7.1 | [16] |
| 8 | Polydispersed sample | 350 | 40–140 | $5.8\times10^{-14}$ | 0.7 | [22] |

Table 6
Radiation forcing (RF), atmospheric lifetime and global warming potential of low boiling HFPEs, as compared with fluids of the older generation (CFCs, PFCs) and with potential substitutes (HFC, HFE)

| | RF ($W/m^2$) | Lifetime (*y*) | MW | Time horizon (*y*) | GWP vs. $CO_2$ | Reference |
|---|---|---|---|---|---|---|
| CFC 11 ($CFCl_3$) | 0.3 | 50 | 137.5 | 100 | 5400 | [23] |
| PFC $C_6F_{14}$ | – | 3200 | 338 | 100 | 7400 | [25] |
| HFC 227ea ($C_3F_7H$) | – | 36.5 | 170 | 100 | 2900 | [25] |
| HFE 449-s1 ($C_4F_9OCH_3$) | 0.37 | 5 | 250 | 100 | 500 | [24] |
| $HCF_2OCF_2H$ | 0.545 | 14 | 118 | 100 | 3699 | [17], this work |
| $HCF_2OCF_2OCF_2H$ | 0.873 | 13.6 | 184 | 100 | 3692 | [16,23], this work |
| $HCF_2O\ CF_2CF_2OCF_2H$ | 1.007 | 7 | 234 | 100 | 1725 | [16,23], this work |
| $HCF_2OCF_2OCF_2CF_2OCF_2H$ | 1.358 | 7.1 | 300 | 100 | 1840 | [16,23], this work |

of the lifetime is expected with further increase in molecular weight.

### 4.3. Global warming potential

Global warming potential of hydrofluoropolyethers has been estimated for the lower boiling components of the H-Galden family using the atmospheric lifetimes reported in [16], and the radiation forcing determined by C.J. Nielsen [23]. The calculation has been done by means of the formula reported by Wallington et al. [24]. Table 6 shows the GWP of the three HFPE molecules. As a comparison, data for greenhouse gases like CFC 11 and PFC $C_6F_{14}$, and for proposed new generation substitutes, hydrofluorocarbons and hydrofluoroethers with short lifetime, are also reported.

It is apparent from the data in the table the substantial contribution given to the GWP of HFPE by the high value of the radiation forcing (RF). The infrared absorption in the earth emission window of the fluorinated ethers, as shown in Fig. 2 is quite strong, and is responsible for the high RF values. The dependence of the RF upon molecular weight is evident. On the other hand, the calculated values per unit weight are nearly constant, their variation being less than 10% for all the molecules we have considered. The calculated GWP values are thus mostly dependent upon the atmospheric lifetimes.

The expected amount of the single elements in the crude HFPE molecular weight distribution curve has been reported above, and indicates that the average value of the GWP (100 years, vs. $CO_2$) of the low boiling fractions of HFPE ranges between 1800 (fraction B) and 2000 (fraction A).

## References

[1] D. Sianesi, G. Marchionni, R.J. De Pasquale, in: R.E. Banks (Ed.), Organofluorine Chemistry: Principles and Commercial Applications, Plenum Press, New York, 1994.

[2] A.R. Ravishankara, S. Solomon, A.A. Turnipseed, R.F. Warren, Science 259 (1993) 194.

[3] R.A. Morris, T.M. Miller, A.A. Viggiano, J.F. Paulson, S. Solomon, G.J. Reid, J. Geophys. Res. 100 (1995) 1287.

[4] D. Sianesi, A. Marracini, G. Marchionni, US Patent 5 149 842 (1992).

[5] G. Marchionni, P.A. Guarda, M. Paganin, US Patent 5 488 181 (1996).

[6] G. Marchionni, G. Spataro, E. Strepparola, Eur. Patent Appl. EP 695 775 (1996).

[7] M. Visca, R. Silvani, G. Marchionni, CHEMTECH 27(2) (1997) 33.

[8] G. Marchionni, P.A. Guarda, US Patent 5 744 651 (1998).

[9] S. Radice, M. Causa', G. Marchionni, J. Fluorine Chem. 88 (1998) 127.

[10] R. Silvani, G. Spataro, G. Marchionni, US Patent 5780 414 (1998).

[11] J.L Adcock, S.B. Mathur, W.A. Van Hook, H.Q. Huang, B.H. Wang, Proceedings of the ACS 10th W Fluorine Conference, St. Petersburg, FL, 1991.

[12] A. Suga et al., Proceedings of the ACS 12th W Fluorine Conference, St. Petersburg, FL, 1995.

[13] Ausimont internal toxicological data.

[14] AFEAS Worksop on Kinetics and Mechanisms for the Reaction of Halogenated Organic Compounds in the Troposphere, Dublin, Ireland, 1993.

[15] E.C. Tuazon, Environ. Sci. Technol. 31 (1997) 1817.

[16] F. Cavalli, M. Glasius, J. Hjorth, B. Rindone, N.R. Jensen, Atmos. Environ. 32(21) (1998) 3767.

[17] N.L. Garland, L.J. Medhurst, H.H. Nelson, J. Geophys. Res. 98 (1993) 23107.

[18] K.J. Hsu, W.B. De More, J. Phys. Chem 99 (1995) 1235.

[19] N. Christidis, M.D. Hurley, S. Pinnock, K.P. Shine, T.J. Wallington, J. Geophys. Res. 102 (1997) 19597.

[20] W.B. DeMore, Private Communication.

[21] M. Glasius, Master Thesis, Odense University (DK), 1995.

[22] C. Bruhl, T. Peter, G. Moortgat, D. Boglu, R. Meller, G. Brasseur, I. Isaksen, P. Crutsen, Model Studies to Ozone Depletion Potential and Greenhouse Effect of Halogenated Hydrocarbons with Focus on CFC Substitutes, Max Planck Institut fur Chemie, Mainz, 1993.

[23] C.J. Nielsen, Private communication.

[24] T.J. Wallington, W.F. Schneider, J. Sehested, M. Bilde, J. Platz, O.J. Nielsen, L.K. Christensen, M.J. Molina, L.T. Molina, P.W. Wooldridge, J Phys. Chem. A 101 (1997) 8264.

[25] IPCC WGI, 1995: Climate change 1995. The science of climate change: Contribution of working group I to the second Assessment Report of the Intergovernmental Panel on Climate change. J.T. Houghton, L.G. Heisa Filho, B.A. Callender, N. Hassin, A. Kattenberg and K. Maskell (Eds.), Cambridge University Press, Cambridge, U.K.