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# Synthesis and characterization of perfuoropolyethers from perfluoromethylvinylether

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## Abstract

The synthesis of a novel perfluoropolyethers (PFPEs) family has been carried out by the low temperature photooxidation of perfluoromethylvinylether. The macromolecular chains are terpolymeric in nature, being constituted by random sequences of the following groups: the regular –$CF_2CF(OCF_3)O$–, the orthoestereal –$CF(OCF_3)O$–, and the acetalic –$CF_2O$–. The presence of an ethereal oxygen in the short side chains represents the main structural difference with other PFPE families studied up to date [G. Marchionni, G. Ajroldi, G. Pezzin, in: S.L. Aggarwal, S. Russo (Eds.), Comprehensive Polymer Science, 2nd suppl., Pergamon Press, London, 1996.]

Several fractions have been obtained, in the present work, by a single sample of the new PFPE, and some of their most important physical and molecular properties have been determined by a variety of different techniques. The properties change regularly with chain length, as expected. The group contribution analysis previously applied by our group to other families of PFPE has been found to be applicable also to chains of infinite length of the present family, which contains oxygen in the side chain.

*Keywords:* Perfluoromethylvinylether; Photooxidation; Perfluoropolyethers; Group contributions; Thermal stability

## 1. Introduction

The perfluoropolyethers (PFPEs) known and commercialized up to date are the series of different Fomblin® produced by Ausimont, of Krytox® produced by Du Pont, and of Demnum® produced by Daikin.

As far as the Fomblin® are concerned, when obtained from the photochemical reaction of oxygen with perfluoroethylene they are called Fomblin Z®, and, when obtained from perfluoropropene, Fomblin Y®. The dependence of their physical and rheological properties on composition and molecular weight have been described in some recent papers and reviews [1–4].

From the same photochemical reaction, in which the reacting monomer is perfluoromethylvinylether, a series of copolymers (here called Fomblin® J) are obtained, and their chemical structure, together with the corresponding physical and rheological properties, related to chain length and composition, are described in the present work. The same photochemical synthesis is also effective for some other perfluoroalkylvinylethers [5].

In comparison to the other PFPEs, the main structural difference of the new copolymers is the presence of an ethereal oxygen in the short lateral chains. This paper correlates structure and chain length with properties, and describes also similarities and differences with the properties of the already known series of Fomblin®, Krytox® an Demnum® perfluoropolyethers.

## 2. Photooxidative synthesis

The Fomblin J oils are produced through the reaction of liquid perfluoromethylvinylether $CF_3$–$OCF$=$CF_2$ with oxygen, at a quite low temperature, under ultraviolet irradiation of wavelength from 200 to 300 nm.

$$CF_3-OCF{=}CF_2 + O_2 \underset{T\approx -40^{\circ}C}{\overset{h\nu}{\rightarrow}} T-O[CF_2CF(OCF_3)O]_n \times [CF(OCF_3)O]_m[CF_2O]_q\text{–}[O]_p\text{–}T \quad (1)$$

In the polymer chain the units –$CF_2CF(OCF_3)O$–, –$CF(OCF_3)O$–, and –$CF_2O$– are randomly distributed, as shown later, and some of them are connected along the chain by peroxide bridges rather than by simple oxygen atoms.

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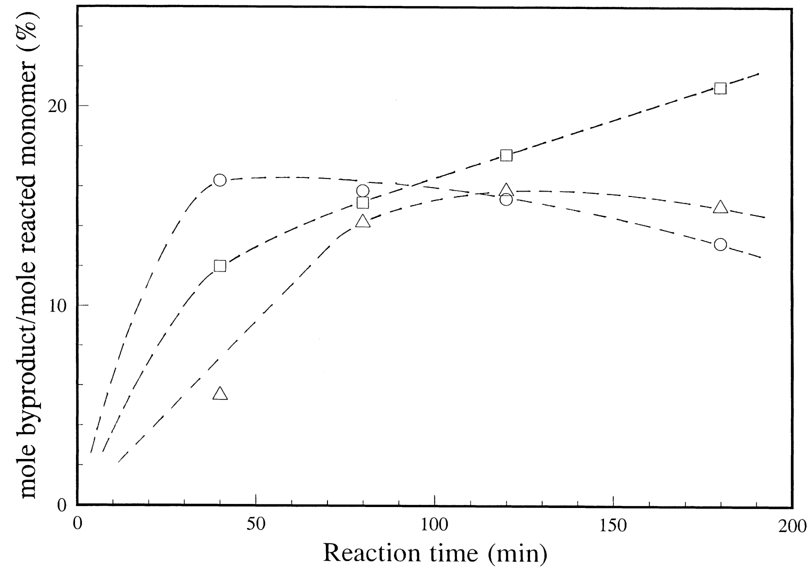


Fig. 1. Gaseous products as a function of the reaction time: (□) $CF_3O$ COF, (△) $COF_2$, and (○) $CF_3O\overset{O}{CF\text{-}CF_2}$.

The terminal groups –T are trifluoromethyl groups $-CF_3$, or fluoroformate groups –COF, or even acid fluoride groups $-CF_2COF$.

The polymer yield is about 50%: the most important byproducts are low molecular weight products such as trifluoromethylfluoroformate $CF_3O{-}COF$, trifluoromethoxy-trifluoroethyleneoxide $CF_3O\overset{O}{CF\text{-}CF_2}$, and carbonyl fluoride $COF_2$.

The amount of low molecular weight sideproducts vary somewhat during the course of the reaction, as shown in Fig. 1. Their formation is explained on the basis of the decomposition of the two different intermediate alkoxy radicals

$$R_fO{-}CF(OCF_3){-}CF_2O^{\cdot} \rightarrow R_fO{-}CF(OCF_3)^{\cdot} + COF_2 \qquad (2)$$

$$R_fO{-}CF_2CF(OCF_3)O^{\cdot} \rightarrow R_fO{-}CF_2^{\cdot} + CF_3OCOF \qquad (3)$$

which undergo extensive C–C fragmentation to give the final in-chain orthoester and acetalic units.

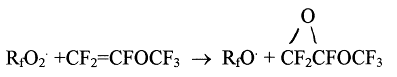
On the contrary it is interesting to note that C–O fragmentation reaction of the alkoxy radicals

$$R_f{-}OCF_2CF(OCF_3)O^{\cdot} \rightarrow R_f{-}OCF_2COF + CF_3O^{\cdot} \qquad (4)$$

$$R_fO{-}CF(OCF_3)O^{\cdot} \rightarrow R_f{-}OCOF + CF_3O^{\cdot} \qquad (5)$$

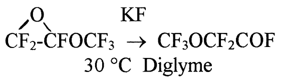
is less favored and has a low probability in comparison with the competing radical addition to another molecule of perfluoroolefin (chain growth reaction). This results in a negligible amount of chain transfer events, and to a relatively high molecular weight of the chains (10 000–50 000). This behavior, which is consistent with the slightly higher bond energy of C–O with respect to C–C, is confirmed by the comparison of data on reactivity, yield, viscosity and byproducts observed in the photo-oxipolymerization of perfluoromethylvinylether and of perfluoropropene, which are reported in Table 1.

The rather abundant epoxide formation in the case of vinylether, can be ascribed either to a direct epoxidation reaction or to the tendency of this olefin toward the reaction



$$R_fO_2^{\cdot} + CF_2{=}CFOCF_3 \rightarrow R_fO^{\cdot} + \overset{O}{CF_2CF}OCF_3 \qquad (6)$$

This epoxide, contrary to the tetrafluooxirane is rather stable, at least at room temperature, with respect to the isomerization to acylfluoride, which however, can be easily carried out by contact with nucleophilic reagents, i.e.

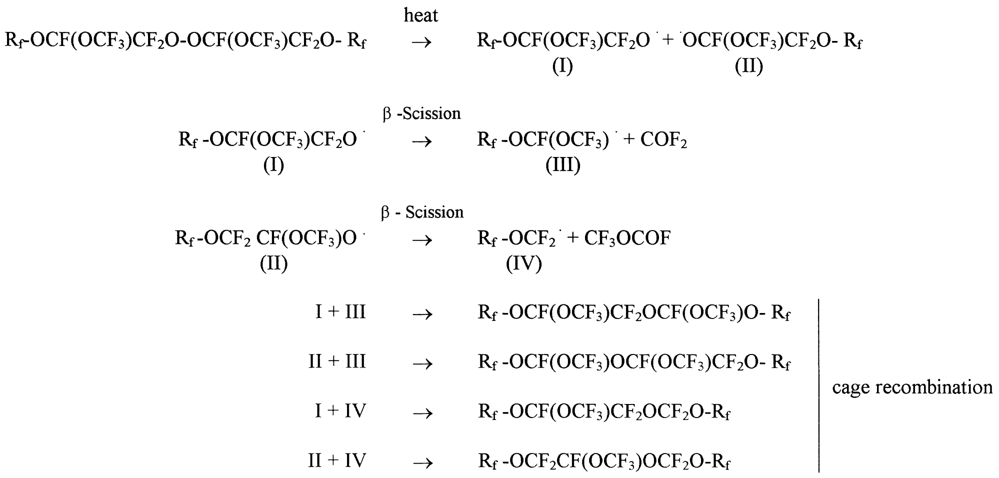


$$\overset{O}{CF_2\text{-}CF}OCF_3 \xrightarrow[30\,°C\ \text{Diglyme}]{KF} CF_3OCF_2COF \qquad (7)$$

Table 1
Reactivity, yield, viscosity and byproducts of the photooxidative polymerization of perfluoromethylvinylether (PFMVE); comparison with perfluoropropene (HFP)

| Monomer | PFMVE | HFP |
|---|---|---|
| Raw polymer produced (g) | 21.4 | 30.0 |
| Peroxidic oxygen (g/100 g) | 1 | 0.3 |
| C1/C2 | 0.81 | 0.15 |
| Kinematic viscosity at 20°C ($cm^2/s$) | 2130 | 340 |
| Selectivity | | |
| Raw polymer (%) | 49 | 87 |
| $COF_2$, $CF_3OCOF$ (%) | 23 | 10 |
| Epoxide (%) | 28 | $\leq 3$ |

Reactor volume=50 ml; reaction time=3 h; $T=-40°C$; optical path=1 mm; Hanau lamp=125 W; oxygen flow rate=3.8 l/h; Monomer=87 g.
C1: $-OCF_2-$, $-OCF(X)-$; C2: $-OCF_2CF(X)-$; X: $-OCF_3$; $-CF_3$.



Scheme 1. Pathway for the removal of peroxide linkages from peroxidic polyethers.

## 3. Thermal treatment and fluorination

The unstable peroxidic bonds present along the chains have to be eliminated by thermal degradation at temperatures around 240°C. The weight losses following peroxide decomposition can reach 30–40% and are a function of the concentration of peroxides. Byproducts of the reaction are $COF_2$ and $CF_3OCOF$.

The reaction mechanism is given in Scheme 1, where only the main peroxidic structure is considered.

In the course of thermal treatment fluoroformates are converted to acid fluorides

$$R_f{-}OCF(OCF_3)CF_2OCOF \overset{\text{heat}}{\rightarrow} R_f{-}OCF(OCF_3)COF + COF_2 \quad (8)$$

A subsequent direct fluorination completely converts the carbonyl groups to inert perfluoromethoxy end-caps

$$R_f{-}OCF(OCF_3)COF + F_2 \rightarrow R_f{-}OCF_2OCF_3 + COF_2 \quad (9)$$

$$R_f{-}OCF_2COF + F_2 \rightarrow R_f{-}OCF_3 + COF_2 \quad (10)$$

After thermal treatment and fluorination the Fomblin J fluid is composed of the following three different substructures

- (A) $-CF_2CF(OCF_3)O-$ (regular unit),
- (B) $-CF(OCF_3)O-$ (ortoestereal unit), and
- (C) $-CF_2O-$ (acetalic unit).

## 4. Characterization

### 4.1. Fractionation and molecular properties

A relatively large polymer sample was fractionated at 15°C and at the initial concentration of 15%, by using the well-known fractional precipitation method, where trichlorotrifluoroethane was the solvent and methanol the precipitant. The fractions, in the form of viscous oily samples, were dried under vacuum at 50°C for 2 h before characterization.

Number average molecular weights $M_n$ were measured by vapor pressure osmometry (VPO), with a Knauer osmometer, at 37°C, in the same solvent.

Molecular weight distributions were obtained by GPC analysis, using a Water 201 apparatus, using for calibration Fomblin Z perfluoropolyether samples of narrow molecular weight distribution [3,6].

### 4.2. NMR and IR spectroscopy

The chemical composition of the fractions and of the unfractionated sample was obtained from $^{19}F$ nuclear magnetic resonance (NMR) measurements, carried out in a Varian XL 200 spectrometer. The infrared spectra were obtained from a Nicolet 20S XB Spectrometer.

### 4.3. Physical properties

The density $\rho$ of the samples was determined picnometrically at selected temperatures in the range from −40°C to 40°C.

The glass transition temperatures $T_g$ were measured by differential scanning calorimetry (DSC).

The viscosity $\eta$ was obtained from the value of the kinematic viscosity $\nu$ (and from the density $\rho$):

$$\eta = \rho\nu.$$

The $\nu$ values were measured at various temperatures with Cannon–Fenske capillary viscometers, according to the ASTM D 445 standardized method.

### 4.4. Thermal and chemical stability

Thermogravimetric (TGA) and DSC measurements were used to evaluate the thermal stability of the samples in the presence of degradation catalysts. The TGA apparatus was the Du Pont 9900 Thermogravimetric Analyzer equipped with a Knudsen cell [7]; temperature was increased at a rate of 10°C/min. Two different kind of catalyst have been used: $\gamma$-$AlF_3$ and a mixture $SiO_2/Al_2O_3$ 75/25 by weight.

The chemical stability was tested by measuring the viscosity changes after treatment of the samples, at 70°C and for 24 h, under vigorous stirring with $H_2SO_4$ (98%), $KMnO_4$ (6%), and KOH (40%).

## 5. Results and discussion

### 5.1. Fractionation, molecular weight, and polymer composition

The fractionation data and the physical characteristics of the fractions, collected in Table 2, show the regularity of the fractional separation and the constancy of the composition among polymeric chains of different length. The fractions obtained have a decreasing molecular weight $M_n$, and the fractionation process has been regular, even if relatively effective, as indicated by the fact that their viscosity average molecular weights, when summed up, give a cumulative sum quite close to that of the unfractionated sample. Moreover their physical properties change regularly, or remain constant, with varying molecular weight, as expected.

The molecular weight distribution (MWD) of the unfractionated sample being relatively narrow ($M_w/M_n=1.48$, $M_z/M_w=1.34$), the fractions are also narrowly distributed.

As far as their composition is concerned, it is seen that the (A), (B) and (C) units content of the five fractions investigated are substantially constant, i.e. independent of chain length, and practically identical to that of the unfractionated sample. Similar results have been previously obtained for other perfluoropolyether fractions investigated [1]

### 5.2. NMR and IR spectra

A typical $^{19}F$ NMR spectrum (fraction no. 9, $M_n=3080$) is plotted in Fig. 2. The main features are the following:

1. The peaks at about −100 ppm (relative to the $CFCl_3$ standard reference) are attributed to the –CF– group of the regular A unit, whereas the peaks of the $-CF_2-$ group of the same unit are located at about −88 ppm. As expected, integration shows indeed that the peaks area are in the 1/2 ratio.
2. The pendant $-OCF_3$ group of the ortoestereal unit (B) is characterized by the well resolved peak at −57.5 ppm, which is flanked by two smaller peaks at −56.8 and −58.4 ppm, clearly attributable to the main chain terminal groups $-OCF_3$ [8]. The intense peak of the abundant $-OCF_3$ pendant group belonging to the (A) structure lies

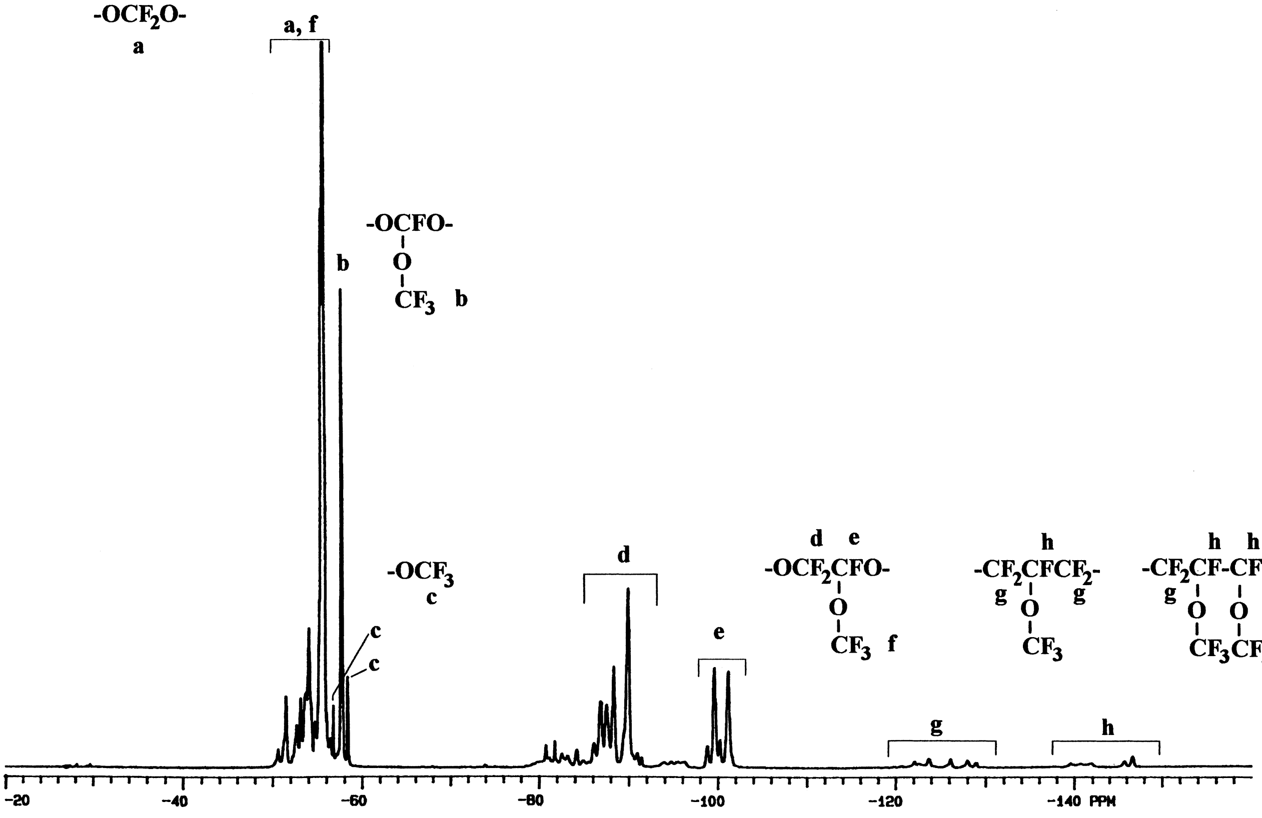


Fig. 2. $^{19}F$ NMR spectrum of Fomblin J, fraction (9).

Table 2
Fractions: composition, molecular properties, density and bulk viscosity at 293 K, and glass transition temperature (onset)

| Fraction | Composition by $^{19}$F NMR | | | | $M_n$ | GPC | | | Density ($g/cm^3$) | Viscosity (mPa s) | $T_g$ (K) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $-OCF_2-$ (% mol) | $-OCF_2CF(OCF_3)-$ (% mol) | $-OCF(OCF_3)-$ (% mol) | $-OR_f-$[a] (% mol) | VPO (g/mol) | $M_n$ (g/mol) | $M_w$ (g/mol) | $M_w/M_n$ | | | |
| 1 | 0.37 | 0.46 | 0.14 | 0.03 | 7200 | 5640 | 7860 | 1.39 | 1.8765 | 509 | 176.5 |
| 2 | | | | | 6830 | 5500 | 7400 | 1.34 | 1.8774 | 469 | 177.2 |
| 3 | 0.38 | 0.45 | 0.15 | 0.02 | 6080 | 5040 | 6930 | 1.37 | 1.8768 | 416 | 176.9 |
| 4 | | | | | 5160 | 4730 | 6090 | 1.29 | 1.8758 | 336 | 175.4 |
| 5 | 0.38 | 0.45 | 0.15 | 0.02 | 4780 | 5070 | 6410 | 1.26 | 1.8754 | 354 | 175.7 |
| 6 | | | | | 4080 | 4380 | 5460 | 1.25 | 1.8751 | 272 | 174.6 |
| 7 | 0.38 | 0.44 | 0.15 | 0.03 | 3950 | 4250 | 5130 | 1.20 | 1.8723 | 296 | 173.8 |
| 8 | | | | | 3490 | 3740 | 4440 | 1.18 | 1.8690 | 155 | 172.8 |
| 9 | 0.39 | 0.43 | 0.14 | 0.04 | 3080 | 3310 | 3790 | 1.15 | 1.8652 | 129 | 172.0 |
| 10 | | | | | 1730 | 2050 | 2440 | 1.19 | 1.8521 | 42.6 | 163.7 |
| Whole | 0.39 | 0.43 | 0.15 | 0.03 | 3650 | 3740 | 5520 | 1.48 | 1.8700 | 224 | 174.5 |

[a] $R_f$: $-CF_2CF(OCF_3)CF_2-$ and $-CF_2CF(OCF_3)CF(OCF_3)CF_2-$ (see text and Fig. 2).

at about −55.5 ppm, and there one finds also the strong signals of the various acetalic $–OCF_2O–$ groups. By subtracting the contribution due to the structures whose peaks lie at about −100 ppm, the molar contributions of the groups to the above area are readily obtained. The peaks of the $–OCF_3$ pendant groups belonging to structures such as

$–OCF_2CF(OCF_3)CF_2–$

and

$–OCF_2CF(OCF_3)CF(OCF_3)CF_2–$

whose amount is relatively limited (about 3% molar, see Table 2), lie between −51 and −59 ppm. The formation of these substructures is ascribed to the occurrence of some out of cage coupling of carbon radicals (III and IV in Scheme 1).

Signals of the $–CF_2–$ and $–CF–$ units for the same sequences are located at about 120–130 ppm and 140–145 ppm, respectively. The overlapping of signals coming from different $–OCF_3$ (terminals and pendant) groups in the same spectral range does not allow to measure with a sufficient accuracy, as normally done with other copolymeric perfluoropolyethers, the number average molecular weight from the terminal group concentration.

The infrared spectrum of Fomblin J is compared in Fig. 3 with those of Fomblin Y and Z. Stretching absorptions of the $–CF_2–$, $–COC–$ and $–CC–$ groups lie in the infrared spectral region from 1000 to 1300 $cm^{-1}$. Two small bands at 895 and 924 $cm^{-1}$ are found in the spectrum of the J sample; by comparison with the IR spectra of Z and Y structures, where the terminal groups are $–OCF_3$. On the basis of IR data presented by Pacansky [9], the 895 $cm^{-1}$ band is attributed to the same terminals also for J material, while the 924 $cm^{-1}$ band, could be reasonably assigned to a normal mode of the vibration, which involve mainly the $–OCF_3$ pendant group [10].

### 5.3. Physical properties

#### 5.3.1. Density

An example of the chain length influence on density $\rho$, shown in the form of a density–temperature plot, is reported in Fig. 4 for different fractions.

It is seen that at all explored temperatures an increase of molecular weight corresponds to an increase in $\rho$, as found for the other perfluoropolyethers [1]. The comparison is plotted in Fig. 5, again in the form of a density–temperature plot, but for polymeric samples of similar viscosity (about 250 mPa/s).

The density of the newly synthesized terpolymers Fomblin J lays between that of the linear copolymers Z and the branched ones Y. The dependence of the reciprocal of density, the specific volume $V_s$, at 293 K, is reported as a function of the reciprocal of the number average molecular weight in Fig. 6. The average molar volume $V_0$ of the repeating unit of molecular weight $M_0$ and the molar volume $V_e$ of the terminal groups are obtained from the coefficients of the linear regression:

$$V = nV_0 + 2V_e, \tag{11}$$

where $n$ is the chain length, in terms of number of monomeric units.

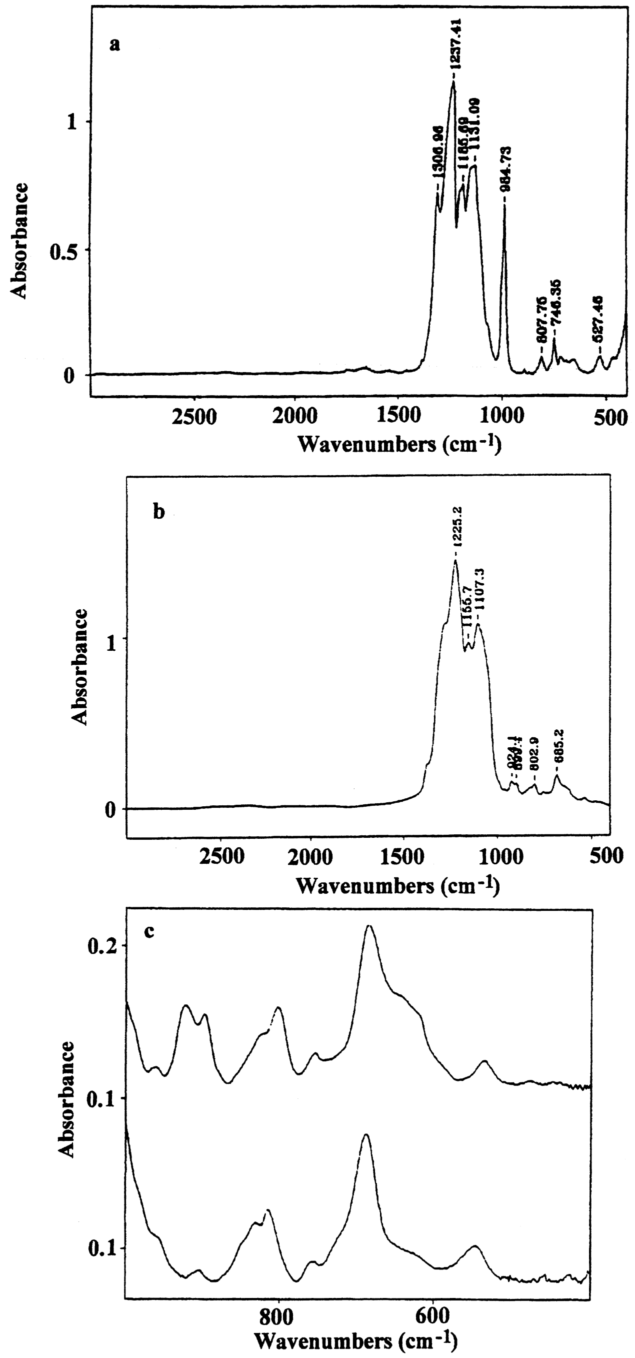


Fig. 3. Infrared spectra for Fomblin J (a), Fomblin Y (b), and comparison of the spectra of Fomblin J and Z (c) in the wavenumber range 500–900.

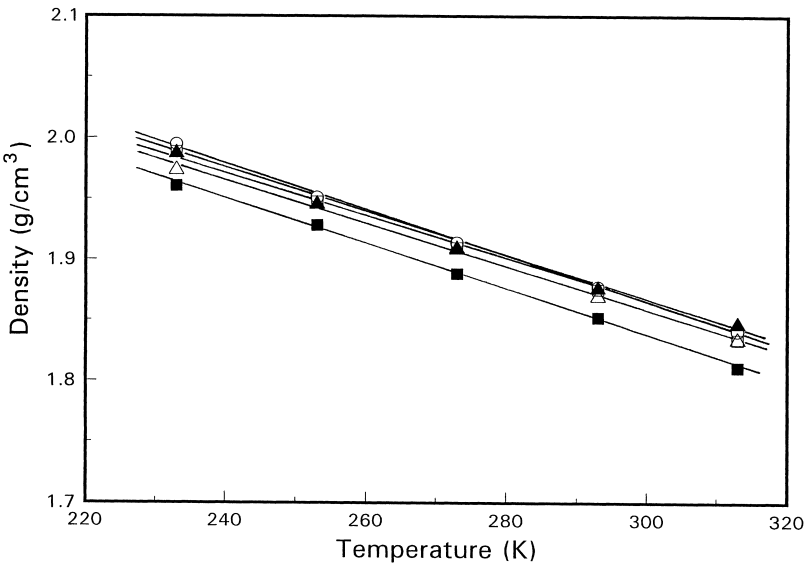


Fig. 4. Dependence of density on temperature for some Fomblin J fractions: F2 (○), F4 (△), F6 (□), F8 (△), F10 (■).

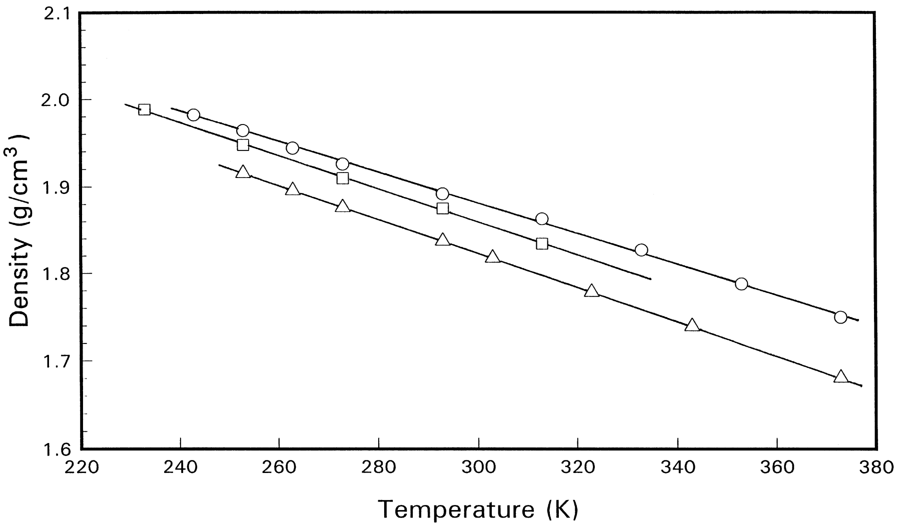


Fig. 5. Dependence of density on temperature for different Fomblin structures having the same bulk viscosity at 293: Fomblin Y (○), Fomblin J (□), Fomblin Z (△).

The data for the J sample are reported in Table 3, where they are compared with those obtained in a previous work [4] for other perfluoropolyethers structures.

The $V_0/M_0$ ratio in Table 3, first column, varies only of about 4% with changing the basic molecular structure, a result which can be taken as evidence that the perfluoropolymers and copolymers of the table do not differ sensibly as far as their intermolecular interactions are concerned. Similarly the excess volume of the end groups is relatively constant at about 11 ml/mol, reflecting the fact that the chemical structure of the groups is similar in the different PFPE families [1]. The corresponding $V_e/V_0$ values vary by a factor of about 2, due to the large change in $V_0$, which is less than 50 ml/mol for the Fomblin Z copolymers, and about twice that value for all the other samples.

Table 3
Molar volume data for backbone and end groups of some perfluoropolyethers at 298 K

| Sample | $V_0/M_0$ (ml/g) | $M_0$ (g/mol) | $V_0$ (ml/mol) | $V_e$ (ml/mol) | $V_e/V_0$ |
|---|---|---|---|---|---|
| Fomblin Z/A | 0.5362 | 83.3 | 44.67 | 9.7 | 0.23 |
| Fomblin Z/B | 0.5390 | 86.4 | 46.57 | 13 | 0.28 |
| Fomblin Z/C | 0.5422 | 92.5 | 50.15 | 12.3 | 0.25 |
| Demnum | 0.5275 | 166 | 87.56 | 12.5 | 0.14 |
| Fomblin Y | 0.5196 | 161 | 83.66 | 11 | 0.13 |
| Krytox | 0.5180 | 166 | 85.99 | 12.7 | 0.15 |
| Fomblin J | 0.5298 | 123.8 | 65.59 | 8.8 | 0.13 |
| Fomblin K | 0.5317 | 140.6 | 74.76 | 8.9 | 0.12 |

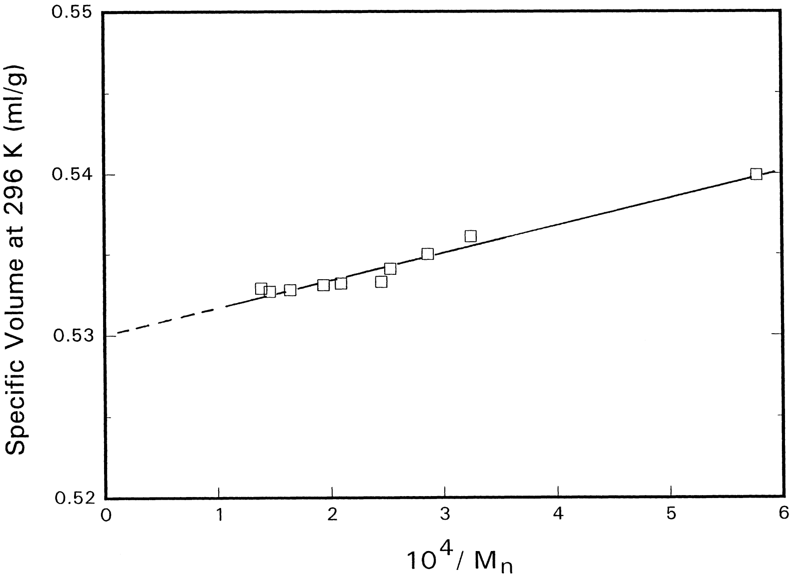


Fig. 6. Specific volume at 293 K as a function of reciprocal number average molecular weight $M_n$ for Fomblin J fractions.

A group contribution analysis was also carried out, and the value found for the contribution to the molar volume at 298 K of the >CFOCF$_3$ group in a chain of infinite chain length is reported in Table 4, where it is compared with the corresponding literature values for the hydrogenated homologous group [11]; data for other PFPE families are also given [1]. The trend is regular in the sense that the increment found on going from the >CFCF$_3$ to the >CFOCF$_3$ group is corresponding, with a reasonable agreement, to the oxygen group contribution.

### 5.3.2. Glass transition

The dependence of $T_g$ on average molecular weight $M_n$ is plotted in Fig. 7 in the highly expressive form of $T_g$ vs $M_n$, and in Fig. 8 in the linearized form of $T_g$ vs reciprocal $M_n$, as required by the well-known equation:

$$T_g = T_{g,\infty} - K_g/M_n, \tag{12}$$

where the symbols have obvious meanings.

The dotted lines in Fig. 8, and the data collected in Table 5, show schematically where the Fomblin J data are located with respect to those of the Z and Y perfluoropolyethers, and it is clear that as far as the glass transition temperature is concerned the J terpolymers lay halfway the two PFPE families obtained from tetrafluoroethylene (Fomblin Z) an hexafluoropropene (FomblinY).

The group contribution analysis was carried out also for $T_g$ according to the equation:

$$T_{g,\infty} = \left(\sum Y_{g,i}\right)/M \tag{13}$$

(where $M$ refers to the repeating units, and $Y_{g,i}$ is the relative characteristic transitional parameter of the group), and the results are reported in Table 4. It is important to observe that while the introduction of an ethereal oxygen in the side chain increases the value of the group for hydrogenated vinylethers, in the case of perfluorinated materials the group contribution is slightly lowered or, within the experimental error, remains practically constant.

Such a result is in good agreement with the negative contribution to $T_g$ of the ethereal oxygen in the main chain to the glass transition reported in a previous paper [4].

The datum found in the present work can be considered in any case sufficiently reliable, because it predicts a glass transition temperature of 230 K for the polyperfluoromethylvinylether, which compares sufficiently well with the experimental datum of 248 K reported in [12].

Table 4
Group contributions at 298 K to volume and glass transition temperature

| Group | $V_i$ (cm$^3$/mol) | | $Y_{gi}$ (kg/mol) | |
|---|---|---|---|---|
| X | F | H | F | H |
| –CX$_2$– | 25.84 | 16.45 | 10220 | 2700 |
| –CX(CX$_3$)– | 50.26 | 32.70 | 28230 | 8000 |
| –CX(OCX$_3$) | 58.92 | 40.80 | 27890 | 11900 |
| –O– | 10.23 | 8.50 | −2100 | 4000 |

Table 5
$T_g^\infty$ and $K_g$ data for different series of PFPE oils

| Series | $T_g^\infty$ (K) | $10^4\ k_g$ (K) |
|---|---|---|
| Fomblin Y | 216 | 5.4 |
| Fomblin Z[a] | 142 | 1.5 |
| Fomblin K | 199 | 3.6 |
| Demnum | 172 | 3.3 |
| Krytox | 219 | 5.5 |
| Fomblin J | 182 | 3.1 |

[a] $p/q$=0.7.

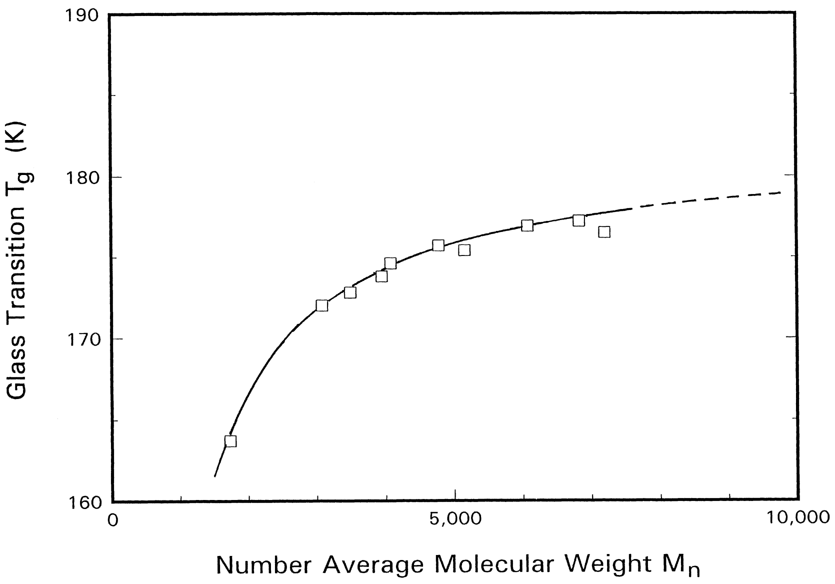


Fig. 7. Dependence of $T_g$ on number average molecular weight $M_n$ for Fomblin J fractions (□).

Moreover our data predict $T_g$=198 K for the homopolymer poly-trifluoromethoxy-trifluoroethyleneoxide; a reasonable value, given the fact that the presence of an ethereal link in the side chain results in a decrease of 21 K with respect to Krytox, i.e. polyperfluoropropyleneoxide) ($T_g$=219 K) [4].

### 5.3.3. *Viscosity*

The newtonian shear viscosities measured at 293 K for the fractions and for the whole polymer are plotted as a function of the weight average molecular weight $M_w$ in Fig. 9. The average slope is 2.11±0.11, i.e. it lies in between the two limiting slopes of 1 and 3.5 expected for molecular weights lower and higher than a critical molecular weight $M_c$. When one takes into account the fact that the $T_g$'s of fractions are all different (and lower than the limiting value $T_g^{\infty}$) the result becomes understandable. When a new $\eta - M_w$ plot is generated at a reference temperature of $T_g$+100 K, as reported in the same Fig. 9, the trend looks very different. At high $M_w$ a steep increase of the slope is observed, while for 4000<$M$<7000 the slope is approximately 0.8±0.1; at lower $M$ the slope again increases. Even though the experimental data are insufficient to define clearly the critical value of $M_w$, the data seem to indicate that $M_c$ should be close to 8000 as previously found for Fomblin Z copolymers [1].

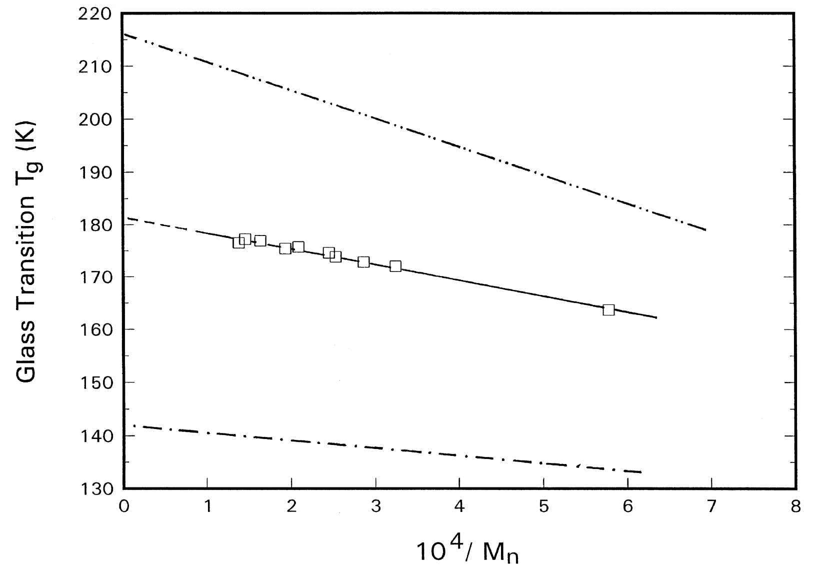


Fig. 8. $T_g$ vs $1/M_n$ for different Fomblin structures: Fomblin J (□), Fomblin Y (-···-) and Z (-··-).

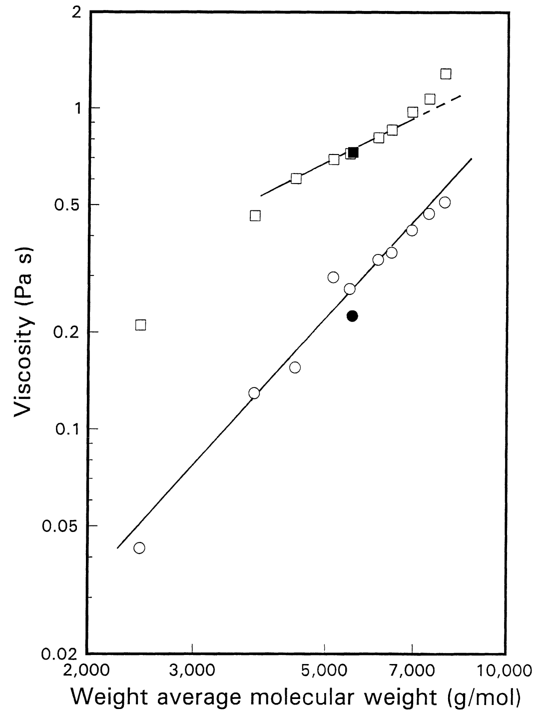


Fig. 9. Relationship between zero shear viscosity and molecular weight $M_w$ at 293 K: (○) fractions, (●) whole polymer, and at $T_g$+100 K: (□) fractions, (■) whole polymer.

The dependence of viscosity on temperature is shown in Fig. 10; as previously found with other PFPEs the WLF equation can be successfully used to describe the viscosity temperature curves. The average values of the fractional free volume at $T_g$ and of the free volume expansion coefficient calculated for all the fractions and the whole polymer from the $C_1$ and $C_2$ parameters of the WLF equation [1] are 0.038 and $5.6\times10^{-4}$, respectively; they compare well with data obtained for Fomblin Y (0.038 and $7.8\times10^{-4}$) and for Fomblin Z (0.041 and $6.5\times10^{-4}$). A general feature of PFPE polymers seems to be that the free volume at $T_g$ is larger than the "universal" value of 0.025 and also the coefficient for the free volume expansion is slightly higher (the so-called "universal" value is $4.8\times10^{-4}$).

Since the viscosity–temperature relationship can be described also in terms of activation energy for the viscous flow $\Delta E$, the relative data were also calculated. The $\Delta E$ value increases, as expected, with molecular weight, and for molecular weights higher than 4000 levels off at 40 kJ/mol, which lies in between the values found for linear copolymers (Fomblin Z, $\Delta E$=22 kJ/mol) and copolymers with a side chain (Fomblin Y, $\Delta E$=50 kJ/mol).

### 5.4. Thermal and chemical resistance

It is a well-known fact that the thermal resistance of PFPE is severely affected by the presence of Lewis acid reagents.

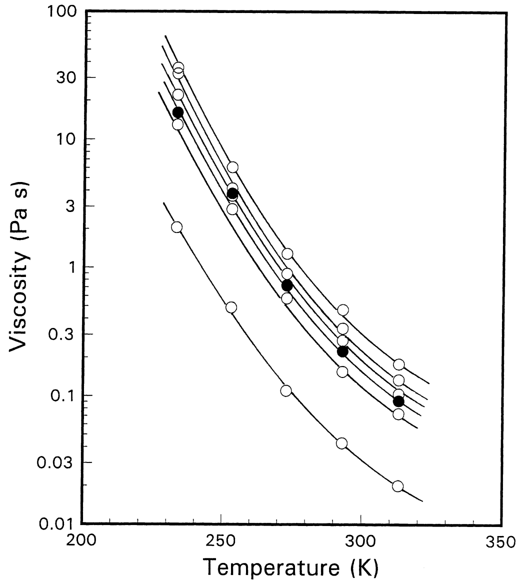


Fig. 10. Dependence of zero shear viscosity on temperature: (○) fractions 2, 4, 6, 8, 10, (●) whole polymer.

The γ-$AlF_3$ catalyst seems to be more effective than the silica/alumina mixture in the degradation reaction of Fomblin J, as shown in Table 6. The weight loss increases with increasing the amount of added catalyst, as expected.

The influence of the chemical structure on degradation was also investigated; data obtained for Fomblin Z, where the group –$CF(OCF_3)$– is not present, are also shown for comparison purpose in Table 6. The reactivity of –$CF_2O$– and –$CF_2CF_2O$– moieties is per se large under these experimental conditions [1], and the presence of the –$CF(OCF_3)O$– and –$CF_2CF(OCF_3)O$– moieties increases, as expected, the reactivity.

A detailed study of the degradation mechanism is at present in progress. Preliminary data obtained by analyzing by NMR $^{19}F$ Fomblin J samples after different residence times at 240°C in presence of 2% of a silica/alumina mixture support TGA data. The moiety –$CF(OCF_3)O$– is found to be the most reactive. As the NMR analysis enables the quantitative determination of the –$OCF_3$ and –COF end groups with the reaction extent, the following reaction mechanism is suggested:

Table 6
Thermal resistance of Fomblin fluids

| Catalyst concentration (%) | Weight loss at 250°C (%) | | | |
|---|---|---|---|---|
| | $SiO_2/Al_2O_3$ | | γ-$AlF_3$ | |
| | Fomblin J | Fomblin Z | Fomblin J | Fomblin Z |
| 0 | 20 | 15 | 20 | 15 |
| 1 | 30 | 23 | 65 | 30 |
| 10 | 60 | 23 | 100 | 50 |

Weight loss at 250°C from dynamic TGA (scanning rate 10°C/min).

Table 7
Chemical resistance of Fomblin fluids

| Chemical agent | Temperature (°C) | Concentration (%w) | Time (h) | Fomblin Z | Fomblin Y | Fomblin J |
|---|---|---|---|---|---|---|
| $H_2SO_4$ (98%) | 70 | 50 | 24 | No change | No change | No change |
| $KMnO_4$ (6%) | 70 | 50 | 24 | No change | No change | No change |
| KOH (40%) | 70 | 50 | 24 | No change | No change | No change |
| Alc. KOH (40%) | 70 | 50 | 24 | No change | No change | No change |

No change means no significant change in acidity of the recovered fluid; change in viscosity within 2%.

$$\begin{array}{c} -OCF_2CF(OCF_3)OCFXOCF_2CF(OCF_3)O- + MY_n \\ \downarrow \\ [-OCF_2CF(OCF_3)OCXOCF_2CF(OCF_3)O-] + MY_nF^- \; . \\ \downarrow \\ -OCF_2CF(OCF_3)OCOX + CF_3CF(OCF_3)O- + MY_n \end{array} \tag{14}$$

As an intermediate product a carbocation is formed.

Some data about the chemical resistance of Fomblin J to acids, strong oxidants, and bases are reported in Table 7, where the performance of this new polymer is compared with that of known PFPE's.

The different structure and the presence of the perfluoromethoxy side group do not impair the resistance against chemicals.

## 6. Conclusions

The present work describes the properties and the molecular characteristics of several fractions of a low molecular weight random terpolymer obtained from the low temperature photooxidation of perfluoromethylvinylether.

The results indicate that the molecular weight dependence of all the properties is regular, in line with the results obtained in the investigation of other PFPE families [1]. Some of the physical properties explored, in particular in the limiting (high molecular weight) volume and glass transition temperature, can be treated as additive, i.e. they are given, with remarkable accuracy, by the sum of group contributions. These properties, in other terms, are controlled only by the composition.

With the exception of the higher sensitivity to the action of Lewis acid reagents, the thermal and chemical stability of the samples are not sensibly changed, with respect to similar PFPE, by the different structure and, in particular, by the presence of the perfluoromethoxy side groups.

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