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Linear perfluoropolyether difunctional oligomers: chemistry, properties and applications

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Abstract

The synthesis of telechelic perfluoropolyether oligomers (PFPE) is described. The preparation of these fluorinated derivatives of the structure

$R_h-CF_2(OCF_2)_q(OCF_2CF_2)_pOCF_2-R_h$

was performed by condensation or nucleophilic reactions starting from PFPE precursors bearing carboxylic or alcoholic functional groups. A large variety of selective synthetic routes have been explored, differences in comparison with conventional hydrogenated molecules emphasized, and the related mechanisms elucidated. High yields and selectivities were generally observed, this enables to isolate oligomers of high purity, whose properties can be easily fine-tuned by varying the structural parameters. Some interesting chemical and physical properties are shown; and potential, highly innovative applications briefly discussed.

Keywords: Telechelic oligomers; Perfluoropolyether; Synthesis; NMR spectroscopy; Chemical/physical properties; Applications

1. Introduction

The synthesis of α,ω-difunctional fluorinated oligomers is a very interesting route to macromolecules having unique properties, thanks to their structure constituted by an internal fluorinated chain and terminal reactive hydrogenated segments. The fluorinated moiety guarantees thermal and chemical stability, while the chain-ends are available for further reactions or chain growth through addition/condensation.

The selection of the different segments of the macromolecule (i.e. their length and chemical structure) allows the design of products having a wide range of behaviour. They can be applied as such or formulated in a variety of highly innovative applications. Moreover, the availability of fluorinated macromolecules opens up new perspectives in the area of advanced elastomeric and thermoplastic materials.

The scientific literature reports many synthetic routes for the production of these molecules: I_2 initiated radical telomerization of perfluoroolefins [1,2], anionic oligomerization of oxirane and oxetane rings [3,4], and the photo-co-polymerization of oxygen and perfluoroolefins [5]. This last process offers distinctive advantages in terms of productivity, selectivity and quality control of the final products; when C_2F_4 is used, fluorinated chains characterized by the following structure are obtained:

$$-CF_2(OCF_2)_q(OCF_2CF_2)_pOCF_2- \quad (I)$$

The present work deals with the synthesis and characterization of difunctional telechelic macromolecules having the above-mentioned internal fluorinated chain.

Many scientific reports are available, describing the photo-synthesis process, post-treatment conditions and some of the main functionalization reactions for the synthesis of perfluoropolyether-macromonomers (PFPE). Their chemical/physical properties have been widely investigated as well as the dependence from the chemical structure, as recently reviewed by Marchionni et al. [6].

Exhaustive works have been carried out on PFPE-macromolecules bearing as reactive groups acyl fluoride –COF, methyl ester $-COOCH_3$, methylol $-CH_2OH$; this last group is obtained by chemical reduction of the corresponding ester under mild conditions [7–9].

Generally, the presence of the perfluorinated chain α to the reactive group strongly modifies its reactivity. This makes possible a variety of synthetic routes which often can be carried out easier, and with more favourable reaction rates and yields, if compared to the reactions of the corresponding hydrogenated molecules.

The selection of fluorinated chain lengths, whose MW generally ranges from 1000 to 4000, offers a further possi-

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bility of fine-tuning of the final performances. As a general rule, within each class of derivatives, the increase of the fluorinated chain length shifts the properties to those typical of a perfluorinated molecule, while its shortening produces an opposite effect; i.e. it makes the properties closer to conventional hydrogenated molecules.

The methyl ester derivative ZDEAL (II) and the corresponding alcohol ZDOL (III) are key precursors for a large number of derivatives bearing functional groups of different nature or unreactive end-capped segments.

$$\mathbf{CH_3OC\text{-}CF_2(OCF_2)_q(OCF_2CF_2)_pOCF_2\text{-}COCH_3\ (II)}$$

$$HOCH_2-CF_2(OCF_2)_q(OCF_2CF_2)_pOCF_2-CH_2OH \quad (III)$$

$$H(OCH_2CH_2)_nOCH_2CF_2(OCF_2)_q(OCF_2CF_2)_p \times OCF_2CH_2O(CH_2CH_2O)_nH \quad (IV)$$

An exhaustive list of ZDEAL and ZDOL reactions by type of compound synthesized is difficult, and outside the scope of the present work. Rather we prefer to point out the high potential of these interesting precursors discussing two general classes of reactions. The first one includes reactions in which the fluorinated macromolecule condenses with another molecule and low molecular weight by-products are formed (generally water, alcohols and acids). Within these class esterifications, starting from ZDEAL or its carboxylic acid and acyl halide, to give organic esters and amination are worthy of note. Other interesting reactions, which produce inorganic esters starting from ZDOL or its ethoxylated derivative (ZDOLTX) (IV) [10], belong to this class; some of them will be described. The second class includes nucleophilic substitution (S_N) from ZDOL. Within this last category, according to the high versatility of ZDOL, two further typologies can be identified: S_N in which ZDOL or ZDOLTX are the attacking species or the substrate of the nucleophilic attack.

Finally, some significant examples of the chemical/physical properties of these macromolecules are reported, they are useful to focus potential uses. Some interesting applications, in which the excellent final performances are strictly connected with the presence of these telechelic PFPE-structures, are also discussed.

2. Results and discussion

Unless necessary, we will represent any symmetric difunctional molecule by writing only half of the chemical structure.

2.1. Condensation reactions

As discussed in Section 1, under this definition we will embrace reactions in which low molecular weight by-products are formed; however, some of them can be also considered as nucleophilic substitution at an aliphatic trigonal carbon.

2.1.1. Esterification

2.1.1.1. Carboxylic esters. Fluorinated carboxylic esters can be easily formed by alcoholysis of the corresponding acyl halides:

$$R_fCOX + ROH \rightarrow R_fCOOR + HX \quad (X = F, Cl) \qquad (1)$$

The electron-withdrawing effect of the R_f chain α to the carboxy group is clearly shown by the IR shift of the carbonyl stretching from 1740 to 1780 cm^{-1}, moving from hydrogenated to fluorinated alkyl esters. This band is further shifted to higher frequencies (1810 cm^{-1}) when, for the alcoholysis reaction, a fluorinated alcohol is used, like R'_fCH_2OH.

The high reactivity imparted by the fluorinated chain allows to convert acyl halides under mild conditions with virtually all alcohols even though sterically crowded. For example, the reaction with *t*-BuOH proceeds without using its alkoxide, as is generally required for the hydrogenated esters [11]:

$$ClOCR_fCOCl + 2(CH_3)_3COH \rightarrow (CH_3)_3COOCR_fCOOC(CH_3)_3 + 2HCl \quad (V) \qquad (2)$$

When the alcoholysis is performed with ZDOL, depending on the selected stoichiometry, three-blocks segmented derivatives, oligoesters, or polyesters can be obtained according to the following general reaction scheme:

$$\begin{array}{c} FOCR_fCOF + HOCH_2RFCH_2OH \\ \downarrow \\ HOCH_2RFCH_2O(OCR_fCOOCH_2RFCH_2O)_nH \\ (VI) \end{array} \qquad (3)$$

A large excess of ZDOL must be present to obtain a condensation degree $n=1$. On the contrary, a polyester is formed (n approaches infinity) if equimolar reagents are converted (any residue –COF end groups of the polymer can be eventually converted by a slight excess of ZDOL).

The extent of this reaction is easily followed by IR analysis. Actually, the stretching of –COF at 1890 cm^{-1} gradually disappears and a new band due to the stretching of highly fluorinated ester is observed at 1810 cm^{-1}. Also ^{19}F NMR analysis is a suitable technique for following the reaction. The disappearance of the $-CO\underline{F}$ signal together with the characteristic shift of the preterminal groups $-C\underline{F_2}CH_2O-$ of ZDOL are diagnostic for the ester formation (see Section 3).

Thanks to the strong acidity of the perfluorinated carboxylic acid, the esterification with primary and secondary alcohol does not require any catalyst. Conventional procedures can be used in order to drive the equilibrium toward ester formation. High yield is always observed, as in the

case of isobutyl ester:

$$R_fCOOH + HOCH_2CH(CH_3)_2 \rightleftarrows R_fCOOCH_2CH(CH_3)_2 + H_2O \quad (VII) \qquad (4)$$

Only with tertiary alcohols the reaction does not proceed, because the steric hindrance of these alcohols completely shifts the equilibrium to the left.

Finally, transesterification of ZDEAL with longer hydrogenated alcohols is an alternative and easy way to obtain a large variety of PFPE-esters.

2.1.1.2. Phosphoric esters. These derivatives are easily achievable by condensation of ZDOL, or its ethoxylated derivative (ZDOLTX), with phosphorous oxychloride ($POCl_3$, reaction (5)) or with pyrophosphoric acid ($O[P(O)(OH)_2]_2$, reaction (6)):

$$R_fCH_2O(CH_2CH_2O)_nH + POCl_3 \rightarrow R_fCH_2O(CH_2CH_2\ O)_nPOCl_2 + HCl \quad (VIII)$$

$$(VIII) + 2H_2O \rightarrow R_fCH_2O(CH_2CH_2O)_nPO(OH)_2 + 2HCl \quad (IX) \qquad (5)$$

$$R_fCH_2OH + O[P(O)(OH)_2]_2 \rightarrow R_fCH_2OPO(OH)_2 + H_3PO_4 \quad (X) \qquad (6)$$

Since when $POCl_3$ is used both the reagents are polyfunctional, oligo- and/or poly-esters can be obtained as side-products. However, appropriate experimental conditions and a large excess of $POCl_3$ make it possible to strongly reduce the chain growth.

The use of pyrophosphoric acid enables one to obtain good selectivity in the monoalkyl-phosphoric ester formation. Actually, in this case, the structure of the pyrophosphoric reagent prevents the oligo-esters formation:

$(HO)_2P(O)OP(O)(OH)_2$ (XI)

Moreover, even if commercial pyrophosphoric acid may contain significant amounts of longer *n*-poly-phosphoric acids of structure:

$(HO)_2P(O)O[P(O)(OH)O]_{n-2}P(O)(OH)_2$ (XII)

only minor amounts of bis-PFPEphosphoric ester are observed. The reason for this behaviour is probably due to the steric hindrance imparted by the first fluorinated chain bonded to the P atom which prevents further attack on the same position by a second molecule of the fluorinated alcohol. This mechanism is confirmed by a comparison of the ^{31}P NMR spectra of molecules obtained by reacting ZDOLTX with $POCl_3$ and pyrophosphoric acid (curves a and b, respectively, in Fig. 1). This last reaction gives only minor bis-esters by-product whose signals resonate at −2.6/−3.0, whereas the monoester signal is located at −1.5/−2.0. Interestingly these peaks are split into an apparent triplet and a doublet, respectively; this is especially evident in sample a. These multiplets do not originate from coupling phenomena but rather they are due to some structural irregularities of the fluorinated precursor. Namely ZDOLTX has an ethoxylation degree slightly higher than 1 (typical average values range from 1.2 to 1.8). This means that end-capped segments may contain 1 or 2 ethylenoxy units: ^{31}P NMR can distinguish these different phosphoric esters. In fact the two signals of the monoester (maximum peak at −1.8 and −1.6 ppm) can be attributed to the molecules containing mono-ethoxylated and bis-ethoxylated chains, respectively, whereas the triplet, well evident in product a, results from the statistical combination of the species, i.e. diesters which contain equal or different fluorinated substituents. This gives rise to the three partially overlapped signals observed in the spectrum. Their intensity ratio (1:2:1) agrees well with the theoretical value calculated considering that ZDOLTX has, in this case, an ethoxylation degree of 1.5.

Finally, both spectra show a small signal of the orthophosphoric acid at −0.6 ppm. The hydrolytic stability of these fluorinated phosphoric esters strongly depends on the vicinity of the fluorinated chain to the P atom. Particularly, the presence of the electron withdrawing fluorinated chain (ZDOL based phosphoric esters) greatly activates the nucleophilic attack at the P centre, whereas the introduction of hydrogenated spacing segments (ZDOLTX based phosphoric esters) strongly improves the stability of the molecule.

2.1.1.3. Boric esters. The reaction of ZDOL with boric acid is a further example of the preparation of fluorinated inorganic esters.

The reaction is easily completed simply by gently warming together the two reagents. The structure of the resulting molecule depends on the selected stoichiometry: higher molecular weight molecules can be synthesized up to a crosslinked polymeric network obtained when equivalent amounts of reagents are allowed to react:

$$\left(-BOCH_2R_fCH_2OBOCH_2R_fCH_2OB- \quad (XIII)\right)$$
$$\qquad\qquad\qquad\qquad\qquad\quad OCH_2R_fCH_2O-$$

If an excess of boric acid is used, the following product is obtained:

$$HOCH_2R_fCH_2OH + 2H_3BO_3 \rightleftarrows (HO)_2BOCH_2R_fCH_2OB(OH)_2 + 2H_2O \quad (XIV) \qquad (7)$$

The equilibrium can be shifted completely to the right by water distillation. The course of the reaction can be monitored by ^{19}F NMR; in fact the typical signals of

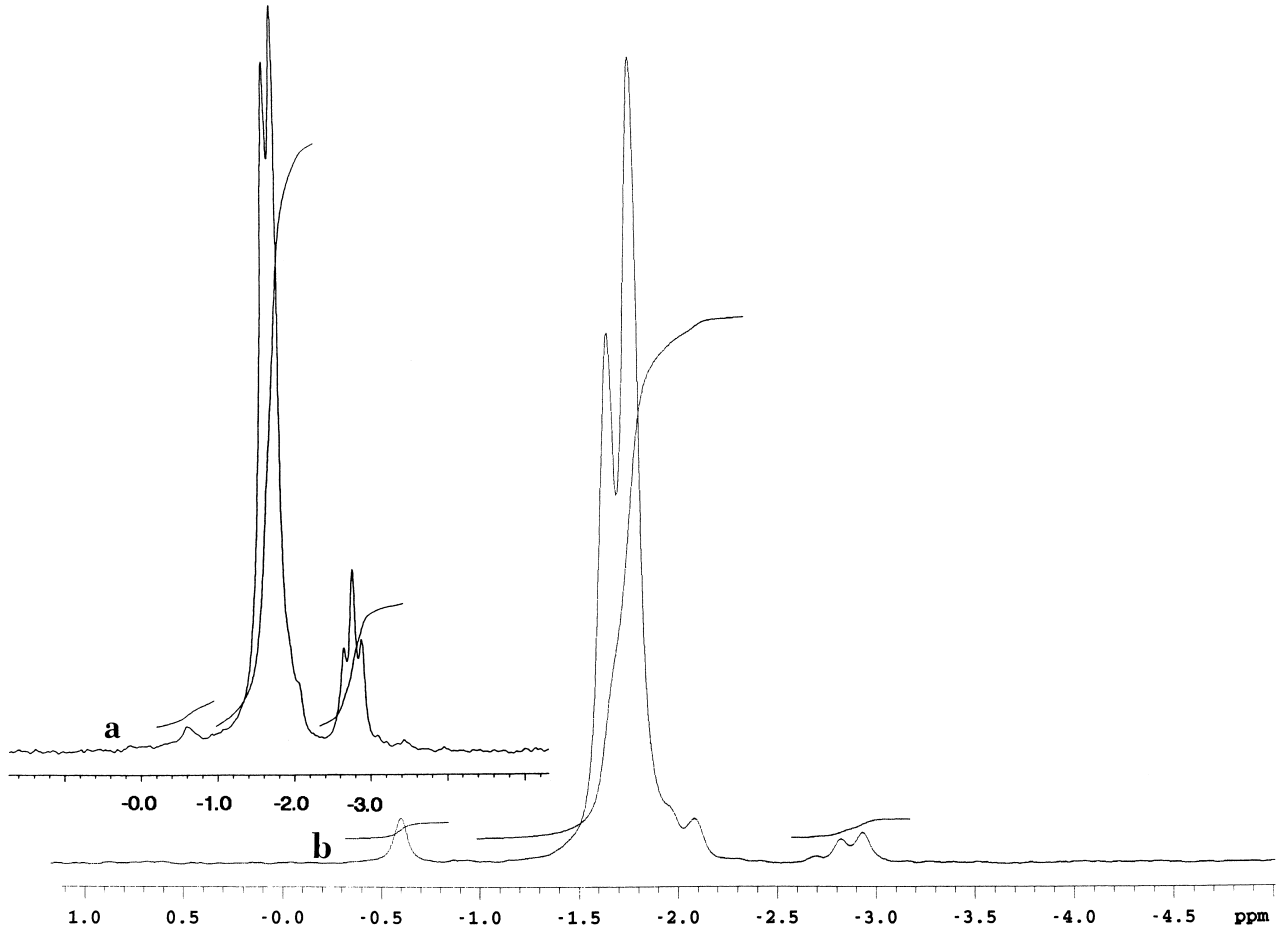
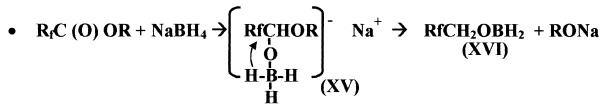


Fig. 1. ^{31}P NMR spectra of PFPE-phosphoric esters using $POCl_3$ (a) and pyrophosphoric acid (b).

CF_2 β to the boric ester group are located at -80.5 ppm ($-OCF_2CF_2O\underline{C}F_2CH_2OB$) and -82.5 ppm ($-OCF_2O\underline{C}F_2$-CH_2OB), whereas in the diolic precursor they resonate at -81 and -83 ppm, respectively.

Also in this case the fluorinated chain enhances the reactivity of the electron poor centre versus nucleophilic species. Consequently, acid- or base-catalysed hydrolysis of the molecule can be easily carried out.

It is interesting to note that fluorinated boric esters are the intermediates of the chemical reduction of fluorinated esters with $NaBH_4$ in ethanol as solvent, probably through the following mechanism which involves a series of nucleophilic attacks at the activated C atom adjacent to the R_f chain:



(8a)

$$R_fCH_2OBH_2 + 2ROH \rightarrow \underset{(XVII)}{R_fCH_2OB(OR)_2} + 2H_2 \quad (8b)$$

$$R_fCH_2OB(OR)_2 + 3H_2O \rightarrow R_fCH_2OH + H_3BO_3 + 2ROH \quad (8c)$$

It should be pointed out that the presence of R_f α to the carboxy group makes the reductive reaction easier. Accordingly, even though sodium borohydride is a very mild reducing agent, it works very effectively in the above-mentioned reaction.

Intermediate (XVI) comes from S_{Ni} of product (XV). This fluoroalkoxyborane is a highly reactive species which immediately forms tris-alkylboric ester (XVII) with the solvent.

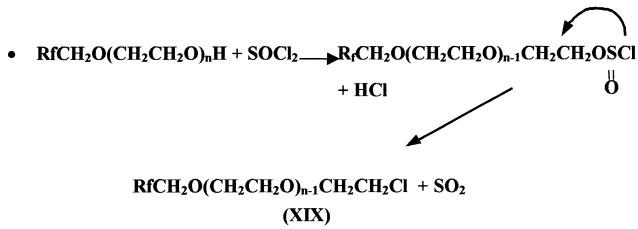
2.1.1.4. Sulfur-containing esters. Chlorosulfite. Some interesting derivatives can be obtained by reacting ZDOL or ZDOLTX with molecules containing sulfur. Among them esters are worthy of note.

For instance, the reaction with an excess of thionyl chloride shows two different pathways according to the nature of the fluorinated alcohol.

In the case of ZDOL the reaction does not proceed through an S_{Ni} mechanism since the first intermediate, fluoroalkyl chlorosulfite (XVIII), is not able to dissociate into an intimate ion pair. This is due to the strong bond energy of the ether linkage β to the R_f. As a consequence, alkyl chloride cannot be formed, while this is possible with ZDOLTX. In this case a behaviour similar to that of con-

ventional hydrogenated alcohols is observed and the fluorinated molecule converts to the corresponding alkyl halide (XIX):

$$R_fCH_2OH + SOCl_2 \rightarrow R_fCH_2OS(O)Cl + HCl \quad (9)$$
(XVIII)



(10)

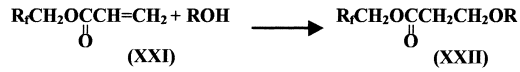
Sulfonic esters. *p*-Toluenesulfonylchloride and trifluoromethanesulfonylfluoride are widely used in nucleophilic substitution for substrates bearing alcohol groups, since OH is a poor leaving group while its sulfonic ester derivatives are much better leaving groups.

Syntheses and reactions of fluorinated tosylates and triflates are described in the literature. For example, tosylates of ZDOL and ZDOLTX have been obtained and their chemical–physical behaviour investigated [10,12]. ZDOLTX tosylate shows approximately the same reactivity of conventional hydrogenated compounds, while ZDOL tosylate is a very stable molecule in which the tendency of the sulfonic ester to act as leaving group is strongly depressed by the fluorinated chain.

In this case, perfluoroalkanesulfonate derivatives (e.g. nonaflate (XX)) can be a valid choice. Actually, the presence of the perfluorinated-alkyl chain α to the $-SO_3$ group greatly increases the effectiveness of this sulfonic ester as a leaving group, making thus possible nucleophilic reactions at the activated CH_2 group of ZDOL (see S_N discussion):

$$R_fCH_2OH + C_4F_9SO_2F \rightarrow R_fCH_2OSO_2CF_2CF_2CF_2CF_3 + HF \quad (11)$$
(XX)

2.1.1.5. Acrylic and methacrylic esters. ZDOL reacts with acryloyl and methacryloyl chlorides to give the corresponding esters [13]. Interestingly, this reaction can proceed further on, and in basic or water media the product can be converted to the corresponding saturated adduct. This reaction, well-known in organic chemistry, is here strongly activated by the fluorinated chain neighbour to the double bond which behaves like an olefin of the type C=C–Z. As a consequence, the reaction is of the Michael type and nucleophilic species attack the side away from the Z substituent:

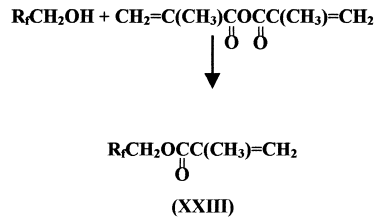


(12)

(where R=H, alkyl group).

The ^1H NMR of fluorinated acrylate (XXI) (Fig. 2) shows the presence of two non-equivalent geminal protons. Not only, all the vinylic protons are mutually coupled, but also the CH α to the carbonyl group couples to the CH_2.

Though anhydrides are somewhat less reactive than acyl halides, fluorinated methacrylic esters can be easily prepared also without acid or base catalysis, thanks to the high reactivity of ZDOL:



(13)

2.1.2. Amination

As already pointed out fluorinated esters are very reactive and versatile reagents. For instance they can be converted to amides. Unlike hydrogenated esters, the reaction does not require any catalyst and proceeds very quickly under mild conditions also with simple esters which generally are not

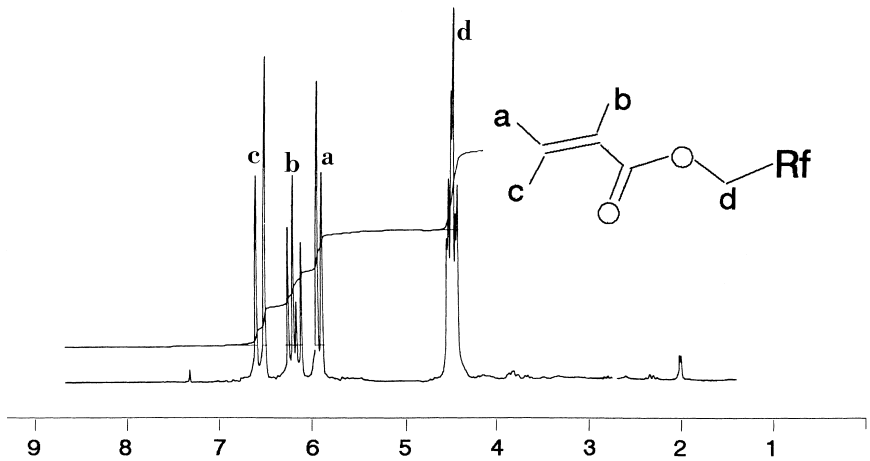


Fig. 2. ^1H NMR spectrum of PFPE–acrylate.

very reactive (R=Me, Et, etc.):

$$R_fCOOR + R'RNH \rightarrow R_fCONR'R + ROH \quad (R', \text{ R alkyl or H}) \tag{14}$$

In principle a large variety of amides can be achieved both with a macromeric (R_h–R_f–R_h) or polymeric structure, if a difunctional amine is used [14,15].

Accordingly, PFPE-amidosilyl derivatives can be formed by reacting ZDEAL with (trialkoxysilyl)alkylamine:

$$R_fCOOR + NH_2(CH_2)_3Si(OC_2H_5)_3 \downarrow R_fCONH(CH_2)_3Si(OC_2H_5)_3 + ROH \quad (XXIV) \tag{15}$$

Only with hindered amines, or with aromatic amines having very low nucleophilicity due to the presence of deactivating substituents (pK_a<4.0), the use of acyl halides is needed. In this case the reaction is highly exothermic. An excess of the same amine can be used as acid acceptor, as given in the following example:

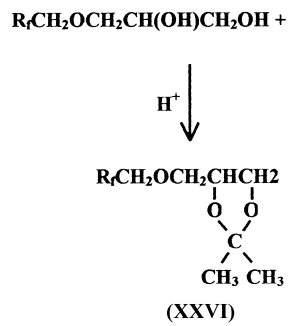
$$R_fCOCl + 2NH[CH(CH_3)_2]_2 \rightarrow R_fCON[CH(CH_3)_2]_2 + HCl \cdot NH[CH(CH_3)_2]_2 \quad (XXV) \tag{16}$$

In Fig. 3 the corresponding ^{1}H NMR is reported. The pattern of the spectrum clearly indicates that there are two couples of non-equivalent methynes and methyls, since the two bulky isopropyl substituents adjacent to the amide group are not free to rotate. Consequently, two conformational isomers are present.

2.1.3. Acetals and ketals formation

Fluorinated acetals or ketals are formed by treatment of alcoholic derivatives with aldehydes or ketones in the presence of acid catalysts. This is a reversible reaction, and acetals and ketals can be hydrolysed by treatment with acid, usually the equilibrium being shifted by water removal.

If fluorinated 1,2-glycols are used, 1-3 dioxolane derivatives can be obtained:



(17)

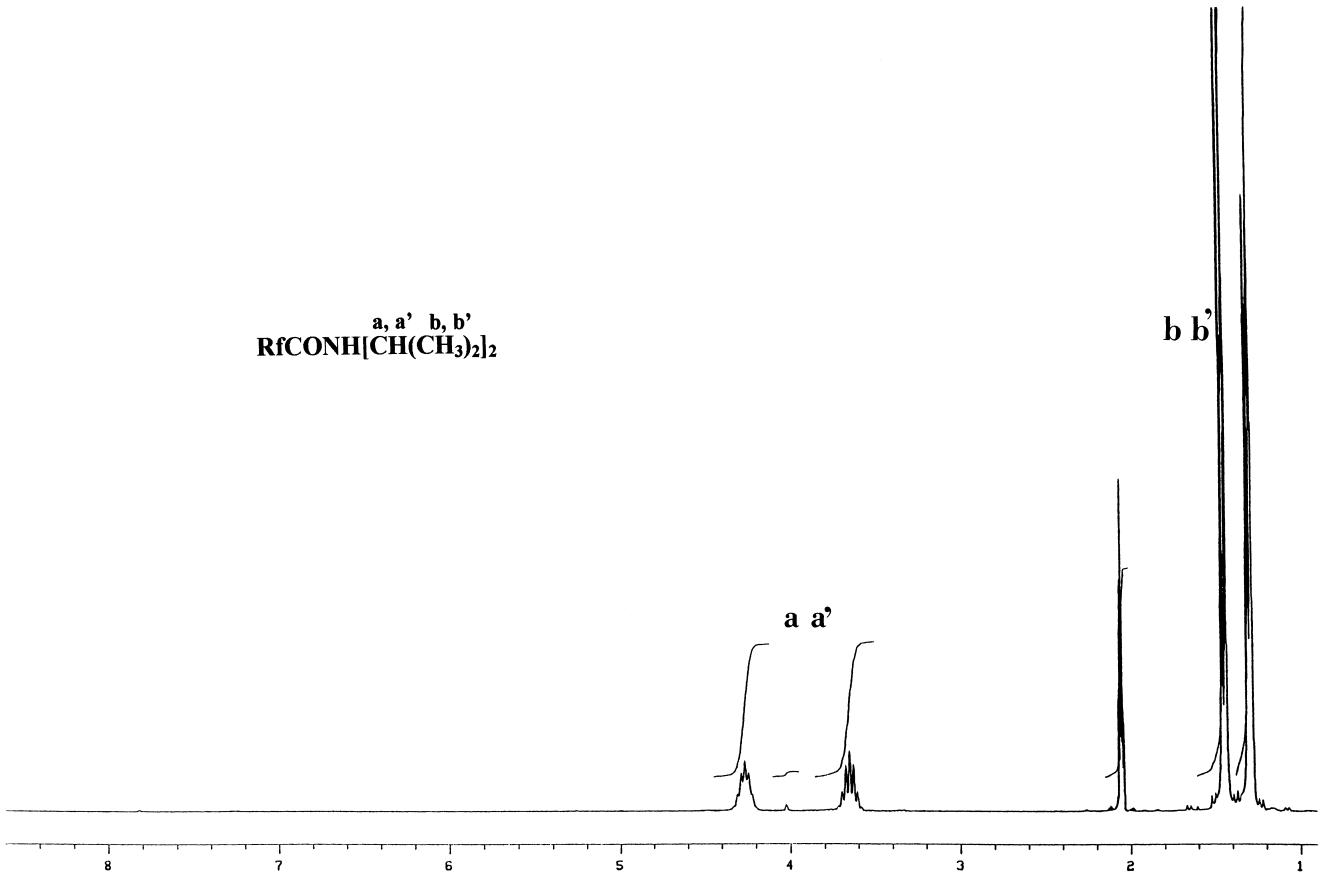


Fig. 3. ^{1}H NMR spectrum of PFPE–diisopropylamide.

Interestingly, this reaction can be used not only to protect alcoholic functions of fluorinated polyols but also it offers to the chemist an easy and reversible way to strongly modify the chemical/physical characteristics of the molecule (viscosity, solubility, polarity, etc). This technique can be used for the purification of mixtures otherwise difficult to separate, for instance for the extraction of salt impurities for extra-pure polyolic products.

^{1}H NMR (CFC 113/acetone as solvents) easily evidences the cyclic ketal by the appearance of the characteristic signals of the two not equivalent CH_3, which resonate at 1.31 and 1.38 ppm.

2.2. Nucleophilic substitution

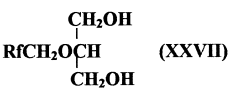
2.2.1. ZDOL as attacking reagent

The acidity of the OH groups of ZDOL makes it easy to obtain the corresponding fluoropolyether alkoxide by acid/base reaction with conventional bases [10]. Unlike other fluorinated alcohols, which easily undergo degradation in strong alkaline media, ZDOL shows a good stability provided that an excess of alcohol is used [10,12].

When no competitive nucleophilic reactions are possible, more conventional base, like NaOH or KOH, can be used; otherwise *t*-BuOK/*t*-BuOH must be preferred.

2.2.1.1. Ring opening reactions. Interestingly, the acidity of ZDOL much higher than that of hydrogenated alcohols allows the synthesis of molecules essentially constituted of mono-alkoxylate derivatives. Actually, the alkoxide intermediate R_f–R_h–O^- (where R_h represents the hydrogenated spacing segment) immediately gives acid/base reaction with the more acid R_fCH_2OH and a new $R_fCH_2O^-$ molecule is available for a further nucleophilic attack, while the chain growth stops.

Oxirane. The alcoholysis of epoxides with ZDOL is a general way to obtain β-hydroxy ethers; based catalysed reactions of ZDOL with ethylene oxide, glycidol or epihalohydrins have been widely investigated [10,16]. Most of these substrates are ''ambident'', that is they may be attacked at two or more positions. However, in the case of asymmetric epoxides the nucleophilic attack shows high regio selectivity and the reaction essentially proceeds at the less hindered carbon atom. However, by-products due to the attack at the more substituted carbon atom are sometimes observed, as in the case of ZDOL reaction with glycidol. In this case the regio selectivity is close to 90% and, besides minor ''bis-adducts'', end-capped segments having the following structure are present:



(XXVII) (18)

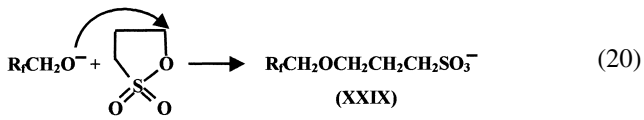
^{13}C NMR of the acetylated sample confirms the presence of this by-product (5–10%), in fact the signal at 84.4 ppm originates from the CH of the structure (XXVII).

On the contrary, very high regio selectivity is observed with propylene oxide:

(19)

Actually, the product derived from the attack at the CH is not observed.

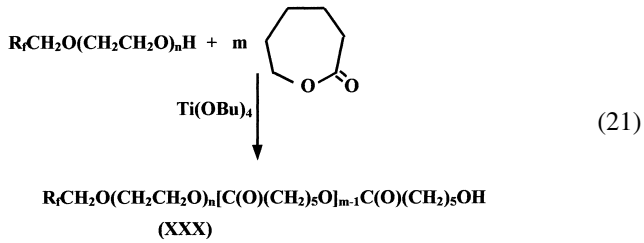
Sultone. ZDOL alcoholate reacts with 1,3-propane sultone forming sulfonic derivatives:



(20)

Also this reaction is highly regio specific, in fact the reaction does not give rise to different structural isomers.

Caprolactone. In a similar way also caprolactone rings react with base catalysed ZDOL or ZDOLTX alkoxide. Experimental conditions and reagents ratio address the course of the reaction. This reaction can be also carried out in the presence of organic titanium compounds like alkoxides (titanate esters). Among the different titanates, titanium(IV) butoxide shows a very high efficiency and PFPE-segmented macromonomers in which poly(ε-caprolactone) end-capped chains are present can be obtained provided an excess of ε-caprolactone is used:



(21)

In this case, due to the large difference of the solubility parameters between the PFPE-chain and the polyester segment, phase segregation occurs as clearly evidenced by calorimetric analysis (Fig. 4). The DSC trace shows the presence of two amorphous phases at −115°C and −70°C (curve a), which correspond to the PFPE and hydrogenated soft phases, respectively. As expected, the crystallization of polyester chain is also observed at 57°C (curve b).

2.2.1.2. Alkoxy-de-halogenation. Williamson reaction. This reaction can be carried out with aliphatic and aromatic substrates and it is the best general method for the preparation of unsymmetrical ethers.

The base catalysed reaction of ZDOL with α,ω dihaloalkanes is described in the literature [10], but other interesting derivatives can be obtained, for example, by reaction of ZDOL with aromatic molecules containing Cl-methyl groups.

This activated substrate makes the reaction quite easy, and generally, quantitative yields are observed. Benzyl or naphthyl derivatives with different substituents on the aromatic rings can thus be obtained. Among them, products

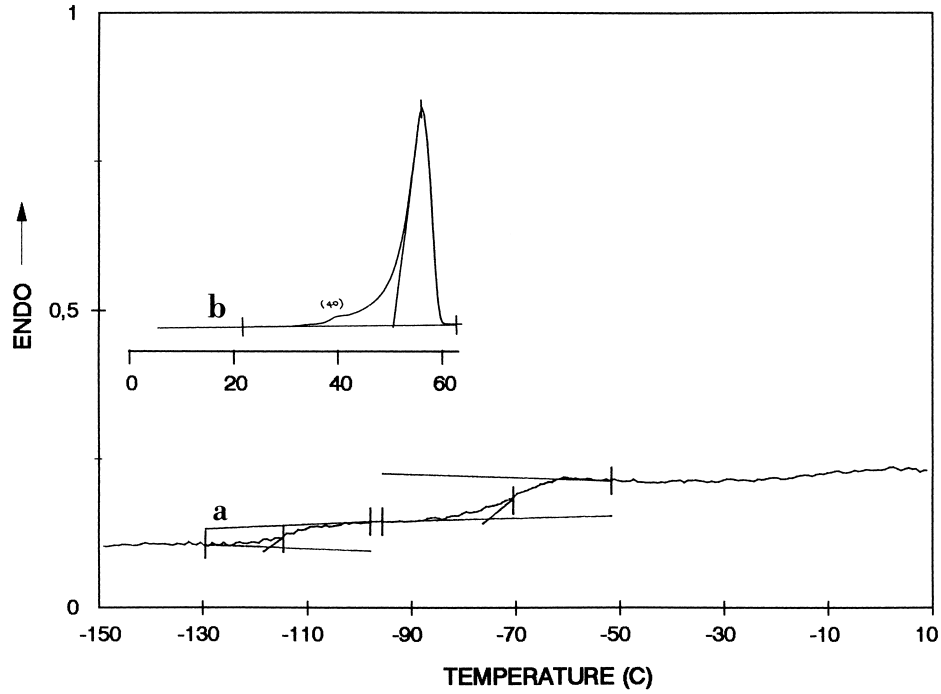
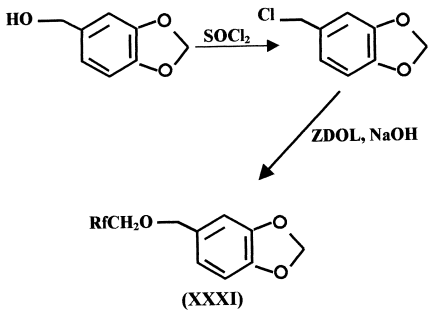


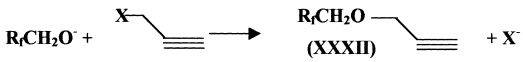
Fig. 4. DSC traces of PFPE–poly(ϵ-caprolactone) end-capped molecule: amorphous phases (a) and crystalline phase (b).

having methylene-di-oxy groups are worthy of note for their unique chemical and physical properties (see applications):



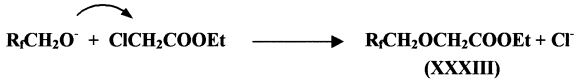
(22)

The reaction of ZDOL with allylic halides is a well-known reaction. This substrate undergoes nucleophilic substitution reactions at a very high rate and diallyl ethers are obtained. Similarly, propargylic substrates offer an interesting way for the synthesis of new unsaturated fluorinated molecules [17]:



(23)

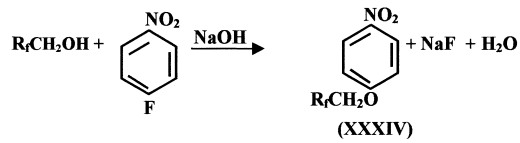
Another interesting example of Williamson reaction is the α carboxy substitution, as in the case of the base catalysed reaction of ZDOL with compounds of formula ZCH_2X (Z is RCO, ROCO) which undergo S_N reactions very rapidly:



(24)

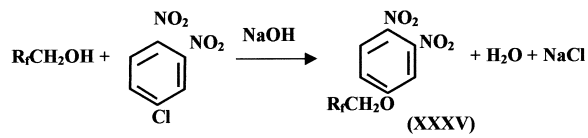
This reaction, which probably proceeds through an S_{N_2} mechanism, makes it possible to convert ZDOL to a carboxylic acid (through a further hydrolysis step) having acidity close to that of conventional hydrogenated compounds.

Aromatic nucleophilic substitution. Reactions of ZDOL that are successful with an aromatic substrate are those in which the aromatic ring is activated by electron-withdrawing groups *ortho* and *para* to the leaving group, as in the following example:

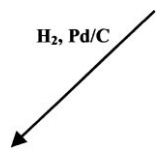


(25)

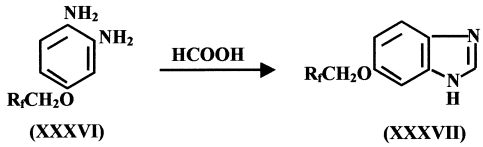
In a similar way fluoroalkoxy-orthodinitro benzene can be synthesized and the corresponding amine easily obtained by reduction. Finally, the fluoroalkoxy-benzimidazole derivative can be prepared by reaction/cyclization with formic acid:



(26)



(27)

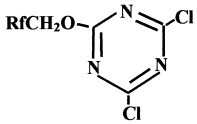


(XXXVI) (XXXVII) (28)

The ^{1}H NMR analyses confirm the expected structures both for intermediates (XXXV), (XXXVI) and final fluoroalkoxybenzimidazole derivative (XXXVII).

A further example of aromatic nucleophilic substitution is given by the reaction of ZDOL or ZDOLTX with heterocyclic compounds, like trichlorotriazines and cyclotrichlorophosphazenes.

The extent of the reaction can be modulated since the stoichiometry and the experimental conditions can drive the synthesis toward the single addition product or to a more extensive Cl substitution, up to a complete conversion of all chlorine atoms. If a 2:1 molar ratio of trichloro-triazine/ZDOL is used, the following compound can be isolated:



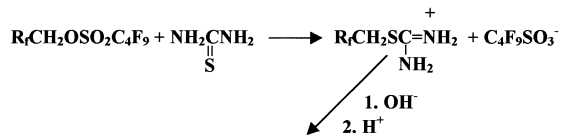
(XXXVIII)

^{13}C NMR (Fig. 5) gives a pattern consistent with the expected structure. In fact all C atoms bearing fluorine resonate in the range 112–128 ppm, CH_2 is observed at 68 ppm, whereas the triazine ring gives two signals at 173 and 176 ppm due to the C bonded to the alkoxy-substituent and to the C–Cl atoms, respectively.

2.2.2. ZDOL and ZDOLTX as substrate of nucleophilic attack

2.2.2.1. Sulfur nucleophiles. The sulfonic esters are ideal derivatives for the synthesis of PFPE-macromolecules in which ZDOL or ZDOLTX undergo a nucleophilic attack. Among them nonaflate derivative is the most reactive (see the discussion about fluorinated sulfonic esters).

2.2.2.2. Mercaptans. A nice procedure for the conversion of ZDOL (through its nonaflate derivative) into a mercaptan is based on the treatment with thiourea to give an isothiouronium salt, which is cleaved to the desired mercaptan by alkali or high-molecular weight amine:



(XXXIX) (29)

The compound (XXXIX) can be obtained in good yields, with only a small amount of by-products, constituted mainly by the corresponding thioether. This side-product is probably formed through a nucleophilic attack of the PFPE–thiolate salt, deriving from the alkaline hydrolysis of the isothiouronium salt, at the activated carbon atom of

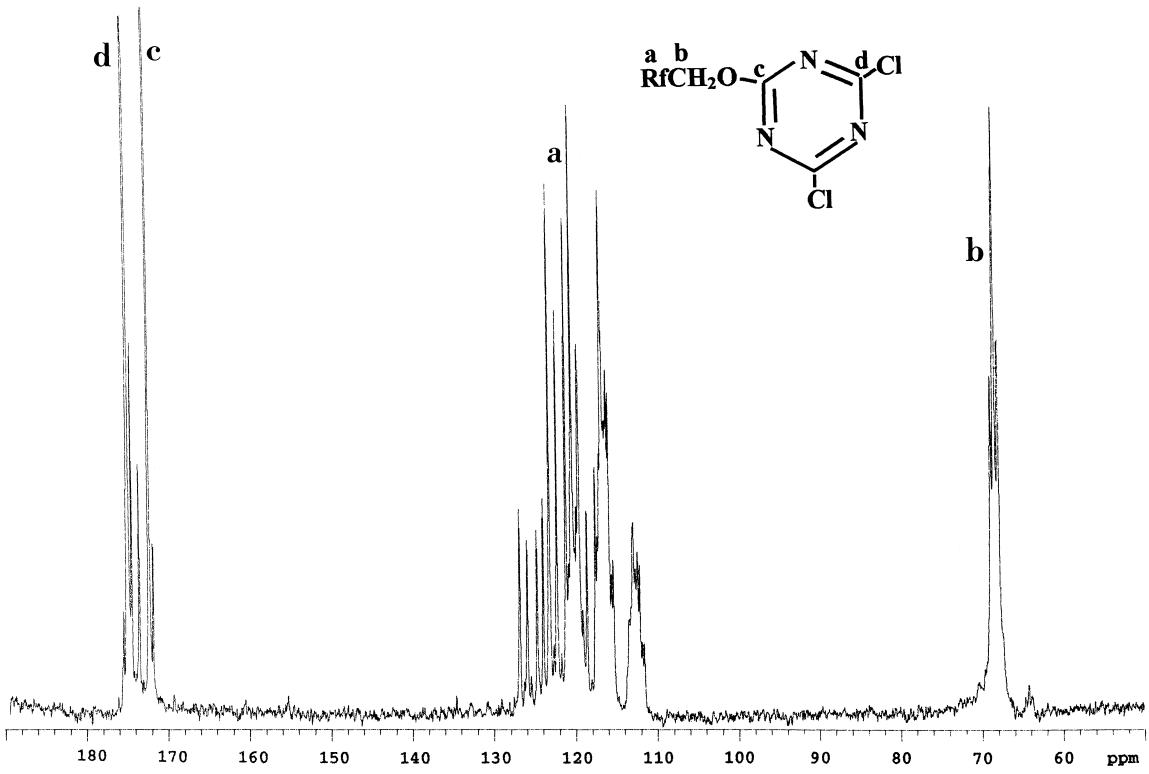
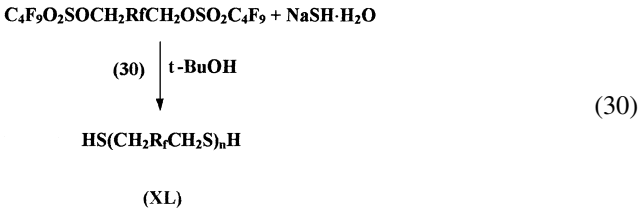


Fig. 5. ^{13}C NMR spectrum of PFPE–triazine.

the salt itself. Both ^{1}H and ^{19}F NMR are highly diagnostic for the reaction monitoring.

2.2.2.3. Sulfides. Symmetrical or asymmetrical PFPE-sulfides can be prepared by nucleophilic attack at the electron poor C atom of the PFPE-nonaflate. The former are obtained by treatment with sodium hydrogen sulfide monohydrate, reaction (30); the latter by reaction with thiolates, reaction (31):



(30)

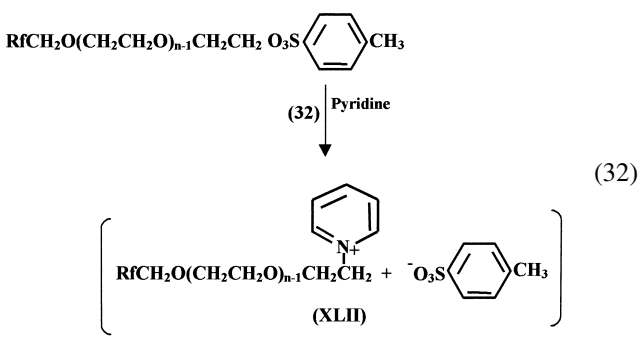
Generally, sodium sulfhydride is a very good reagent for the formation of mercaptans from alkyl halides, sulfuric and sulfonic esters, although sulfides (RSR) are often side products.

However, in the present case a good selectivity in the sulfide formation is observed, probably because the system is not a true solution but rather a micro-phase separation is present. This etherophasicity promotes a further reaction of the products having similar solubility; consequently the PFPE-mercaptan is converted, by reaction with the PFPE-nonaflates, as soon as it is formed. Accordingly, this reaction proceeds through two S_N steps: the first one involves the attack of the SH- moiety at the PFPE-nonaflate, the second being the reaction of the PFPE–thiol intermediate (or its thiolate) with the PFPE-nonaflate. Therefore, the reaction product is the polysulfide (XL), being the chain extension promoted by the difunctional nature of the involved PFPE-species.

Asymmetrical PFPE-sulfides can be obtained in a similar way, even if in this case the reaction proceeds through a one-step process. High yield and selectivity are always observed:

$$R_fCH_2OSO_2C_4F_9 + C_3H_7SH \xrightarrow[2.\ \text{acid}]{1.\ \text{base}} \underset{\text{(XLI)}}{R_fCH_2SCH_2CH_2CH_3} + C_4F_9SO_3H \quad (31)$$

2.2.2.4. Nitrogen nucleophiles. PFPE-quaternary ammonium salts can be prepared by reacting tertiary amines with PFPE-sulfonates (Menschutkin reaction). In this case a PFPE–ammonium sulfonate is formed, like in the case of ZDOLTX-tosylate:



(32)

In the corresponding ^{1}H NMR spectrum (Fig. 6), besides the expected signals of the two aromatic rings, it is possible to distinguish between the molecules having a different degree of ethoxylation. Namely the CH_2 α to the nitrogen atom resonate at 4.9 and 5.0 ppm (for n=2 and 1, respectively); similarly CH_2 β to the nitrogen are located at 4.0 and 4.2 ppm (n=2 and 1, respectively). The CH_2 adjacent to the R_f gives signals at 3.9 ppm (n=1) and 3.8 ppm (n=2), whereas the other signals at 3.6 and 3.7 ppm ($OC\underline{H}_2C\underline{H}_2O$) originate from the molecules containing more than one ethoxylated unit.

In a similar way PFPE-amines can be obtained starting from PFPE-nonaflate even if the reaction with ammonia or primary amines is not usually a feasible method for the preparation of primary or secondary PFPE-amines, since they are stronger bases than ammonia and preferentially attack the substrate. Nevertheless, selective reactions can be performed provided a large excess of amine or hindered primary amines are used.

2.2.2.5. Oxygen nucleophiles. ZDOL nonaflate can undergo nucleophilic attack by oxyanions. In this way it is possible to bond, through ether linkage, a large variety of alcoholic, diolic or polyolic molecules. When the attacking species are polyfunctional the chain growth can be avoided by using a large excess of glycol in the presence of an amount of base stoichiometric with the fluorinated substrate:

$$R_fCH_2OSO_2C_4F_9 + HOCH_2CH_2OH \xrightarrow{\text{base}} \underset{\text{(XLIII)}}{R_fCH_2OCH_2CH_2OH} + C_4F_9SO_3^- \quad (33)$$

However, severe reaction conditions are often required which can cause a partial degradation of PFPE-nonaflate. Actually, at the reaction temperature (80–120°C) base induced HF extraction at the activated CH_2 can occur; this side reaction destroys the base and limits the yields to values not higher than 70–80%.

2.2.2.6. Iodine as nucleophile. Iodine derivatives of ZDOL can be prepared in a similar way. For example, ZDOL nonaflate reacts easily with inorganic iodide dissolved in an aprotic dipolar solvent, like DMF, forming the corresponding iodine derivative in quantitative yield:

$$R_fCH_2OSO_2C_4F_9 + NaI \xrightarrow{DMF} \underset{\text{(XLIV)}}{R_fCH_2I} + C_4F_9SO_3Na \quad (34)$$

2.2.2.7. Carbon nucleophiles. Carbanions generated by simple acid–base reaction can easily form a bond with a carbon atom of a proper PFPE-substrate. As reported in the literature [10] the malonate anion is, from this point of view, a very useful and effective reagent. It reacts with ZDOLTX-tosylate and the corresponding polyfunctional derivative is

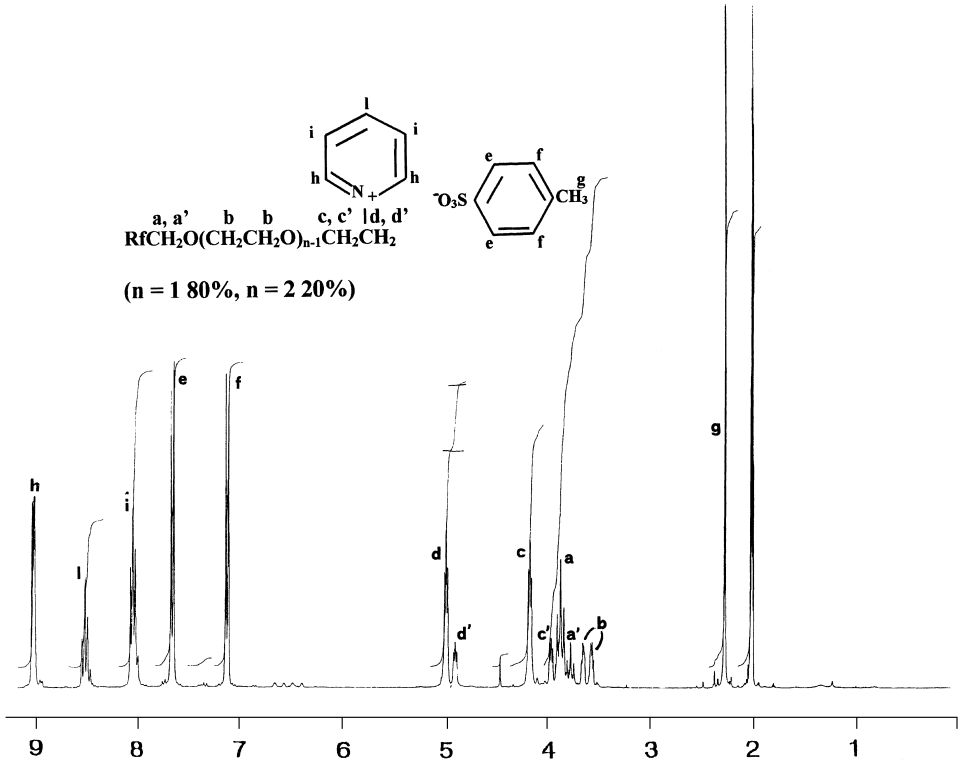


Fig. 6. ^{1}H NMR spectrum of PFPE–ammonium sulfonate.

obtained in a simple way:

$$R_fCH_2OCH_2CH_2CH(COOCH_3)_2 \quad (XLV)$$

The conversion of this substitution reaction is easily monitored by ^{1}H NMR, comparing the area of the signals of the methyne group –CH(COOR)$_2$ and CH_2 adjacent to the PFPE-chain. This reaction shows a high selectivity, whereas the conversion is 80% in the adopted experimental conditions.

3. Experimental

3.1. General comments

The aim of the present work is mainly focused on the definition of general aspects concerning new suitable synthetic routes for the preparation on PFPE-macromolecules bearing either reactive or unreactive hydrogenated end-segments. Therefore in some cases, the overall process was not fully optimized.

Generally, low molecular weight by-products, when present, have been eliminated by conventional techniques. On the contrary, the fluorinated molecules bearing structural heterogeneities, like unreacted terminal groups or different functional groups, are difficult to be purified. Actually, conventional procedures are not easily applicable to difunctional species which may have the proper end-group combined with the undesired one on the same macromolecule. Moreover, the chemical–physical behaviour of these PFPE-macromolecules prevents their purification by distillation or crystallization.

Nevertheless, the selectivity and the conversion were generally high. This makes very promising most of the reactions described in the present study.

The hydrogenated co-reagents and the solvents have been generally used as received, unless specific purification or water-free solvents were required for the syntheses.

3.2. Syntheses

3.2.1. PFPE-oligoesters (VI)

In a three-necked 100 ml flask, equipped with a mechanical stirrer and a dropping funnel, 40 g (37 mmol) of ZDOL (MW 1100) and 5 g of KF were placed under nitrogen. The PFPE–diacylfluoride (MW 900) (30 g, 27 mmol) was then added slowly, at room temperature, through the funnel and allowed to react for 2 h.

The product, recovered after elimination of the KHF_2 by filtration, is a low viscous clear liquid characterized by a typical IR band at 1810 cm^{-1}. The integration ratio among the different CF_2 preterminals is consistent with an oligoester having an MW close to 8000. ^{19}F NMR spectrum (neat sample) δ : -C$\underline{F}_2$CH$_2$OH −81 and −83; -C$\underline{F}_2$CH$_2$OC(O)– −79.5 and −77.5; -C$\underline{F}_2$(O)COCH$_2$– −79.0 and −77.0. The other signals are not diagnostic for the monitoring of the reaction since they are related to the internal fluorinated chain.

3.2.2. Phosphoric esters (X)

3.2.2.1. Use of pyrophosphoric acid. In a three-necked 250 ml flask, equipped with a mechanical stirrer and a dropping funnel, 22.5 g of pyrophosphoric acid are charged and heated at 60°C under stirring. Then 50 g (36 mmol) of ZDOLTX (MW 1400) are added through the funnel over a period of 1.5 h. A viscous reaction mass is obtained which is kept at 60°C for further 30 min. Then 35 ml of isopropyl acetate and 150 ml of HCl 2% are added and the mass stirred for 4 h.

The mixture is cooled at room temperature and a phase separation is observed over a period of 1 h. The fluorinated heavy phase is separated and washed two times with acidic water. Finally, the product (51 g) is dried in vacuo, and analysed by ^{31}P NMR. The NMR agrees with the formation of the PFPE–monoalkyl-phosphoric ester (containing slight amounts of dialkylester and orthophosphoric acid). ^{31}P NMR (CFC 113/methanol) δ:–$CH_2OP(O)(OH)_2$ −1.8 and −1.6; $(–CH_2O)_2P(O)OH$ −2.6/−3.0; H_3PO_4 −0.6.

3.2.2.2. Use of $POCl_3$. In the same reactor previously used 100 g (640 mmol) of $POCl_3$ are charged and heated at 60°C under nitrogen. Then 100 g (71 mmol) of ZDOLTX (MW 1400) are added dropwise over a period of 3 h. HCl evolution is immediately observed. The mass is kept under stirring at the reaction temperature further for 1 h. When the reaction is completed the excess of $POCl_3$ is removed in vacuo. The resulting fluoroalkyl phosphorous oxychloride is transferred into a dropping funnel and added slowly, under vigorous stirring, into a second reactor containing 250 ml of water. Finally, the addition of 100 ml of isopropyl acetate leads to a phase separation. The fluorinated ester (101 g) is purified and recovered by the same procedure described for the pyrophosphoric acid.

The ^{31}P NMR shows the same pattern already observed for the previous compound, even if, in this case, the dialkylester content is higher (18% with respect to 4%).

3.2.3. Boric esters (XIV)

In a three-necked 100 ml flask, equipped with a mechanical stirrer and connected through a valve to a vacuum pump, 50 g (25 mmol) of ZDOL (MW 2000) and 3 g (48 mmol) of H_3BO_3 are charged. The mixture is heated at 100°C for 2 h and the water being formed is removed by vacuum distillation. A viscous clear liquid is obtained.

^{1}H NMR (CDCl3) δ : $R_fC\underline{H}_2OB$ 4.2.

^{19}F NMR (neat sample) δ : $-C\underline{F}_2CH_2OB$ −80.5 and −82.5.

3.2.4. Sulfur-containing esters (XVIII) and (XX)

PFPE–sulfur esters can be easily formed by reacting, at low temperature (0–20°C), ZDOL or ZDOLTX with sulfonyl fluoride or thionyl chloride.

With $SOCl_2$ the reaction is highly exothermic. HCl and SO_2 by-products (the last present only when ZDOLTX is used) can be removed from the reactor by a nitrogen stream. When perfluorobutanesulfonylfluoride is used, the HF side-product can be eliminated by absorption onto KF or, as in the case of the HCl, using an inert gas stream. The final products are low viscous high reactive liquids, with the exception of the stable α,ω-Cl derivative obtained by reacting ZDOLTX with $SOCl_2$. Typical ^{1}H and ^{19}F NMR are as follows:

- $R_fCH_2OS(O)OCH_3$ (fluoroalkyl-methylsulfite), ^{1}H NMR (CFC 113/acetone) δ: CH_2 4.6 m, CH_3 3.1 s.
- $R_fCH_2OSO_2C_4F_9$ (fluorosulfonicester), ^{19}F NMR (neat sample) δ: CF_2 α to CH_2 −79 and −81; CF_2 α, β and γ to the sulfonic groups −110, −121 and −126; CF_3 −82.

3.2.5. Acrylic esters (XXI) and (XXII)

Ten grams of acryloyl chloride (110 mmol) and 100 ml of CFC 113 are charged into a 250 ml reactor. Forty-five grams of ZDOL (MW 1100) (40 mmol) are slowly added to the CFC solution kept at room temperature. Immediately after the reaction mixture is warmed at the refluxing temperature for 20 h. Finally, the excess of acryloyl chloride and the solvent are distilled off. A clear low viscous compound is obtained (48 g).

^{1}H NMR (in CFC 113/$CDCl_3$) δ: geminal vinylic protons 6.6–6.7 (*trans*) and 5.9–6.0 (*cis*); CH α to C=O 6.1–6.3; CH_2 α to R_f 4.4–4.6.

If the fluorinated acrylic ester is treated with an aqueous alkaline solution, a very fast Michael reaction (1,4 addition) takes place and the corresponding hydration product is formed.

^{1}H NMR (CFC 113/$CDCl_3$) δ: CH_2 α to R_f 4.4–4.6; CH_2OH 3.7–3.8 (t); CH_2 α to carbonyl 2.8–2.9 (t).

3.2.6. Amination

3.2.6.1. Amidosilyl derivative (XXIV). In a 100 ml two-necked flask equipped with a mechanical stirrer 40 g (40 mmol) of ZDEAL (MW 1000) is introduced and allowed to react with 18 g (82 mmol) of 3-(triethoxysilyl)propylamine at 40°C. During the reaction, vacuum is progressively applied in order to remove the methanol formed by the reaction. The PFPE–amidosilyl derivative is obtained as low viscous liquid.

^{1}H NMR (methanol) δ: CH_3 1.2 (t); CH_2 α to CH_3 3.8 (q); CH_2 α, β and γ to Si at 0.6, 1.6–1.7 and 3.2–3.3 (all m), respectively.

3.2.6.2. Diisopropylamide (XXV). In a 250 ml three-necked flask equipped with a mechanical stirrer, thermometer, and dropping funnel, 40 g of PFPE–diacylchloride (MW 600) (67 mmol) and 40 ml of CFC 113 are charged under inert atmosphere. The solution is cooled at 0°C and 35 ml (240 mmol) of diisopropylamine are slowly added under stirring over 2 h. Then the reaction mass is spontaneously warmed at room temperature and kept at this temperature,

under stirring, for one night. The solution, further diluted with other CFC 113, is filtered in order to eliminate the diisopropylamine hydrochloride. Finally, the solvent is distilled off and a low viscous fluorinated compound is obtained (45 g).

IR: band at 1690 cm^{-1}.

^1H NMR (acetone) δ: CH_3 1.3 (6H); CH_3 1.4 (6H); CH 3.6–3.7 (1H); CH 4.2–4.3 (1H) (all m).

^{19}F NMR (neat sample) δ: $-CF_2CON$ preterminals two signals at −74 and −72.

3.2.7. Ketals (XXVI)

In a 100 ml four-necked flask, equipped with a mechanical stirrer, dropping funnel, cooling column, and connected to a vacuum pump, 50 g of PFPE–tetraol (36 mmol) (MW 1400) (obtained by epoxidation/hydrolysis of the corresponding PFPE–bis-allylether [16]), 50 ml of acetone and 2 ml of HCl 37% are charged. The solution is refluxed for 2 h, then 5 g of pyridine are added. Solvent, water and excess of pyridine are finally removed by distillation in vacuo. After filtration, a clear low viscous PFPE-ketal is isolated (53 g).

^1H NMR (CFC 133/D6-Acetone) δ: CH_3 1.32 and 1.37 (6H); a complex pattern of signal at 3.5–4.3 (7H) due to the remaining protons (the complexity is originated by the presence of the cyclic ketal which contains a stereogenic centre).

3.2.8. Propoxylate (XXVIII)

In a 200 ml stainless steel pressure reactor 100 g (91 mmol) of ZDOL (MW 1100) and 10 ml of *t*-BuOH/*t*-BuOK solution (5%) are charged. Then 12 g (225 mmol) of propylene oxide is introduced and the mass warmed at 80°C for 14 h. Finally, the reactor is cooled at room temperature, the alkaline solution is treated with a HCl 5% solution, washed two times with 50 ml of distilled water and dried in vacuo at 80°C. A clear low viscous product is isolated (106 g) whose analyses are consistent with the expected structure.

^1H NMR (D_6-acetone) δ: R_fCH_2 and CH 3.9–4.1 (two overlapped m); $OC\underline{H}_2CH$ 3.5–3.6 (qd); CH_3 1.2 (d).

3.2.9. Sulfonic derivative (XXIX)

In a 250 ml three-necked flask 13.5 g (120 mmol) of *t*-BuOK is dissolved in 150 ml of *t*-BuOH freshly distilled.

Fifty grams (50 mmol) of ZDOL (MW 1000) are added drop-wise to the alkaline solution over 2 h. Then a slurry of 12.5 g (100 mmol) of 1,3-propane sultone in 10 ml of *t*-BuOH is charged. The reaction mass is warmed at 60°C and maintained at this temperature for some hours. The solvent is removed by distillation and a white solid is isolated (60 g). The analyses are consistent with the expected sulfonic structure.

^{19}F NMR δ: CF_2 preterminals: −77 and −80.

^1H NMR (D_2O) δ: CH_2 signals at 3.7, 3.5, 2.8 and 1.8 for methylene groups α, γ, δ, ϵ to the R_f chain, respectively.

3.2.10. Methylenedioxybenzene derivative (XXXI)

Eleven grams (72 mmol) of piperonyl alcohol is dissolved in 10 ml of CH_2Cl_2, and cooled at −5°C. Then 9 g (76 mmol) of thionyl chloride is slowly added. A strong evolution of HCl and SO_2 is observed over a period of 12 h.

The mass is warmed at 20°C and 8 g of NaOH 50% is introduced, followed by 40 g (21 mmol) of ZDOL (MW 1900) fed to the reactor over a period of 2 h under vigorous stirring.

After 4 h, 50 ml of water is added, and further washing twice (2×50 ml) makes it possible to separate a heavy fluorinated phase which is dried in vacuo at 80°C.

^1H NMR (CFC 113/D_6-Acetone) δ: aromatic protons 6.8–6.9 (3H, s); O-CH_2-O 6.0 (2H, s); benzylic CH_2 5.6 (s); R_f–CH_2 3.8–3.9 (td).

3.2.11. α-Alkoxyester (XXXIII)

Fifty grams (25 mmol) of ZDOL (MW 2000) is added to a solution of *t*-BuOK 8 g in 50 ml of *t*-BuOH. The temperature is raised to 50°C and 8 g of ethyl chloroacetate (65 mmol) is introduced dropwise over 1 h. The reaction mass is kept at the refluxing temperature for another 8 h, and washed two times with HCl (0.1 N). The fluorinated heavy phase is separated and dried in vacuo. Fifty-five grams of α-PFPEalkoxyethylacetate is isolated.

^1H NMR (D_6-acetone) δ: CH_3 1.3 (t); CH_2 α to ester group 4.1–4.3 (overlapped m); CH_2 α to R_f 4.0 (m).

3.2.12. Para-nitro-fluoroalkoxybenzene and dinitro-fluoroalkoxybenzene (XXXIV) and (XXXV)

Hundred grams (50 mmol) of ZDOL alkolate (potassium salt) (MW 2000) is prepared in a conventional way in *t*-BuOH. Then 22 g (156 mmol) of 1-fluoro-4-nitrobenzene is slowly added, under vigorous stirring, over a period of 4 h; finally the mass is warmed and maintained at the refluxing temperature for 10 h.

Washing twice with acidic water and a final phase separation by a treatment with anhydrous ethanol allow to separate the PFPE-*para*-nitrobenzene derivative. In a similar way, starting from 1-chloro-3,4-dinitrobenzene, the PFPE-dinitrobenzene derivative is obtained.

Para-nitro-fluoroalkoxybenzene. ^1H NMR (CFC 113) δ: H *ortho* to the NO_2 group 8.2 (2H, d); H *ortho* to the fluorinated chain 6.8 (d); CH_2 4.3–4.6 (m).

3.2.13. Benzimidazole (XXXVII)

The PFPE-aromatic dinitro compound is reduced in methanol by hydrogen in the presence of Pd/C as catalyst. The reaction is carried out in an autoclave at room temperature and at initial P_{H_2} of 10 atm. After 24 h a complete conversion of the dinitro derivative is observed.

The corresponding PFPE-amine is isolated by filtration and solvent evaporation.

This amine (50 g, 23 mmol) is treated in a 250 ml flask with 70 ml of formic acid at the refluxing temperature

for 12 h. The reaction mass is neutralized with NH_4OH (10%), diluted with CFC 113 and washed several times with water.

The heavy phase is separated, filtered and the solvent removed by distillation.

The desired product is obtained in good yield (>80%).

^{1}H NMR (neat sample) δ: CH_2 4.4 (m); 2-proton 8.5 (s); 4,5,7-protons 6.6–7.2 (m), NH 7.5–7.7 (broad).

3.2.14. Triazine (XXXVIII)

Thirty grams (163 mmol) of 2,4,6-trichloro-1,3,5-triazine is dissolved in 600 ml of toluene, then 20 g of ''collidine'' (2,4,6-trimethylpyridine) is charged. The solution is cooled at 2°C and 100 g (83 mmol) of ZDOL (MW 1200) is slowly added; the reaction mass is kept at room temperature for 3 h. After filtration and solvent removal by distillation, 120 g of PFPE-triazine derivatives is isolated.

^{13}C NMR δ: all C atoms bearing fluorine 112–128; CH_2 68; $\underline{C}$–O–CH_2 173; C–Cl 176.

3.2.15. Mercaptans (XXXIX)

In a 250 ml flask 70 g (35 mmol) of ZDOL (MW 2000), 8 g (79 mmol) of freshly distilled triethylamine and 100 ml of CFC 113 are charged. Over a period of 2 h, 24 g (79 mmol) of nonafluoro-1-butanesulfonylfluoride is added to the solution at room temperature. After 12 h, 150 ml of water is introduced and phase separation immediately occurs. The heavy organic phase is dried in vacuo and the PFPE-nonaflate isolated.

The PFPE-nonaflate (17 g, 7 mmol) is dispersed in 20 ml of isopropanol, 1.2 g (15 mmol) of thiourea is fed to the reaction mass and the temperature is raised at 80°C under inert atmosphere. After 15 h, by monitoring the reaction by ^{19}F NMR (or IR), a complete conversion of the PFPE-nonaflate to the corresponding isothiouronium salt is observed. The solvent is eliminated by distillation and the compound isolated.

A sample of the PFPE–isothiouronium salt (2.6 g, 1 mmol) is dissolved, under nitrogen, in 10 ml of ethanol and treated with 2.5 ml of NaOH (10%). The mass is reacted for 4 h at 25°C, then 10 ml of HCl (5%) is introduced. The final PFPE-mercaptan is isolated by CFC 113 extraction.

^{1}H NMR (CFC 113) δ: CH_2 2.9 (m); SH 1.5 (t).

^{19}F NMR (neat sample) δ: CF_2 preterminals at −73 and −75.

3.2.16. Sulfides

3.2.16.1. Symmetrical PFPE-sulfide (XL). In a 100 ml flask 10 g of PFPE-nonaflate (4 mmol) is charged with 20 ml *t*-BuOH and 0.6 g (8 mmol) of $NaSH{\cdot}H_2O$ under inert atmosphere. The mixture is heated at the refluxing temperature for 3 h. The PFPE-polysulfide is recovered by solvent removal, several washing with water, and final stripping in vacuo at 80°C.

^{1}H NMR (D_6-acetone) δ: CH_2SCH_2 3.5 (s); $C\underline{H_2}SH$ 2.9 (m); –SH 1.5 (t).

^{19}F NMR (neat sample) δ: CF_2 preterminals −70.5 and −72.5 ppm.

3.2.16.2. Asymmetrical PFPE-sulfide (XLI). In a 100 ml flask 0.22 g of NaH dispersed in 20 ml of THF are charged, followed by 0.6 g (8 mmol) of 1-propanethiol, slowly added. The reaction mass is stirred at room temperature 15 g. Finally, 10 g (4 mmol) of PFPE-nonaflate is fed and the mixture heated at 70°C for 6 h.

The solvent is evaporated and the crude fluorinated derivative is washed several times with water. Finally, the heavy phase is dried in vacuo. Ten grams of PFPE-propyl-sulfide is obtained.

^{1}H NMR (CFC 113/acetone) δ: CH_2 α to R_f 3.2–3.3 (m); CH_2 α and β to S resonate at 2.7(t) and 1.6–1.8 (qt≈sest., since $j_{bc}\approx j_{cd}$), respectively; CH_3 1.0–1.1 (t).

^{19}F NMR (D_6-acetone) δ: CF_2 preterminals −70 and −72.

3.2.17. Quaternary ammonium salts (XLII)

ZDOLTX-tosylate is prepared by treating ZDOLTX with NaOH (50%) in the presence of a solvent and subsequent reaction with an equivalent amount of *p*-toluenesulfonyl chloride.

After phase separation and solvent removal the isolated product is dissolved in ethanol and reacted with pyridine at the refluxing temperature. The solution is dried in vacuo and a waxy fluorinated pyridinium salt is obtained.

^{1}H NMR (D_6-acetone/CFC 113) δ: CH_3 2.1 (s); CH_2 α to N 4.9 and 5.0 (for n=2 and n=1, respectively, m); CH_2 β to N 4.0 and 4.2 (for n=2 and n=1, respectively, m); CH_2 α to R_f 3.8 and 3.9 (for n=2 and n=1, respectively, m); –O$C\underline{H_2}C\underline{H_2}$O–3.6 and 3.7 (m); pyridinium: 2,6H 9.0, 3,5H 8.0–8.1, 4H 8.5–8.6; *p*-toluene sulfonate: 2,6H 7.7, 3,5H 7.1–7.2, CH_3 2.3.

3.2.18. PFPE-monoethoxylated (XLIII)

Eight grams of ethylene glycol (130 mmol) is dissolved in 100 ml of a mixture of *t*-BuOH/bis(trifluoromethyl)-benzene (1:3), followed by the addition of 1.0 g of *t*-BuOK (9 mmol). The reaction mass is warmed at 40–50°C for 30 min, then a solution containing 10 g of PFPE-nonaflate (XX) in 50 ml of *t*-BuOH/bis(trifluoromethyl)benzene (1:3) is slowly added into the reactor. After heating at 90°C for 8 h, the solution reaches neutral pH and ^{19}F NMR analysis evidences a conversion of 70%. Finally, the solvent is evaporated and the crude fluorinated derivative is washed several times with water. The heavy phase is dried in vacuo. Ten grams of PFPE-monoethoxylated is obtained.

^{1}H NMR (neat sample, trifluoro-acetylated) δ: 3.9–4.1 (CH_2 (to the ether group), 4.5–4.6 CH_2 (to the trifluoroacetyl group).

3.2.19. PFPE-iodide (XLIV)

ZDOLTX-tosylate, prepared according to the above procedure, is reacted with a 10% excess of NaI in a solution of DMF (50% w/w) at 150°C. After 5 h the completion of the reaction is evidenced by ^{19}F NMR analysis. The product is isolated by washing several times with water and dried in vacuo.

^{19}F NMR (neat sample) δ: CF_2 preterminals −68 and −70.

4. Chemical–physical properties

The chemical–physical behaviour of these functional macromolecules reflects mainly the properties of the perfluoropolyether backbone. Nevertheless they are, to some extent, influenced by the presence of a specific functional group.

These functional derivatives are liquid, colourless with low refractive index, low vapour pressure, and generally, posess good dielectric properties. Moreover, they are characterized by low values of surface tension, unusually low glass transition temperature, combined with tailored low viscosity. These last characteristics result in an excellent wetting capability for most of the surfaces.

In Table 1 we report the main chemical–physical properties of some of these functional derivatives.

The viscosity of these fluorinated macromolecules is probably one of the most important properties from an applicative point of view and is also the property which is much more influenced by the nature of the functional group [27,28].

Typically, the presence within the structure of many ether bonds and acetalic units like –CF_2O– provides flexibility to the molecule, resulting in a limited variation of the viscosity with the temperature. At the same time the presence of polar end-groups able to interact with each other and even to form intermolecular hydrogen bonds, renders the viscosity much more sensitive to the temperature, leading to lower values of the viscosity index.

As expected, the influence of polar groups decreases by increasing the molecular weight, becoming dominant, in this case, the effect of the perfluoropolyether backbone.

Table 2 shows the values of the viscosity and viscosity index (VI) and in Fig. 7 the viscosity is plotted as a function of the temperature for different functional groups, in comparison with a non-functional perfluoropolyether having the same chemical structure and similar molecular weight. From these data it appears that the relationship between viscosity and temperature is essentially ruled by the polarity of end-groups.

Actually, it is evident that the methylester shows a very high VI and a behaviour similar to the non-functional PFPE; contrarily by increasing the polarity, going from the aromatic to the alcoholic group, the VI drops down, as evidenced by the increasing of the slope of the curves.

From the data of Table 2 the effect of the molecular weight within a homologous series can also be noticed. For example, the aromatic derivatives show a VI which increases proportionally to the length of the internal PFPE chain.

Finally, other inherent properties of the PFPE chain are the excellent photo-stability [29], the high chemical resistance [6] and the very low solubility parameter δ [26].

This unique set of properties suggests the use of these fluorinated macromolecules as reactive or unreactive modifiers for synthetic polymers.

5. Applications

The possibility to link to a perfluoropolyether structure a large variety of functional groups, either reactive or unreactive, provide compounds which can have better performances in the typical applications of perfluoropolyethers, as well as opens the possibility for new applications through the selection of specific functional groups. Some examples of possible fields of application for these macromolecules will be briefly described here.

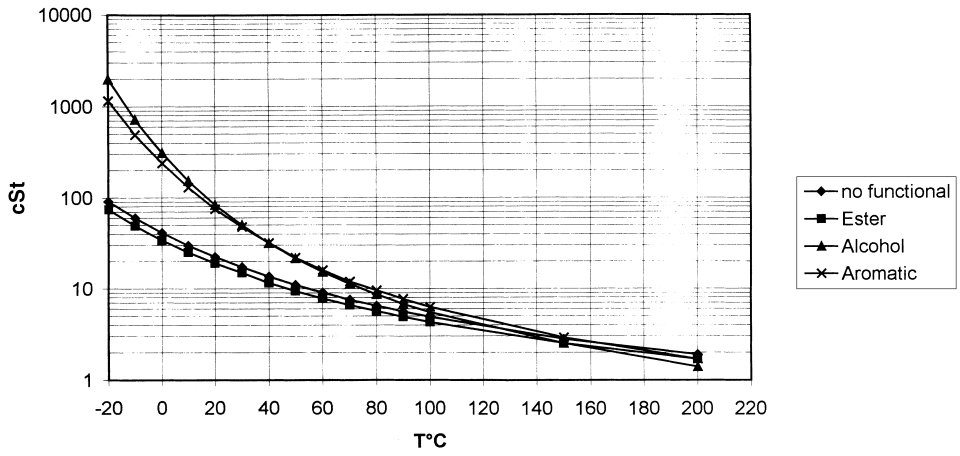


Fig. 7. Perfluoropolyethers: viscosity/temperature relationship.

Table 1
Chemical–physical properties of functional perfluoropolyethers: R_f-F

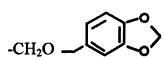
Property	Unit	Functional group (F)					
		Methylester –$COOCH_3$	Acid –COOH	Alcohol –CH_2OH	Alcohol –$CH_2OCH_2CH_2OH$	**Diol** -$CH_2OCH_2CHCH_2OH$ (OH)	**Aromatic** 
Molecular weight	–	2000	2000	2000	2200	2200	2400
Kinematic viscosity at 20°C	cSt	20	60	80	145	2000	75
Specific gravity at 20°C	g/ml	1.77	1.81	1.81	1.74	1.75	1.72
Vapour pressure at 20°C	Torr	3.0E−04	5.1E−05	2.1E−05	3.1E−06	3.0E−06	2.1E−06
Vapour pressure at 100°C	Torr	2.1E−03	2.1E−03	2.1E−03	3.1E−05	3.0E−05	2.1E−04
Dielectric constant	–	3.7	2.3	2.9	n.a.	n.a.	3.3
Refractive index	–	1.298	1.295	1.298	1.316	1.316	1.345
Surface tension	dyne/cm	25	25	24	23	24	25

Table 2
Viscosity index of perfluoropolyethers

Functional group	None	Ester	Aromatic MW 3000	Aromatic MW 2000	Alcohol
Viscosity at 20°C (cSt)	22	19	84	75	83
Viscosity at 40°C (cSt)	14	12	37	32	32
Viscosity at 100°C (cSt)	5	4	8	6	6
Viscosity index	390	346	189	152	110

5.1. Advanced polymers

PFPE macromers are ideal candidates as building blocks for the synthesis of high-performance, new polymeric materials [18–24].

Thus, fluorinated polyurethanes (FPU) are easily achievable starting from ZDOL and ZDOLTX by reaction with hydrogenated diisocyanates and chain-extenders [25,26]. These segmented polymers, containing PFPE chains as the continuous phase, are multi-phase materials characterized by very low glass transition temperature (T_g). Moreover, they show low surface tension (<15 mN/m), improved thermal stability, and chemical resistance. These distinctive properties are coupled to excellent low temperature mechanical and tensile behaviour.

These low temperature properties are noteworthy; in fact FPUs perform as elastomers even at very low temperatures, as indicated in Fig. 8, where compression-set data, obtained by testing the deformation recovery as a function of temperature and time, are reported. It is clear that, even under very severe temperature conditions, after load removal a quite instantaneous recovery of the original dimension results.

5.2. Lubrication of magnetic recording media

Perfluoropolyethers are well known as the most suitable lubricants for the lubrication of metal evaporated hard disks for computers or of videotapes, thanks to their excellent wetting and spreading capabilities, as well as to the possibility to provide excellent lubrication even under the form of very thin film of 10–20 Å [30–34].

The presence of functional groups in the PFPE macromolecule allows the lubricant to interact, or even react, with the surface, resulting in a better adhesion and a more stable lubricant film.

Moreover, the possibility of synthesising different functional groups makes it possible to customize the lubricant for different magnetic systems like disks and tapes and different operating conditions.

In hard-disk application the alcohol and aromatic functionality show the best performances, because the lubricant, strongly bonded to the surface, can withstand the high centrifugal force developed during the high speed rotation of the disk in the drive.

Fig. 9 shows the better resistance to the centrifugal force of aromatic and $–CH_2OH$ end-capped macromolecules in comparison with compounds having $–CF_3$ end groups.

In addition, Fig. 10 shows the capability of the $–CH_2OH$ group to react, under increasing temperature, with the silica overcoat of a magnetic media forming $–CH_2O–Si–O–$ bonds, thus decreasing the coefficient of friction (curve a) and increasing the contact angle with water (curve b).

5.3. Antirust additives for lubricants

Perfluoropolyether fluids or greases perform very well as special lubricants for high temperatures and aggressive environment, but generally they do not provide a satisfac-

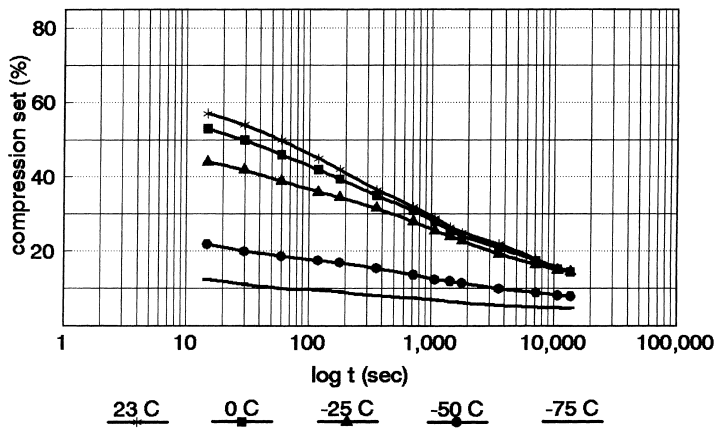


Fig. 8. Thermoset FPU: compression set/temperature relationship.

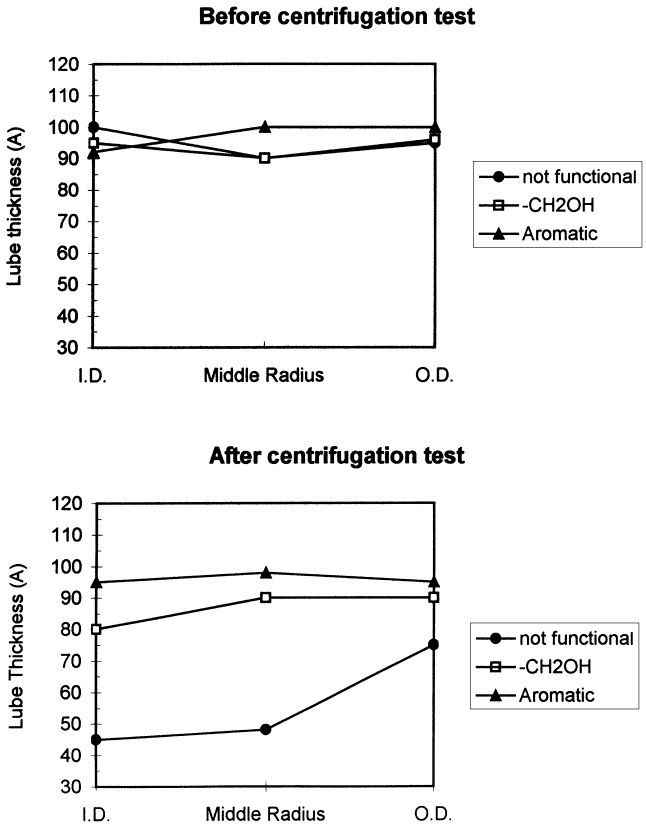


Fig. 9. Magnetic recording media (MRM) PFPE-lubricants: resistance to the centrifugal force.

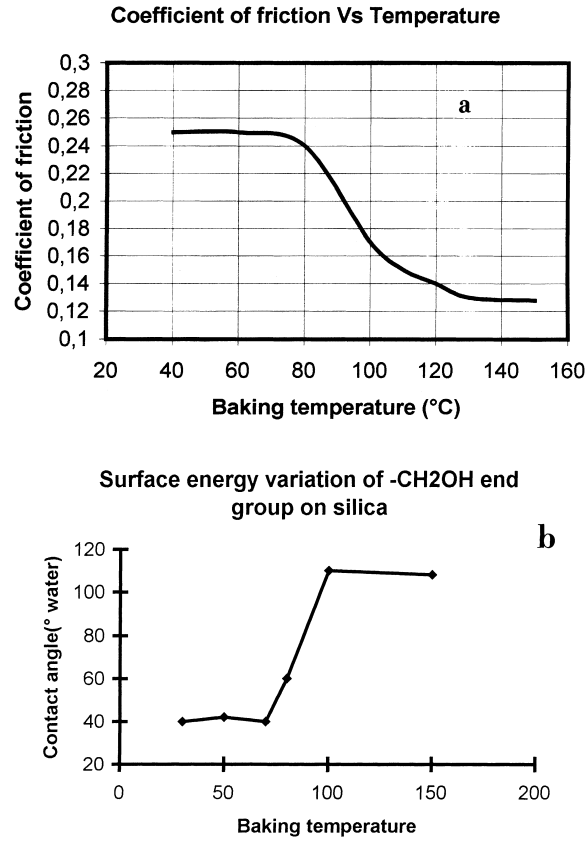


Fig. 10. Magnetic recording media (MRM) PFPE-lubricants: coefficient of friction (a) and contact angle (versus water) (b) of silica substrate treated with PFPE–CH_2OH molecule as a function of the temperature treatment.

tory rust protection, because of their high permeability to gases including oxygen and water vapours.

On the other hand, the conventional corrosion inhibitors, widely used for mineral or synthetic oils, cannot be used due to immiscibility.

On the contrary, these functionalized macromolecules are fully compatible with most of the PFPE lubricants, and when used as additives, can provide good antirust properties to the fluid, thanks to the capability to form a resistant protective layer on the metal surface through the functional group [35,36].

Polar functional groups, like –CN and –COOH, exhibit the best performances when used as additives, whereas functional products bearing –CH_2OH, benzimidazole, benzothiazole groups show a good antirust effect when used as base oils for grease formulation.

In Tables 3 and 4 we report some examples of the antirust properties of these macromolecules when combined both with branched and linear perfluoropolyethers and in grease formulation.

The evaluation of the performance has been carried out on low carbon specimen (C 15) in Fog Chamber for fluids and according to the Emcor DIN 51802 on ball bearings for greases.

The rating ranges from 0 in the absence of rust spot, to 5 for a completely rusted surface. The two numbers refer to both the faces of the metal specimen or to the two bearings used in the test for greases.

From the data of Table 4 the outstanding effect of the PFPE additives on the surface protection is evident.

5.4. Antiwear additives for lubricants

In case of mineral or synthetic lubricants, the antiwear properties can be enhanced by the use of additives, generally based on phosphorous compounds.

The insolubility of these commercial additives in perfluoropolyether lubricants and their relatively poor thermal and chemical stability make their use impossible under the

Table 3
Antirust properties of perfluoropolyether oils

Fluid	Viscosity (cSt)	Additive		Result
		Functional	(%)	
Branched PFPE	250	None	–	5–5
Branched PFPE	250	–CN	2	0–0
Linear PFPE	280	None	–	5–5
Linear PFPE	280	–CN	2	0–0
		–COOH	0.1	

Table 4
Antirust properties of perfluoropolyether greases

Base oil	Viscosity (cSt)	Functional group	Thickener	Result
Perfluoropolyether	250	None	PTFE	5–5
Perfluoropolyether	100	$-CH_2OH$	PTFE	0–0
Perfluoropolyether	100	Benzimidazole	PTFE	0–0
Perfluoropolyether	100	Benzimidazole	PTFE	0–0

Table 5
Wear values of perfluoropolyethers (Four Ball Test ASTM D 4172)

Functional group	Scar diameter (mm)	Wear reduction (%)
None	1.00	–
$-CH_2OH$	0.81	19
$-CH_2OCH_2CH(OH)CH_2OH$	0.73	27
–CONHR	0.65	35
$-CH_2O$-Aromatic	0.60	40

severe operating conditions where PFPEs are generally employed.

The availability, through the synthetic routes described before, of many functional products, generally soluble in perfluoropolyether lubricants with a comparable thermal and chemical stability, represents a big chance to improve the lubrication properties of the fluid.

The wear, during the lubrication of the system, is typically due to the incapability of the lubricant to maintain a continuous film on the metal surface, resulting in a metal–metal contact with a dramatic increase of friction, which causes wear, and ultimately, the failure of the system.

For the above reasons the antiwear properties are, also in this case, strictly related to the capability of the lubricant to be bonded to the surface as strongly as possible.

In Table 5 we report the wear values, determined with the ''Four Ball Test'' according to the ASTM D 4172 for different functional PFPEs.

The experimental results confirm that molecules with groups like –CONHR, $-CH_2OH$ and aromatics, exhibit better antiwear properties when compared with compounds without any functional group. These products are effective to improve the antiwear behaviour of a fluorinated lubricant also when applied in a limited amount, typically 3–5%, as shown in Table 6, where the results of the ''Four Ball Test'' carried out on fluids and greases, with and without functional additives, are summarized [37,38].

6. Conclusions

A great amount of work has been done on the elucidation of the reactivity of PFPE-macromolecules bearing alcoholic or carboxylic end-groups.

The knowledge of their reactivity with many different hydrogenated co-reagents paved the way to a large number of selective synthetic routes and to a deeper understanding of the related reaction mechanisms.

Generally, the PFPE-precursors show unique chemical/physical characteristics; these, in turn, can cause inhomogeneity during reaction, or differences in reactivity between the fluorinated and hydrogenated reacting molecules. Nevertheless, as clearly shown in the present work, it is possible to define proper experimental procedures which allow synthetic routes able to bond the PFPE segment to virtually all hydrogenated molecules. In this way fluorinated macromolecules end-capped by aliphatic, aromatic, heterocyclic and inorganic segments are available for applications in different areas.

The classes of reactions here described (condensation and nucleophilic substitutions) are simply indicative of the high potential, from both a synthetic and an applicative point of view, of these new segmented PFPE-macromolecules.

Their general properties can be easily fine-tuned, simply by varying the internal PFPE-chain length, the number of functional groups per molecule, or the structure of the end-capped hydrogenated segment.

This tailoring ability offers new and unique opportunities in applications where specific and targeted performances are usually required.

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Table 6
Wear values of perfluoropolyether oils and greases (Four Ball Test ASTM D 4172)

Lubricant	Viscosity (cSt)	Functional	(%)	Scar diameter (mm)	Wear reduction
PFPE oil	450	None	–	0.90	–
PFPE oil	450	$-CH_2OH$	4.9	0.70	22.2
		–COOH	0.1		
PFPE grease	–	None	–	1.40	–
PFPE grease	–	$-CH_2OH$	4.9	0.96	31.4
		–COOH	0.1		

References

[1] V. Tortelli, C. Tonelli, J. Fluorine Chem. 47 (1990) 199.
[2] M. Yamabe, K. Arai, J. Kaneko, Jpn. Pat. 7 61 33 206, 1976 (to Asahi Glass); Chem. Abs. 87, 5365d.
[3] J.F. Ding, M. Proudmore, R.H. Mobbs, A. Rashid Khan, C. Booth, C. Price, Makromol. Chem. 193 (1992) 2211.
[4] Y. Ohsaka, T. Tohzuka S. Takaki, Eur. Pat. 1 48 482, 1984 (to Daikin Ind.).
[5] D. Sianesi, A. Pasetti, R. Fontanelli, G.C. Bernardi, G. Caporiccio, Chim. Ind. (Milan) 55 (1973) 208.
[6] G. Marchionni, G. Ajroldi, G. Pezzin, Comprehensive Polymer Science, suppl. 2, Pergamon, New York, 1997, p. 347.
[7] D. Sianesi, G. Caporiccio, D. Mensi, US Pat. 38 47 978, 1974 (to Ausimont).
[8] C. Tonelli, G. Marchionni, P. Gavezotti, R.J. De Pasquale, Soc. Plast. Ind. Fluoropolymer Div., Proceedings of the Fall Meeting, Asheville, NC, September 1992.
[9] D. Sianesi, G. Marchionni, R.J. De Pasquale, in: R.E. Banks et al. (Eds.), Organofluorine Chemistry: Principles and Commercial Applications, Plenum Press, New York, 1994.
[10] M. Scicchitano, S. Turri, C. Tonelli, Die Ang. Makromol. Chem. 231 (1995) 47.
[11] Kaiser, Wooddruff, J. Org. Chem. 35 (1970) 1198.
[12] F. Danusso, M. Levi, G. Gianotti, S. Turri, Eur. Polym. J. 30(12) (1994) 1449.
[13] R.A. Mistsch, J. La Mar Zollinger, US Pat. 38 10 874, 1974 (to 3M).
[14] F. Piacenti, M. Camaiti, J. Fluorine Chem. 68 (1994) 227.
[15] G. Caporiccio, E. Strepparola, G. Bargigia, G. Novaira, G. Peveri, Makromol. Chem. 184 (1983) 935.
[16] S. Turri, M. Scicchitano, C. Tonelli, Polym. J. Sci. 34 (1996) 3263.
[17] Unpublished results.
[18] F. Pilati, M. Toselli, F. Bottino, G. Di Pasquale, A. Pollicino, R.D. Short, C. Tonelli, La Chimica e l'Industria 74 (1992) 678.
[19] F. Pilati, M. Toselli, A. Vallieri, C. Tonelli, Polym. Bull. 28 (1992) 151.
[20] L. Mascia, F. Zitouni, C. Tonelli, J. Appl. Polym. Sci. 51 (1994) 905.
[21] M. Toselli, F. Pilati, M. Fusari, C. Tonelli, G. Castiglioni, J. Appl. Polym. Sci. 54 (1994) 2101.
[22] L. Mascia, F. Zitouni, C. Tonelli, Polym. Eng. Sci. 35(13) (1995) 1069.
[23] F. Pilati, M. Toselli, M. Messori, U. Credali, C. Tonelli, C. Berti, J. Appl. Polym. Sci. 67 (1998) 1679.
[24] A. Priola, R. Bongiovanni, G. Malucelli, A. Pollicino, C. Tonelli, G. Simeone, Macromol. Chem. Phys. 198 (1997) 1893.
[25] C. Tonelli, T. Trombetta, M. Scicchitano, G. Castiglioni, J. Appl. Polym. Sci. 57 (1995) 1031.
[26] C. Tonelli, T. Trombetta, M. Scicchitano, G. Castiglioni, G. Ajroldi, J. Appl. Polym. Sci. 59 (1996) 311.
[27] S. Turri, M. Scicchitano, G. Gianotti, C. Tonelli, Eur. Polym. J. 31(12) (1995) 1227.
[28] S. Turri, M. Scicchitano, G. Gianotti, C. Tonelli, Eur. Polym. J. 31(12) (1995) 1235.
[29] J. Scheirs, G. Camino, L. Costa, C. Tonelli, S. Turri, M. Scicchitano, Polym. Degr. Stab. 56 (1997) 239.
[30] M.A. Scarati, G. Caporiccio, US Pat. 53 82 614, 1995 (to Ausimont).
[31] G. Caporiccio, E. Strepparola, M.A. Scarati, US Pat. 48 89 939, 1989 (to Ausimont).
[32] G. Caporiccio, E. Strepparola, M.A. Scarati, US Pat. 48 08 472, 1989 (to Ausimont).
[33] G. Caporiccio, E. Strepparola, M. A. Scarati, US Pat. 47 57 145, 1988 (to Ausimont).
[34] G. Caporiccio, E. Strepparola, M.A. Scarati, US Pat. 47 21 795, 1988 (to Ausimont).
[35] E. Strepparola, M. Alfieri, P. Gavezotti, US Pat. 49 41 987, 1990 (to Ausimont).
[36] E. Strepparola, P. Gavezotti, C. Corti, US Pat. 51 69 548, 1991 (to Ausimont).
[37] C. Corti, P. Savelli, US Pat. 51 24 058, 1992 (to Ausimont).
[38] L. Montagna, E. Strepparola, M. Quallo, US Pat. 53 76 289, 1994 (to Ausimont).