Synthesis of fluorinated polyethers

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UNIVERSITY OF DURHAM
Department of Chemistry

A thesis entitled

SYNTHESIS OF FLUORINATED POLYETHERS

by

Andrew K. Joel, B.Sc.
(Graduate Society)

A candidate for the degree of Doctor of Philosophy
1992

To the memory of my father.

... "I realised I *had* to act before the entire will and vitality of the free Western world was sapped and polluted and clotted and made rancid by this diabolical substance, *fluoride*. The absolutely fantastic thing is that the *facts* are there for anyone who wants to see them. Do you know anything about fluorides, Group Captain Mandrake?"

Mandrake stroked his mustache. He said, "Well, not actually, sir..."

From 'Doctor Strangelove, or How I Learned to Stop Worrying and Love the Bomb,' by Peter George, from a screenplay by Stanley Kubrick, Peter George and Terry Southern.

Acknowledgements

I would like to thank Professor Dick Chambers for his help and advice throughout this period of research.

I must also thank my mother for her support through the last four years, and indeed the numerous years before I embarked on this course, and also, for proof reading this work.

My grateful thanks for financial support to the US Air Force for funding the first three years, and also to British Nuclear Fuels for the last year, while I have been writing this thesis.

For the good times (and occasional lack of bread, *etc.*) I would like to thank the residents of the Cave, past and present, Alex, Lee, Nigel, Steve and Tom, and also the other inmates of CG115, Alan, Graham, Howard and all the others too.

For services within the department I thank Dr J.P.S. Badyal, Mrs. M. Butterfield, Dr. M. Jones, Dr. A. Kenwright, Mr. L. Lauchlan, Dr. R. Matthews, Mrs. J. Say, Miss L.M. Turner and especially Mr T.F. Holmes, as a friend as well. I am also indebted to Dr J. Becher of Odense University, Denmark for the ^{252}Cf PDMS work on the 18-crown-6 derivatives, and to Ms L. Gschwender and Dr C.E. Snyder of Wright Laboratory, Wright Patterson Air Force Base, Ohio for viscosity and supercritical fluid chromagraphy analysis.

Finally I would like to thank my girl friend Sara for making me happy when everyone around me was so sad!

Memorandum

The work described in this thesis was carried out at the University of Durham between October 1988 and May 1992. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

Copyright

Part of this work has been accepted for publishing in the *Journal of Fluorine Chemistry*, and has been presented by the author at:

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Padua, Italy.

Nomenclature

Throughout this thesis an ‘F’ in the centre of a ring is used to denote that all unmarked bonds are to fluorine.

The following abreviations are also used:

CTFE	Chlorotrifluoroethylene
DBPO	Dibenzoyl peroxide
DEPEG	Diethyl poly(ethylene glycol)
ESCA	Electron spectroscopy for chemical analysis
FEP	Fluorinated ethylene-propylene (HFP/TFE copolymer)
HF	Hydrogen fluoride
HFA	Hexafluoroacetone
HFCB	Hexafluorocyclobutene
HFP	Hexafluoropropene
OFCP	Octafluorocyclopentene
PDMS	Plasma desorption mass spectrometry
PFP	2*H*-Pentafluoropropene
PFPE	Perfluoropolyether
PMMA	Poly(methyl methacrylate)
PTFE	Polytetrafluoroethylene
PTHF	Diethyl polytetrahydrofuran
TBPO	*tert*-Butyl peroxide
TFE	Tetrafluoroethylene
VDF	1,1-Difluoroethene (vinylidene fluoride)

Abstract

Synthesis of Fluorinated Polyethers

The addition of ethers and polyethers to fluoroalkenes (especially hexafluoropropene, but also chlorotrifluoroethene, decafluoro-3,4-bis(trifluoromethyl)-hex-3-ene, 1,1-difluoroethene, hexafluorocyclobutene, octafluorocyclopentene and pentafluoropropene) and hexafluoroacetone was investigated. Studies involving model compounds, such as diethyl ether and oxolane, indicated that this general reaction proceeded with ease when initiated by UV light, using acetone as both solvent and photosensitiser. High field NMR studies allowed a high degree of structural and also mechanistic information to be derived. It was established that the diadducts of HFP with diethyl ether and with oxolane form by two different processes, the former with a surprising degree of stereocontrol.

Additions of polyethers to fluoroalkenes were performed and, using the information gained from the model compounds, approximate structures for the new materials were derived. These materials have interesting properties and were shown to migrate to the air interface in acetone solutions of poly(methyl methacrylate) and also in paint by ESCA.

Cyclic analogues of these materials (derived from crown ethers) were also synthesised, and evidence for the formation of corresponding alkali metal complexes was obtained by mass spectrometry, though the complexes could not be isolated.

Both the cyclic and acyclic materials were successfully fluorinated, using elemental fluorine at room temperature, in an unusual solvent system. NMR and other analysis were performed on these perfluoropolyethers.

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CHAPTER ONE
PERFLUOROPOLYETHERS

1.1 Fluorine in Organic Chemistry

The whole field of organofluorine chemistry is a vast and expanding one, encompassing compounds and materials with a very broad range of interesting properties. Much work has been done, for instance, in the area of biochemistry, adding a fluoroalkyl group to an already biologically active pesticide to give significantly higher activity through increased lipophilicity.[1] Another area of interest is anti-viral and anti-cancer chemistry in which the small size of a fluorine atom, comparable to that of hydrogen, allows a hydrogen atom to be replaced by fluorine without any significant distortion of the molecular shape. The anti-cancer agent 5-fluorouracil has the correct geometry to bind at an enzymic site just as uracil itself, but the fluorine atom prevents reaction and the enzyme remains blocked.[2] The work contained herein is primarily concerned with perfluorinated organic compounds, *i.e.,* materials in which all the hydrogens in the corresponding hydrocarbon derivative have been replaced by fluorine.

1.2 Perfluorinated Materials

Perfluorinated materials exhibit a number of commercially very interesting properties.[2] The electron pairs of the fluorine atoms in polytetrafluoroethylene (PTFE) give it its unique 'non-stick' properties and also cause this and other perfluorochemicals to be highly resistant to a vast range of chemicals. Thermal stability is another feature, the fluorine-carbon bond being particularly strong (485 kJ mol^{-1} in tetrafluoromethane).[3] PTFE coatings have been used as hose and pipe lining, and on fabrics (Gore-Tex) as well as on cooking utensils. Other applications of PTFE include gaskets, wire insulation and thread seal tapes.[4] Perfluoroelastomers have found a market as seals in specialised environments, especially as O-rings.[5]

Low molecular weight materials have found many applications as inert fluids. Perfluorinated liquids have been used as cooling fluids, especially in the electronics industry where compatibility with a range of materials and stability to electrical and magnetic fields are very important.[6] Vapour phase soldering is another major role for these fluids; advantages include rapid heat transfer, low variations in temperature and the generally good condition of the item after processing (*i.e.*, devoid of fluid residue and chemically unaltered).[7] These materials are also characterised by unusually low intermolecular forces, giving a very low surface tension and so good wetting ability.

Perfluorocarbons are particularly non-polar materials and so are good solvents for gases, including oxygen and carbon dioxide. This, together with their biological inertness, has provoked a good deal of interest in their use as "blood substitutes" or more properly as artificial erythrocytes or oxygen carriers.[8-11] Although they dissolve oxygen and carbon dioxide very well they are however immiscible in water and so are used as emulsions. It is therefore necessary to add surfactants, the nature and amount of which determines particle size and so the oxygenating ability of the mixture. Perfluorocarbon emulsions have several advantages over natural blood plasma such as lower viscosity, allowing oxygen supply to ischemic organs (*i.e.*, with a reduced blood flow) and cancer tumours.[11] The latter is beneficial as it can give marked improvement in chemo- and radio-therapy responses. They are also more resistant to infection and have a prolonged shelf life (counted in years in some cases). There are some drawbacks, for instance there have been toxicologic problems with the surfactants, which are not necessarily biologically inert, nevertheless some perfluorocarbon emulsions are available commercially and have been used in a number of cases.[11]

Although "blood substitutes" is the most well known area in which perfluorocarbons are used for oxygenation, other applications have been suggested. It has been shown that mice and cats can breathe a perfluorocarbon solution of oxygen and survive,[12] and this idea of breathing a liquid has been used to inflate the lungs of a prematurely born baby.[13] Although the baby eventually died, due to other attempts to correct the lung disorder, it was kept alive an extra 19 hours by the perfluorocarbon treatment. Also it has been suggested that perfluorocarbons could be injected into the blood stream of divers to "mop up" nitrogen that has been dissolved under pressure to avoid decompression sickness (the bends).[8] In the supply of oxygen to micro-organism cultures in biotechnology applications, perfluorocarbons have also proved useful.[10]

1.3 Perfluoroethers

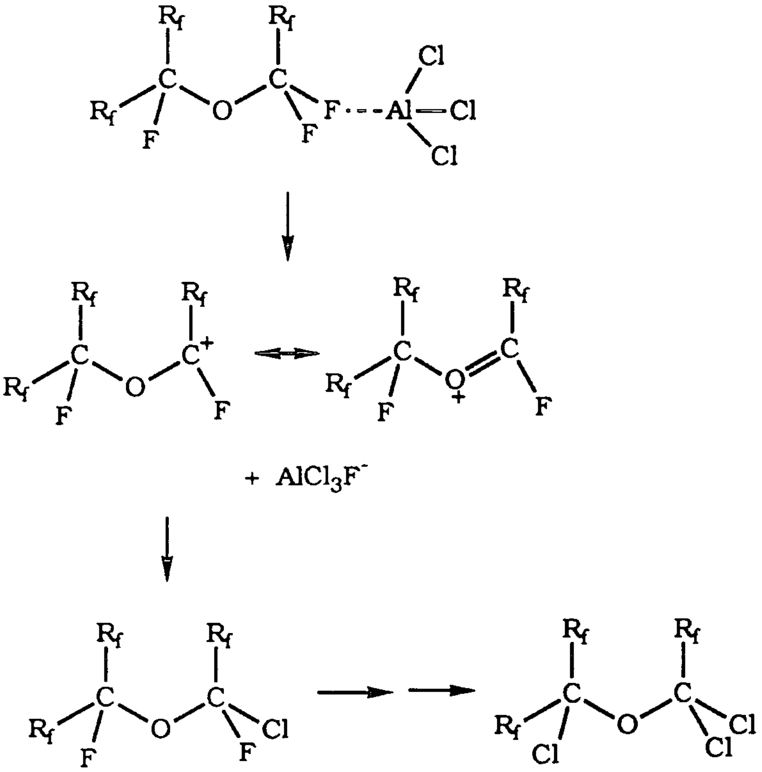
Perfluoroethers represent an important class of inert fluids for many of these applications.[6,14] They have many of the properties of perfluorocarbons such as thermal stability and very low toxicity, their chemical reactivity is only marginally greater. They have lower boiling points than their non-fluorinated analogues, similar to that of a perfluorocarbon with the same number of carbons, see for example table 1.1.[14] They have significantly lower melting points however, and this greater liquid range makes them superior to the perfluorocarbons in many applications.

The only known reaction of perfluoroethers is attack at the α-fluorines with aluminium trichloride at temperatures above 150°C, to form compounds in which all the α-fluorine atoms are replaced by chlorine, scheme 1.1.[15-17] Where there are now two chlorine atoms on both the α-carbons cleavage occurs as shown in scheme 1.2. The reaction relies on the Lewis acid nature of aluminium trichloride, which pulls the fluoride ion from the substrate. The resultant carbocation on the substrate is stabilised by lone pair interactions from oxygen.

Compound	m.p./°C	b.p./°C	pour point* /°C
$(C_4F_9)_2O$	†	102	-100
$(C_4H_9)_2O$	-95	142	
C_8F_{18}	†	100	-42
$(C_6F_{13})_2O$	-90	181	-90
$(C_6H_{13})_2O$	55	228	
$C_{12}F_{26}$	76	175	42

Boiling, melting and pour points of perfluoroethers, ethers and perfluorocarbons

Table 1.1



Scheme 1.1

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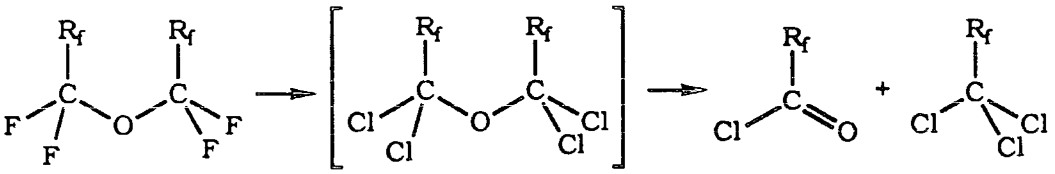
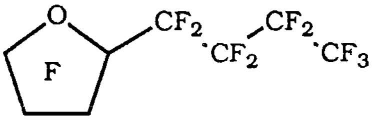
* Pour point is the temperature below which a material will not pour under perscribed conditions.

† These compounds have no well defined melting points, pour points are provided for comparative purposes instead.

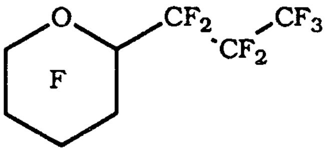


Scheme 1.2

Perfluoroethers are marketed by the 3M company as part of the Fluorinert range of liquids (perfluorocarbons and perfluorotertiaryamines make up the rest of the range).[6] The products FC-72, FC-77, FC-104 and FC-75 are primarily the perfluorinated analogues of 2-*n*-butyltetrahydrofuran and 2-*n*-propyltetrahydropyran, and are synthesized together by electrochemical fluorination in a one step fluorination and cyclisation process from octanoic acid, or octanoic acid fluoride. Electrochemical fluorination is discussed further in the next chapter. Some of the physical properties of these fluids are listed in table 1.2.[6]



Perfluoro(2-*n*-butyltetrahydrofuran)



Perfluoro(2-*n*-propyltetrahydropyran)

	FC-72	FC-77	FC-104	FC-75
Average molecular weight	340	415	435	420
Density/g ml^{-1}	1.68	1.78	1.76	1.76
Boiling point/°C	56	97	101	102
Pour point/°C	-90	-110	-65	-88
Kinematic viscosity/cSt	0.4	0.8	0.8	0.8
Surface tension/mN m^{-1}	12	15	14	15
Volume resistivity/Ω cm	$1.0x10^{15}$	$1.9x10^{15}$	$8.4x10^{15}$	$8.0x10^{15}$

Properties of some commercially availabe perfluoroethers

Table 1.2

1.4 Perfluoropolyethers

Perfluoropolyethers (PFPE) behave as would be expected for high molecular weight perfluoroethers, for instance similar thermal stability and resistance to chemicals, but are a lot less volatile and more viscous. They are still liquids at molecular weights over 10 000 due to the flexibility from the oxygen atoms.[18]

PFPEs have found many applications and potential applications such as lubricants and greases in particularly hostile environments. Their compatibility with chemicals has given them a wide market, for instance in the oxygen producing and using industries, where applications already include the lubricant for liquid oxygen pumps.[19] Similarly they have been used in the nuclear industry where inertness towards uranium hexafluoride and fluorine is of the utmost importance, for instance as a lubricant for centrifuge isotope separation.[19]

For vacuum technology PFPEs are important in areas requiring very clean vacuums such as electron microscopy[20] and mass spectroscopy.[21] They have also been used in low pressure chemical vapour deposition (CVD) in the semi-conductor industry.[20] Although they only give vacuums down to 3×10^{-8} mbar (polyphenyl ether can produce vacuums below 10^{-9} mbar), they have advantages in that they do not polymerise at all when hot or bombarded with energetic particles and so give greater reliability and longer life of the machinery. Chemical compatibility is clearly also very beneficial.

Having a low surface tension allows very thin films to be formed with PFPEs. Consequentially they have found uses as lubricants for magnetic recording media between the head and magnetic material. Films of thicknesses down to 50Å have been reported.[22] Coupled with the ease of dissolving oxygen, this has also led to suggested applications in cosmetics[23] and monument protect.[19] In both cases a very thin film would permit protection and still allow oxygen to pass through letting the skin or stone breathe.

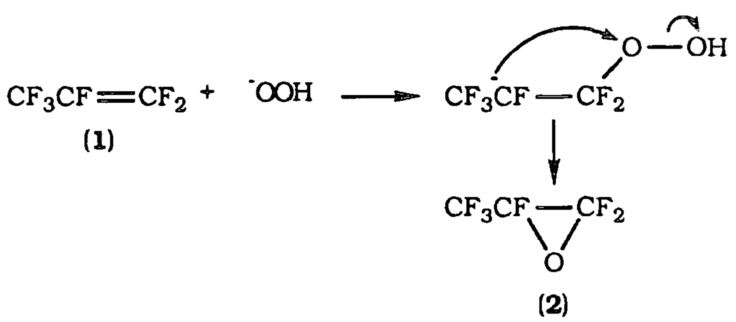
Good thermal stability has led to other fields of application such as oils for gas-turbine engines and hydraulic fluids for aircraft (where non-flammability is important),[24] whilst high dielectric constants make them suitable for use in transformers and rectifiers as insulating fluids.[19] They have also been used as the stationary phase of GC columns[19] and as an additive to improve the ease of removing vulcanised rubber from its forming mold.[25]

1.41 Commercial perfluoropolyethers

Commercially available PFPEs are available under three trade names, Krytox, Fomblin and Demnum, manufactured by Du Pont, Montefluos and Daikin Industries respectively. Whilst all have the same general properties, they do vary, for example, in viscosity and stabiliy to heat and metals.

1.411 Krytox

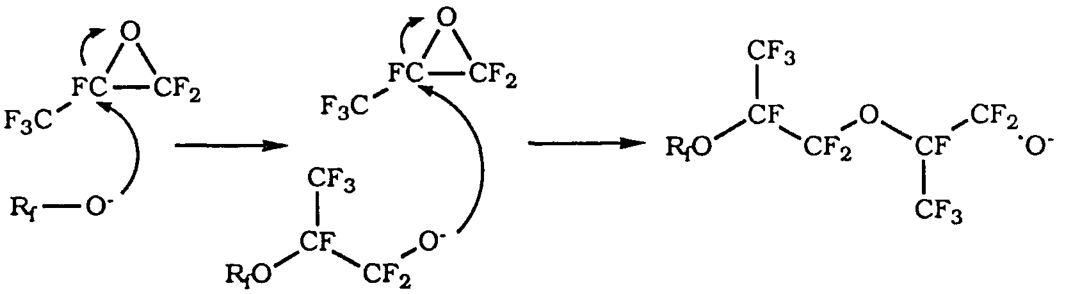
Krytox was the first PFPE produced commercially and is made by the anionic polymerisation of perfluoroalkene oxides, hexafluoropropene oxide (HFPO) (**2**) and tetrafluoroethylene oxide (TFEO). Considerable effort was made to synthesise these monomers, but until the mid-sixties only carbonyl compounds could be formed. Eventually HFPO (**2**) was prepared by oxidation of hexafluoropropene (HFP) (**1**) with hydrogen peroxide, with careful control of the temperature and pH, scheme 1.3. The reaction was performed in an aqueous methanol/potassium hydroxide mixture at -30°C, the pH maintained above 8.[26] Yields were subsequently improved by reacting HFP directly with oxygen at 130 - 165°C, 20 atm in the liquid phase. A number of products are recovered, the exact ratios depending on the conditions used.[27]



Scheme 1.3

Oxidation of tetrafluoroethylene (TFE) was somewhat more problematic as the product is very unstable to ionic reagents and heat (above about -65°C it forms trifluoroacetyl fluoride, HFPO is stable up to 150°C). Also mixtures of oxygen and TFE are potentially explosive. However TFEO is now manufactured commercially by the UV irradiation of TFE, oxygen, air and a nitrogen/bromine mixture (40 - 60 ppm bromine in nitrogen). FC-43[*] is used as a solvent, the bromine acts as a sensitiser.[27]

HFPO was the first monomer polymerised, originally with activated charcoal, to give a material with a broad distribution of molecular weights.[28,29] Use of fluoride ion to initiate the reaction has led to living polymers, allowing molecular weights up to 12 000 and narrow molecular weight distributions to be achieved, scheme 1.4. Cæsium fluoride is used to initiate the reaction, solvated with tetraglyme. Tetraglyme also allows emulsion conditions to form for the polymerisation process. The temperature is maintained below -30°C to suppress fluoride ion transfer, scheme 1.5.



Scheme 1.4

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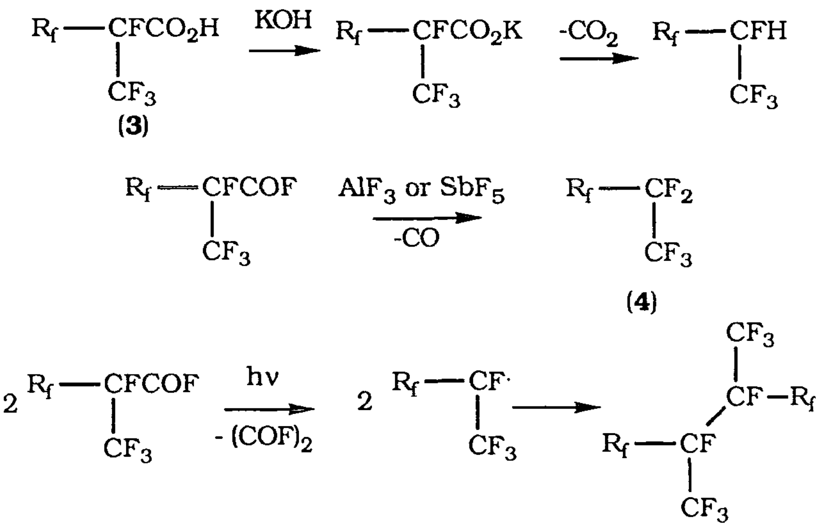
[*] FC-43 is a perfluorinated fluid of the fluorinert range, molecular weight 670, boiling point 174°C. Its major component is perfluoro(tri-*n*-butyl)amine.

$$R_fCF_2O^- \rightarrow R_fCOF + F^-$$

Scheme 1.5

It was found advantageous to add HFP to the system to aid mass and heat transfer, also fluoride ion transfer was reduced. The HFP was found to oligomerise, but the anions were not incorporated into the polymer, presumably for steric reasons. The HFP and its oligomers could all be used in further reactions. TFEO is best polymerised with an electron beam or X-rays at -196°C to form high molecular weight materials. Allowing TFEO to warm up from -196°C on active charcoal gave polymers of molecular weights up to 2500.[27]

The polymerisation process gives a material with an acid fluoride end groups (**3**). This can be eliminated in three ways. By heating the carboxylic acid derivative in aqueous potassium hydroxide a terminal hydrogen results. Alternatively a fully fluorinated material (**4**) is produced if the material is treated with aluminium trifluoride or antimony pentafluoride, in a process involving loss of carbon monoxide. Finally, if the product of polymerisation is irradiated with UV light a coupling reaction takes place, joining two acid fluoride terminated polymer chains together, with loss of ethanedioyl fluoride, scheme 1.6. This must be done at temperatures below 100°C to avoid reduction in polymer length through loss of trifluoroacetyl fluoride from the polymer end.

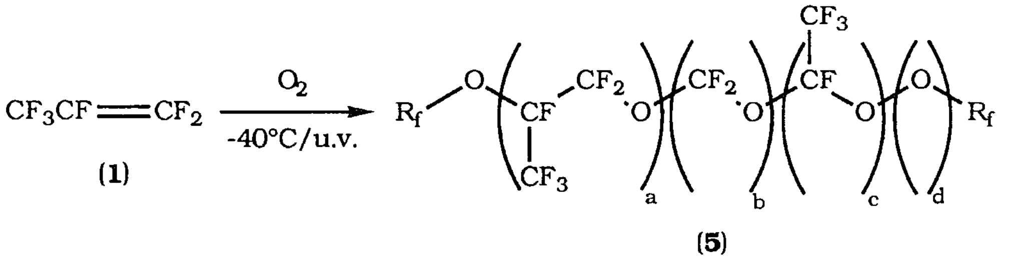


Scheme 1.6

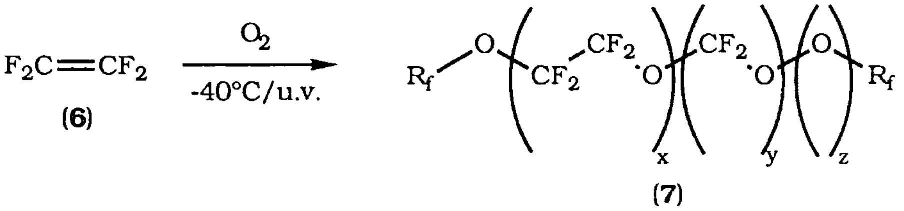
Seven grades of Krytox are available, molecular weights ranging from 2000 to 7000, with the expected variation in viscosity, volatility and other properties. The grades available are (with viscosities at 38°C); Krytox 143AZ (18 cSt), 143AA (36 cSt), 143AY (55 cSt), 143AB (85 cSt), 143AX (150 cSt), 143AC (270 cSt), and 143AD (495 cSt).[30] These materials have been mixed with low molecular weight PTFE to form a range of inert greases, designated Krytox 240AZ, 240AB, 240AC, and 240AD.[31] Inert greases of this type have already been employed in aerospace applications, and in other severe environments.

1.412 Fomblin

The manufacture of Fomblin involves the photopolymerisation of perfluoroalkenes, specifically HFP (**1**) or TFE (**6**) , in the presence of oxygen irradiated with UV at wavelengths around 3200Å, schemes 1.7 and 1.8. Peroxide linkages are removed by heating and acyl fluoride end groups by the action of elemental fluorine.



Manufacture of Fomblin Y
Scheme 1.7



Manufacture of Fomblin Z
Scheme 1.8

This route is preferable to that employed by Du Pont as the oxidation and polymerisation may be performed in one step, however, there is a much lower degree of uniformity in the polymer chain. The presence of single difluoromethylenes between oxygens has important consequences for the material's nature, which will be discussed later.

The two ranges of PFPEs are available. Fomblin Y is derived from HFP and has a ratio of *a* to *b* of about 20, it was the first PFPE manufactured by Montefluos. Fomblin Z is produced from TFE[32,33] with the ratio of *x* to *y* is around 0.8. Having a much large proportion of oxygen carbon bonds and a linear structure Fomblin Z is characterised by a very low vapour pressure and pour point, and a very high viscosity index. It should be realised that the process for the manufacture of Fomblin Z can be hazardous, TFE and oxygen make a potentially explosive mixture.

The photooxidativepolymerisation processes have been studied extensively. As none of the starting materials absorb UV light it is believed that the bulk of the reaction occurs only after acyl fluorides, peroxides or another photosensitive material have formed through an otherwise minor dark reaction. Unless a photosensitiser is used a short induction period is therefore required. Initiation can then occur *via* two processes:

$$R_{f2}O_2 \rightarrow 2R_fO\bullet$$

$$R_fCFO \rightarrow R\bullet + \bullet CFO$$

Scheme 1.9

Despite the ease of polymerisation of TFE no reaction is observed between fluoroalkyl radicals and TFE, rather the fluoroalkyl radicals react with oxygen only, while fluoroalkoxy radicals react specifically with fluoroalkene.

$$R\bullet + O_2 \rightarrow RO_2\bullet$$

$$RO\bullet + M \rightarrow ROM\bullet$$

$$RO2\bullet + M \rightarrow ROOM\bullet$$

$$RO_2\bullet + M \rightarrow RO\bullet + MO$$

$M = C_2F_4$, C_3F_6

Scheme 1.10

Termination occurs through one of the following three processes, primarily the first.

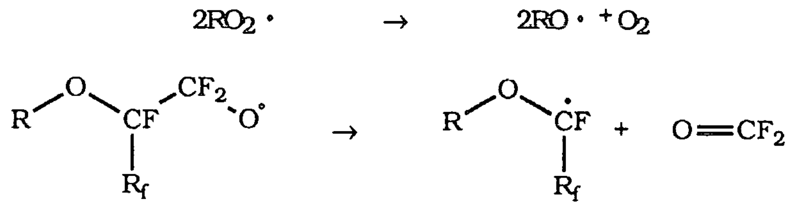
$$2RO_2\bullet \rightarrow R_2O_2 + O_2$$

$$2\bullet CFO \rightarrow (CFO)_2, CO + CF_2O$$

$$RO\bullet + \bullet CFO \rightarrow ROCFO$$

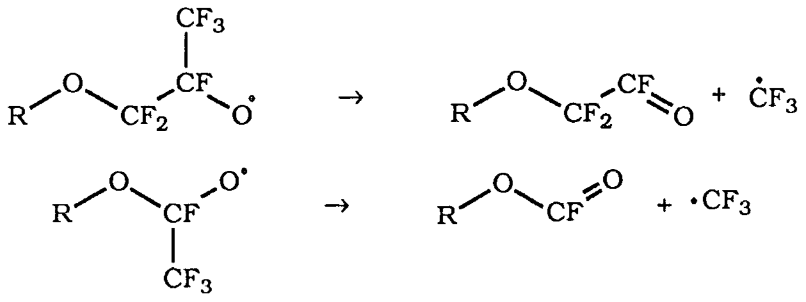
Scheme 1.11

Two further reactions can occur which can alter the radical at the chain end without extending the chain length, scheme 1.12. The second is particularly important as it causes the presence of single difluoromethylene units between oxygens in the chain, which has a pronounced effect on the material's properties. Finally chain termination reactions may take place in the manufacture of Fomblin Y, scheme 1.13. These involve the loss of trifluoromethyl radicals from the chain end, which may well initiate further polymerisation chains.



R_f = F, CF_3

Scheme 1.12



R_f = F, CF_3

Scheme 1.13

Montefluos market a range of PFPEs based on this process. The lower molecular weight materials are known as Galden fluids and are used primarily in the electronics industry, like the perfluoroethers mentioned earlier.[34] Fomblin Y materials, derived from the photo-oxidation of HFP, are available in 8 grades, separated by distillation, Fomblin Y 02, Fomblin Y 04, Fomblin Y 06, Fomblin Y 25, Fomblin Y 45 and Fomblin YR, the latter being the residue after distillation.[19] Their average molecular weights range from 1 200 to 6 500 and their other properties vary accordingly. A range specifically aimed at health care is also produced, Fomblin HC/04, Fomblin HC/25 and Fomblin HC/R.[23,35] Table 1.3 details the grades available with their average molecular weights for the primary grades of Fomblin Y.

Y 02	Y 04	Y 06	Y 16	Y 25	Y 45	YR	HC/04	HC/25	HC/R
1 200	1 500	1 800	2 500	3 000	4 100	6 500	1 500	3 200	6 600

Molecular weights of commercially available Fomblin Y

Table 1.3

Fomblin Z is available in 3 grades, Fomblin Z 03, Fomblin Z 15 and Fomblin Z 25. A grease formed from Fomblin Z and PTFE is also marketed as Fomblin Z LHT.[22]

Several other materials are available, including one that combines TFE and HFP, Fomblin KR, and so has properties intermediate between Fomblin Y and Fomblin Z, and another, Fomblin MR, similar to Fomblin Z but with the ratio of m to n greater than one.[36] There are materials based on Fomblin Z differing in the the end groups, providing a range of difunctional PFPEs. In certain applications these may have improved lubricating properties, the functional groups giving a degree of bonding to the surfaces, keeping the lubricant in place.[22] These PFPEs can also be combined through reactions at the end-groups, to produce new, higher molecular weight materials, possibly with cross-linking agents too. Figure 1.1 shows some of the end groups available.

$-CF_2OCF_3$

Fomblin Z

$-CF_2COOR$

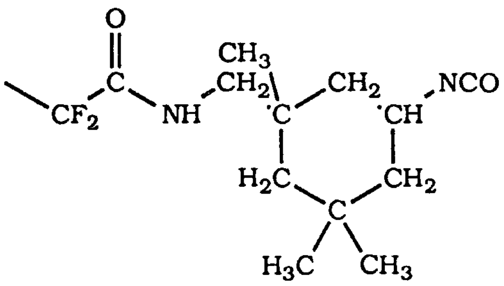
Fomblin Z-DEAL

$-CF_2CH_2OH$

Fomblin Z-DOL

$-CF_2CH_2O(CH_2CH_2O)_nH$

Fomblin Z-DOL TX



Fomblin Z F DISOC

Figure 1.1

Ausimont* have used an end-capped Fomblin Z derivative, either mono- or di-brominated, as a telogen to produce higher molecular weight materials,[37] employing di-*tert*-butyl peroxide (DTBO) as an initiator in chlorofluorocarbon or perfluorocarbon solvents. Telomers have been made from 1,1-difluoroethylene, HFP, TFE, combinations of these, and mixtures with hydrocarbon alkenes, with typically 15 telomer units incorporated.

1.413 Demnum

Daikin Industries marketed the first linear PFPE having tri(difluoromethylene)oxy repeating units (**10**). It is prepared from 2,2,3,3-tetrafluorooxetane (**8**) by fluoride ion

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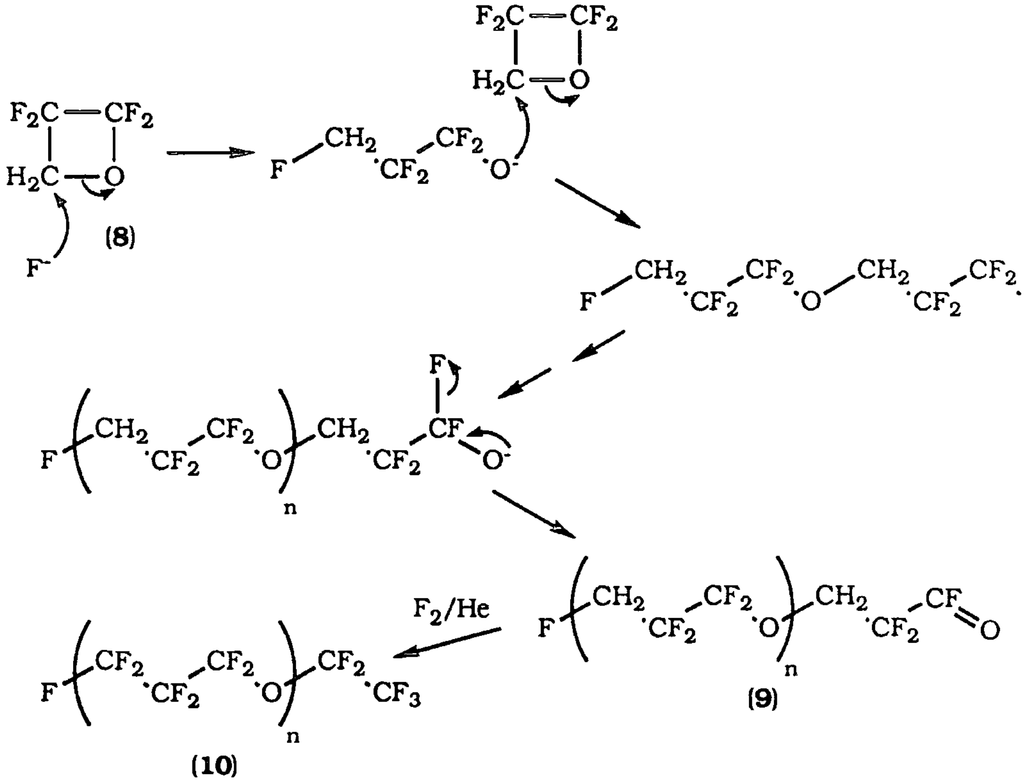
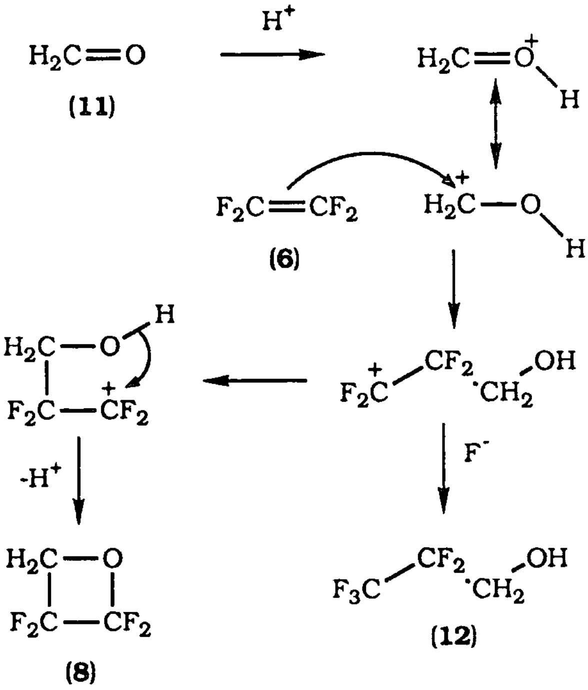
* Ausimont S.p.A. is the new name of the Montefluos company.

induced polymerisation, with either cæsium fluoride or antimony pentafluoride, to produce a polyfluorinated polymer (**9**), scheme 1.14.[38] The polymer is then fluorinated with elemental fluorine whilst irradiated with UV light. 2,2,3,3-Tetrafluorooxetane is prepared as a by-product from the reaction of hydrogen fluoride on formaldehyde (**11**) and TFE (**6**), the major product being 2,2,3,3,3-pentafluoropropanol (**12**), scheme 1.15.



Scheme 1.14



Scheme 1.15

Demnum is marketed in 4 grades, S20, S65, S-100 and S200 corresponding to average molecular weights of 2700, 4500, 5600 and 8400.[39] The numerical designations refer to the kinematic viscosity at 40°C. Like Krytox and Fomblin these grades show a range of properties, suitable for a range of applications. A grease is also marketed, Demnum Grease, in three grades, L65, L100 and L200, formulated from Demnum and low molecular weight PTFE.

1.414 Properties of commercial perfluoropolyethers

All three products are available in a range of molecular weights, from 1500 to 15 000, with a corresponding range of properties. Table 1.4 gives details of typical materials,[19,30,39,40] while table 1.5 gives some properties of the commercially available greases.[19,31,39]

The table shows that, in terms of lubricating power, Fomblin Y is the superior material. It has the lowest viscosity values, but also the viscosity index of Fomblin Y is very high. Viscosity index is an empirical measure of the variation of viscosity with temperature, compared with two standards, a 'good' one at 100 and a 'poor' one at 0. It can therefore be predicted that Fomblin Y will perform well across a large range of temperatures. Furthermore, the material has a low pour point, indicating that the material can be used at both high and low temeratures. This is undoubtedly due to the presence of such a large oxygen to carbon ratio, giving significantly greater flexibility to the polymer.

Due to their potential as high temperature lubricants much work has been done investigating the thermal stability of PFPEs, especially in conjunction with materials frequently encountered in jet engines such as iron alloys. Although PFPEs show no decomposition below 300°C, 350°C in some cases, this temperature is significantly lowered in the presence of metals and metal oxides. Zehe and Faut established that the decomposition process involves reaction at a metal oxide site on the surface, which chelates with the oxygens of the PFPE.[41] Fluoride ion transfer then occurs towards the more electron deficient carbon, which forms acid fluoride groups (no evidence was found for migration of the fluoride ion to the metal). These in turn react with the metal surface to form metal fluoride sites. The decomposition then accelerates as the metal fluoride catalyses the break down faster than the metal oxide.

Fluorinated oil Grade	Krytox 143AA	Fomblin Y-16	Fomblin Z 03	Demnum S-20
Average molecular weight	2 450	2 500		2 700
Kinematic viscosity/cSt				
20°C	80	150	29.2	53
38°C	36	56	17.7	25
99°C	5.4	6.8	5.6	
Viscosity index	90	70	317	150
Density/g cm^{-3}	1.88	1.89	1.824	1.86
Pour point/°C	-50	-45	-90	-75
Surface tension/dyne cm^{-1}	16.7	19	23	17.7
Refractive index n_D^{20}	<1.300	1.2967	1.290	1.290
Specific heat capacity (38°C)/ kJ kg^{-1} $°C^{-1}$	1.00	1.0	0.96	1.0
T_g/°C	-75	-72		-115
Volatility, % weight loss				
149°C, 6.5 hr	2			
204°C	26			
260°C	93			
149°C, 22 hr		<8	7.3	
100°C, 72 hr				0.2
200°C				4

Properties of commercially available PFPEs

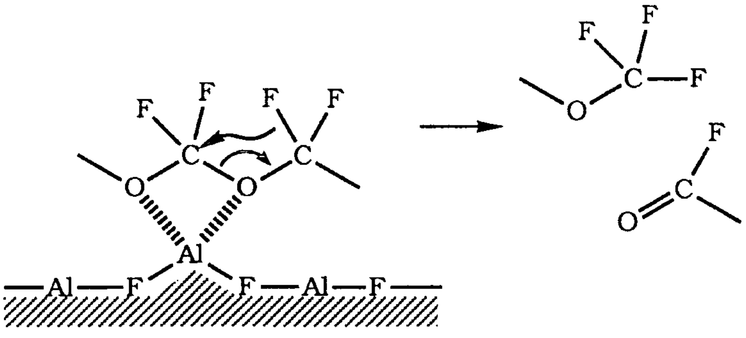
Table 1.4

Kasai and Wheeler have looked at the latter stage of the process, studying the reaction with aluminium trichloride of PFPEs with molecular weights in the range 6000 - 8000.[42] They showed that this process is most favourable at sites with one difluoromethylene between oxygens, as the cation formed is stabilised by the two oxygens as shown in scheme 1.16. Such sites occur in both Fomblin fluids, but are especially prevalent in Fomblin Z, both decomposed to some degree at 200°C, Fomblin Z completely. In other cases the second difluoromethylene destabilises the cation. Due to the ring size in the chelated form, tri(difluoromethylene) units between oxygens, such as those in Demnum, are the next most likely to decompose, scheme 1.17. Thus although both Demnum and Krytox decomposed at 250°C, total loss of material was observed in Demnum in about 15 minutes compared with 80 minutes for the Krytox sample. Fomblin Y had gone in less than 10 minutes.

Fluorinated Grease	Krytox 240AC	Fomblin UT 18	Fomblin Z LHT	Demnum L100
Appearance	white		white	white
Texture	buttery		buttery	
Viscosity/cSt	270	160	150	
Density/g cm^{-1}	1.93	1.93	1.84	
Penetration* at 25°C/mm 10^{-1}				
unworked	274	280	270	280
worked (60 strokes)	282	280	270	280
worked (10^4 strokes)†	312	310	270	260-290
Operating temperature/°C		-30 to 150	-80 to 200	
Volatility, % weight loss				
149°C, 22 hr		3.7	2	
204°C	2	9	5	<1
260°C	8			
Mechanical stability/mm 10^{-1} penetration after 10^4 strokes	312	310	270	260-290

Properties of commercially available PFPE greases

Table 1.5



Scheme 1.16

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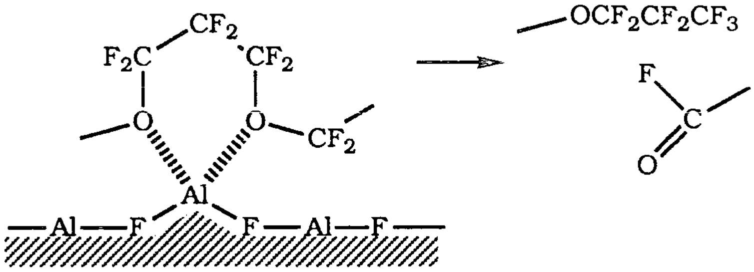
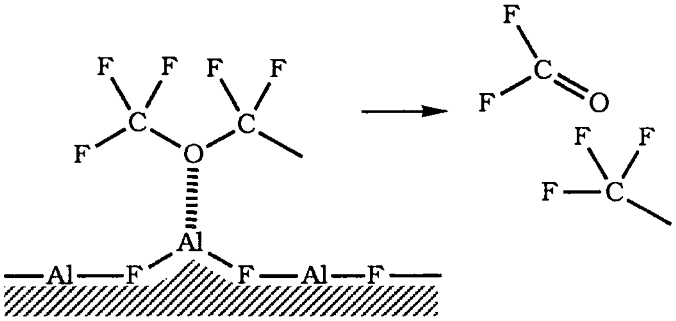
* Distance of penetration of a standard gemetry and mass into the grease in 5 s; higher penetration indicates lower viscosity.

† *I.e.*, a measure of mechanical stability.



Scheme 1.17

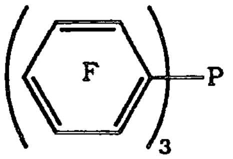
Unlike Fomblin and Demnum, Krytox decomposes from the ends, the trifluoromethoxy and pentafluoroethoxy groups being more prone to decomposition than a di(difluoromethylene) unit between oxygens. Migration of the fluoride ion is towards the polymer, scheme 1.18, which is important as the potentially reactive acid fluoride will be part of the volatile component and will quickly be removed from the system. After some decomposition the PFPE is just as inert as before, if of lower molecule weight. It was also observed that pendant trifluoromethyl groups lowered susceptibility to decomposition, presumably because their steric bulk destabilises the chelated ring on the aluminium.



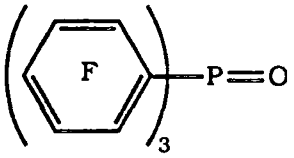
Scheme 1.18

PFPEs are equally prone to decomposition in contact with metals with oxide coatings. Snyder and Dolle have studied Krytox in contact with metals, such as silver, tool steel and stainless steel.[43] After several experiments at 370°C for 24 hours they found that weight change of the metal and viscosity change of the PFPE were both significantly higher when in contact with air, especially wet air, as opposed to nitrogen, wet or dry, due to the formation of the metal oxide. It can be seen that, while a high oxygen to carbon ratio gives particularly good lubricating properties, it also leads to less stable materials. The choice of one PFPE over another must therefore be made with a consideration of the requirements of the application.

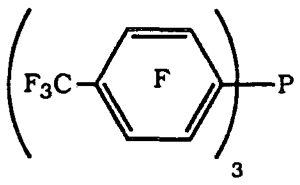
Snyder and Dolle proposed four additives that can be combined with PFPEs that can greatly enhance their stabilities towards metals at high temperature.[43] Significantly lower weight changes were observed with between 0.05% and 0.5% additive. For example addition of 0.10% tris[4-(pentafluorophenoxy)tetrafluorophenyl]phosphine, in a 24 hour test at 340°C led to a weight loss of 0.03 mg cm^{-2} from a stainless steel sample, compared with 4.52 mg cm^{-2} in its absence. It is thought that the additives complex preferentially with the metal oxide sites, effectively blocking the sites. The four proposed additives are detailed in figure 1.2.



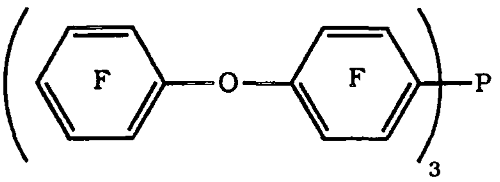
Tris(pentafluorophenyl)phosphine



Tris(pentafluorophenyl)phosphine oxide



Tris(4-heptafluorotolyl)phosphine



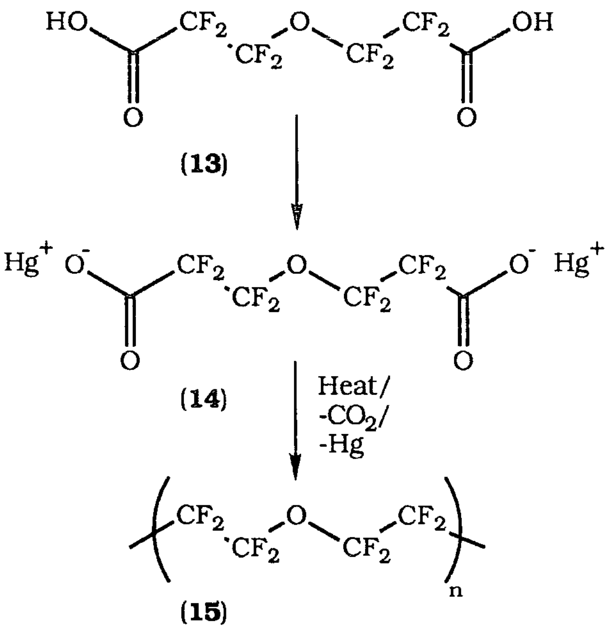
Tris[4-(pentafluorophenoxy)tetrafluorophenyl]phosphine

Figure 1.2

1.42 Other syntheses of perfluoropolyethers

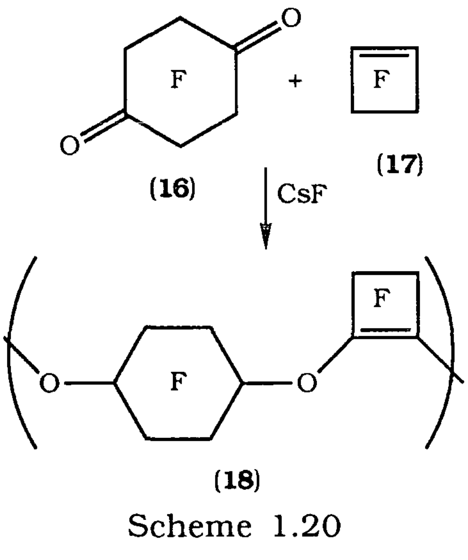
Some other groups have published patents and papers on the synthesis of a variety of PFPEs, although none are currently commercially available. The work of Lagow and co-workers, using elemental fluorine, is discussed in the next chapter and is the most comprehensive.

The 3M company published patents detailing the synthesis of PFPEs from diacid ethers (**13**).[44,45] The diacids were converted into the silver or mercury salt (**14**) and pyrolysed at 300 - 400°C to decarboxyate and couple the substrate, for example scheme 1.19. Linear PFPEs (**15**) were obtained, with 4 to 20 carbons between oxygens, the material obtained from the reaction shown was quoted as being a tough rubber like solid, which was not brittle above -80°C.



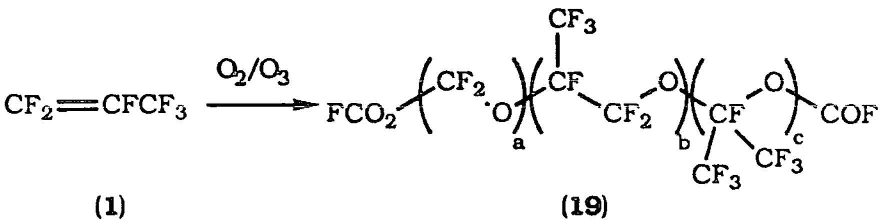
Scheme 1.19

Doorenbos *et al.*,[46] for Dow Chemicals, synthesised perfluorocyclohexan-1,4-dione (**16**), which was subsequently copolymerised with fluoroalkenes, hexafluorocyclobutene (**17**), decafluorocyclohexene, chlorotrifluoroethylene and tetradecafluoroheptene, to produce a clear, colourless oil (**18**), scheme 1.20. The reaction shown was performed in diglyme with cæsium fluoride at room temperature.



Scheme 1.20

Another patent by the 3M company describes a process for producing PFPEs by refluxing perfluoroalkenes in an atmosphere of ozone or a mixture of ozone and oxygen.[47] For instance, the reaction of HFP with ozone (2-5%) in oxygen, scheme 1.21, gave a material with little peroxide linkages (**19**), and molecular weights in the range 6000 to 10 000.

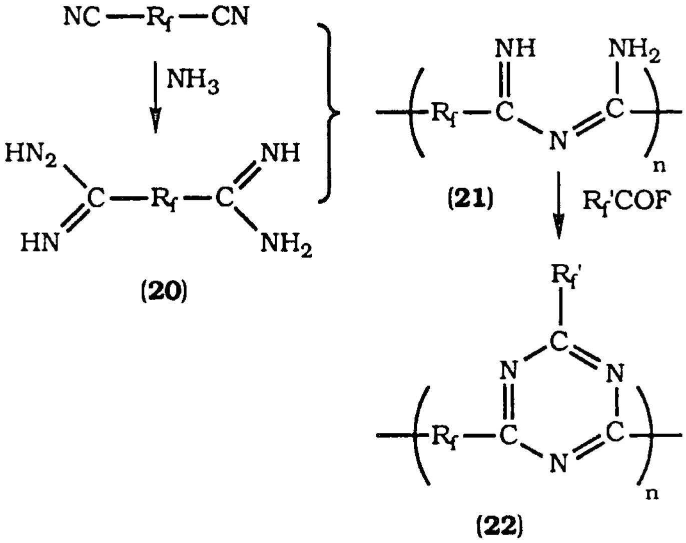


(1) (19)

(principle structural units)

Scheme 1.21

The Asahi Chemical Industry Company, Ltd have recently described a process for dramatically increasing the molecule weight of Krytox-like materials, a process very similar to that used by DePasquale *et al.* a decade ago, scheme 1.22.[48,49] A difunctional initiator is used to produce poly(HFPO) in the normal way and the acid fluoride end groups converted to cyanide groups by the reaction of ammonia, followed by dehydration. Some of this is reacted further with ammonia to produce the diamidine material (**20**), which forms a polyimidoylamidine (**21**) with more of the dicyanomaterial. Finally an acid fluoride terminated PFPE is introduced to complete the triazine ring (**22**). Molecular weights over 1 million were reported.



(20) (21) (22)

Scheme 1.22

CHAPTER TWO
TECHNIQUES OF FLUORINATION

2.1 Early Fluorination Techniques

Much of the early work to produce perfluorocarbons was performed in the vapour phase with elemental fluorine. Usually both the substrate and fluorine gas would be diluted in helium or nitrogen over a metal packing (generally copper, sometimes silver-plated). This could be heated (to keep the reactants as a vapour) or cooled (to limit the reaction). The metal packing moderates the reaction by dissipating heat and breaking up the reaction chains. Ethane, methane, chloroethane, benzene and acetone were all successfully fluorinated in this way by Bigelow and co-workers.[50]

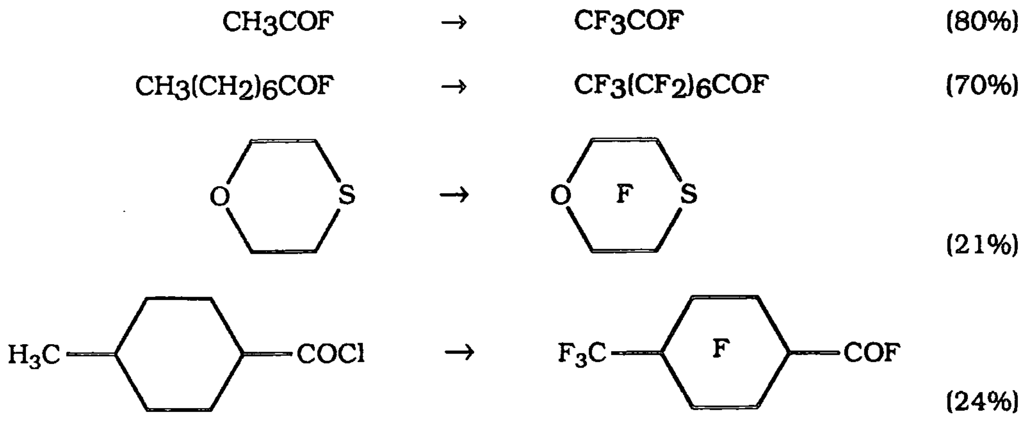
Solution phase fluorinations have been performed by Bockemüller in carbon tetrachloride, using fluorine diluted in carbon dioxide, though solvent reactions were found to be a problem. Miller attempted liquid phase fluorination, but was only successful with materials already significantly resistant to fluorination, and with low vapour pressures and melting points. Some solid phase fluorinations have also been attempted, generally with little success.[50]

These early experiments suffered greatly from low yields and complex mixtures of products, due to fragmentation during reaction, and it was generally believed that direct fluorination was a clumsy and unsubtle technique. Recently, methodologies have been developed that have to a greater extent overcome these problems, however historically electrochemical and high valency metal fluoride fluorination gained importance first and it is worthwhile looking briefly at both these techniques.

2.2 Electrochemical Fluorination

An alternative method of producing perfluorinated compounds was devised during the war as part of the Manhattan Project, though it was some time later that any work was published. This was electrochemical fluorination (ECF), which involved passing a current though a suspension or solution of the substrate in anhydrous hydrogen fluoride (HF), the perfluorinated product forming at the anode. Hydrogen gas was evolved at the cathode. Formation of fluorine gas was avoided by keeping the voltages low.[51]

ECF has the advantages that compounds are exhaustively fluorinated and there is a degree of retention of functional groups (such as acid fluoride, ether bridges, thioether bridges and tertiary amines). Rather than generating elemental fluorine from HF and using that as the reagent, HF is used directly as the source of fluorine atoms. However there are drawbacks. The anode is gradually consumed, and tarry deposits appear. There is also an explosive hazard from oxygen-containing compounds and water, and degradation and fragmentation are prevalent. Nevertheless ECF is used industrially and some examples of materials fluorinated this way are shown in scheme 2.1.[51]



Scheme 2.1

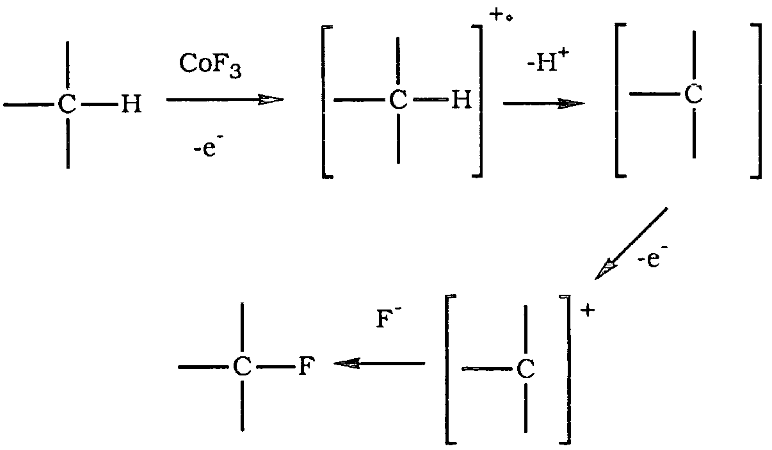
2.3 High Valency Metal Fluorides

Technology has also been developed involving high valency metal fluorides, predominantly cobalt trifluoride, as perfluorination agents. The enthalpy change of the reaction of cobalt trifluoride is significantly lower than that of fluorine and so the process is easier to control. Indeed best results have sometimes been obtained when working at high temperature (440°C).[52] Fluorination with cobalt trifluoride can be viewed as conceptually the same as direct fluorination using cobalt difluoride as a catalyst, scheme 2.2. Fluorine reacts first with the cobalt difluoride to form the trifluoride, the latter then reacts with the substrate to produce the perfluorinated material and cobalt difluoride.

$$\begin{array}{rcl} F_2 + CoF_2 & \rightarrow & CoF_3 \\ CoF_3 + R\text{-}H & \rightarrow & CoF_2 + R\text{-}F + HF \\ \hline F_2 + R\text{-}H & \rightarrow & R\text{-}F + HF \end{array}$$

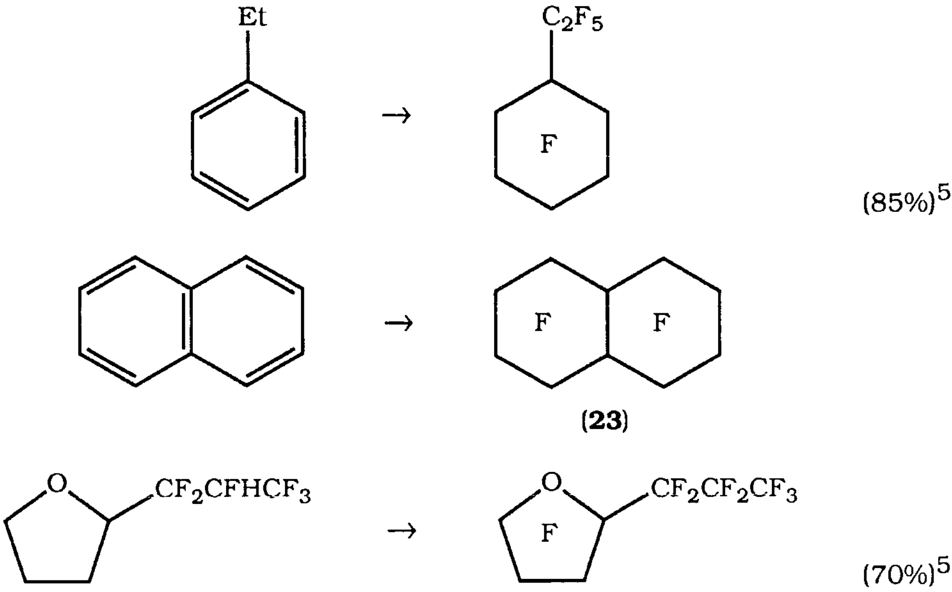
Scheme 2.2

The mechanism of the reaction is similar to ECF, the material being oxidised by cobalt trifluoride rather than at the electrode. It is a four step process involving two oxidation steps, a loss of a proton step and acquisition of fluoride ion, scheme 2.3.[53]



Scheme 2.3

Perfluorodecalin (**23**) is manufactured commercially by ISC Chemicals Ltd *via* this technique,[10] and other examples are also shown in scheme 2.4.



Scheme 2.4

Several other metal fluorides have also been considered as reagents for fluorination. Silver difluoride and lead tetrafluoride have been used to prepare some saturated perfluorinated ring systems from the corresponding aromatic hydrocarbon. Though less reactive manganese trifluoride has been used to synthesis perfluorocyclohexane from benzene albeit in low yield. Other metal fluorides of interest have included cerium tetrafluoride and uranium hexafluoride.[55] Recently Holloway *et al.* presented work utilising the fluorides and oxide fluorides of metals such as vanadium, molybdenum, rhenium and uranium to fluorinate hydrohaloalkanes and showed that there is quite a range of reactivity, and selectivity, available with these reagents.[56] Plevey and co-workers have also published results from the fluorination with complex metal fluorides, such as potassium tetrafluorocobaltate,[57] potassium hexafluoronickelate,[58] potassium tetrafluoroargentate,[59] and cæsium tetrafluorocobaltate.[60]

2.4 Direct Fluorination

In recent years the use of elemental fluorine has been looked at anew, and techniques have been devised to control the reaction. To explain their development it is necessary to look at the thermochemical considerations behind them. In the table below the values of ΔH and ΔG, in kJ mol^{-1} at room temperature, are listed for each step of the fluorination process.[61]

				ΔH/kJ mol^{-1}	ΔG/kJ mol^{-1}
Initiation	F_2	→	$2F^\bullet$	+157.7	+123.6
	$F_2 + RH$	→	$R^\bullet + HF + F^\bullet$	+16.3	-24.4
Propagation	$RH + F^\bullet$	→	$R^\bullet + HF$	-141.4	-151.2
	$R^\bullet + F_2$	→	$RF + F^\bullet$	-25.5	-284.9
Termination	$R^\bullet + F^\bullet$	→	RF	-446.8	-407.9
	$R^\bullet + R^\bullet$	→	R-R	-350.6	-294.1
Overall	$RH + F_2$	→	RF + HF	-430.5	-432.6

Table 2.1

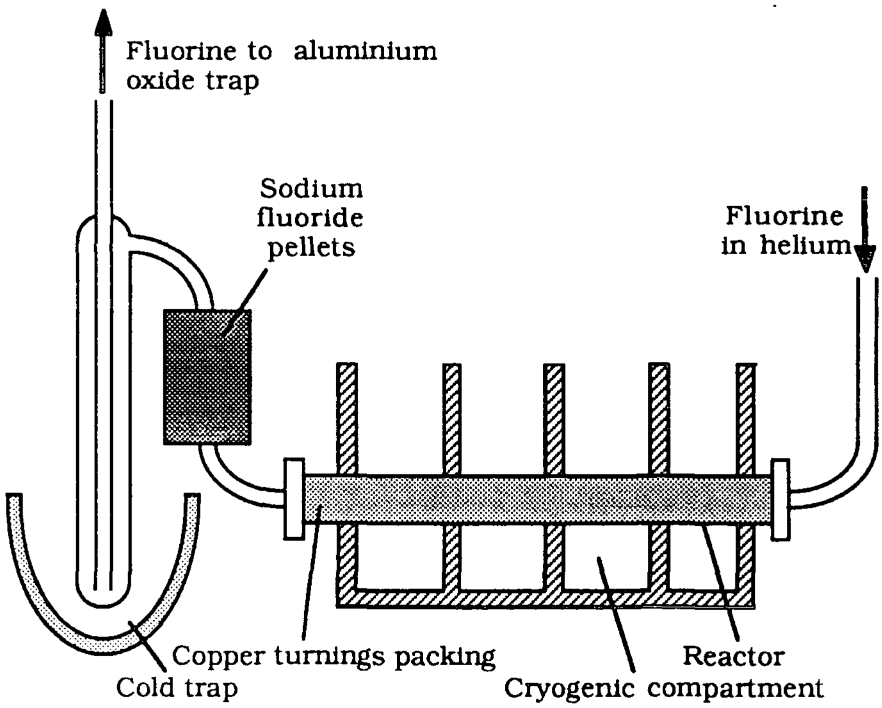
A few points should be realised. Firstly it can be calculated that less than 1% of fluorine is dissociated into fluorine atoms at room temperature, this compares with around 4% at 325°. One important method of limiting the reaction is therefore to lower the temperature, and so reduce the first initiation step. It should also be noticed that no single step is exothermic enough to cleave carbon-carbon bonds, and so if each reaction is sufficiently isolated molecular fragmentation should not occur. This is generally done by high dilution of the fluorine gas in either nitrogen or helium, causing a drop in the statistical likelihood of multiple reactions occurring within the same molecule in a short time. Other important developments involve the removal of energy from the reaction site before bond cleavage can occur. Typical solutions involve using a metal packing as a heat sink and using substrate molecules with large numbers of degrees of freedom, *i.e.*, able to translate the energy to another part of the molecule as rotational or vibrational energy. The use of dilute substrates helps to reduce the degree of oligomerisation by preventing the second termination reaction from occurring.

There is an alternative set of problems due to the relative inertness of the intermediary materials that has also to be overcome to achieve perfluorination. These highly polyfluorinated, but not perfluorinated, materials have a high electron density surrounding them, the result of the many non-bonding electrons of the fluorine atoms. Hence there is a great tendency for them to be shielded from further attack of fluorine molecules, preventing further fluorination. This can be overcome by raising the temperature and fluorine concentration, and by using UV irradiation, to promote the first initiation step, increasing the probability of reaction.

Due to the reactive nature of fluorine the degree of selectivity in its free radical reactions tends not to be great and it is generally thought not to be suitable for regiospecific reactions. However several papers have been published that show that this is not the case and with proper care in the choice of conditions and substrates selective reactions in good yield can be achieved.[62-64] This is not a major concern if the substrate is to be perfluorinated, but selectivity of free radical reactions is discussed in later chapters.

2.41 Cryogenic direct fluorination

The technique devised by Lagow *et al.*[61,65-67] entails using very low fluorine concentrations, usually at very low temperatures. The 'LaMar' process involves evaporating the substrate into a cryogenic reactor, figure 2.1, that is a nickel tube packed with copper turnings, the whole of which lies in a compartmentised box. The box is made of steel and insulated with polyurethane foam. Each compartment is maintained at a set, but different, temperature, and so a series of temperature gradients is produced typically ranging from -78°C to room temperature (fluorine itself boils at -188.14°C[3]).



The cryogenic reactor system

Figure 2.1

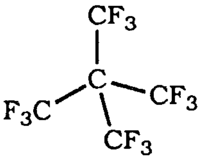
As the substrate becomes more fluorinated it becomes more volatile and so moves further through the apparatus, giving a continually renewed surface for fluorination. The copper turnings provide a heat sink and a large surface area, and may also catalyse the reaction by the formation of copper fluorides in a similar process to the cobalt trifluoride fluorination. Over the course of the reaction the concentration of fluorine in helium is slowly raised, and the temperature of the compartments adjusted. The perfluorinated product, after passing through a sodium fluoride scrubber to remove HF, is collected in a cold trap if sufficiently volatile or otherwise recovered from the reactor.

Using this process Lagow and co-workers have synthesised a vast range of perfluorinated compounds, from PFPEs to hexafluoroacetone. Some examples of this work are presented.

Fluorination of saturated hydrocarbons

The following fluorocarbons were made by fluorination of the corresponding hydrocarbon precursors at -78°C, excepting the second which was at 0°C.[61] Some substituted adamantanes were also fluorinated.

1.



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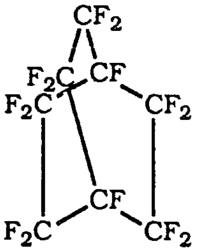

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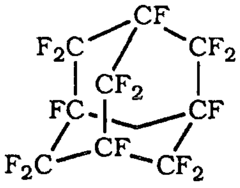

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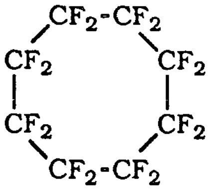
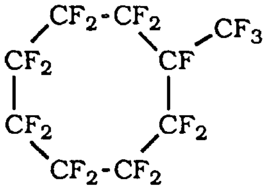


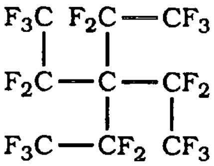
The hydrocarbon precursors to fluorocarbons 5 to 7 were all fluorinated at -40°C to 60°C in reasonable yields. The materials were fluorinated on sodium fluoride, a hydrogen fluoride scavenger.[68] This technique was used in many of Lagow's later reactions, especially for less volatile starting materials.

5.

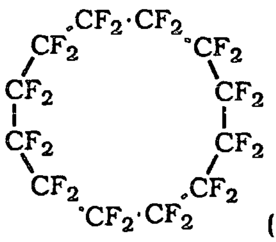


(19.0%)

6.



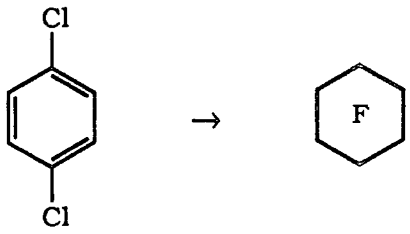
(15.1%)

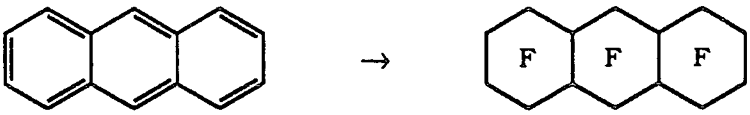
7. 

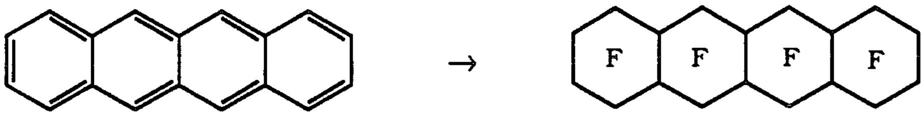
(6.0%)

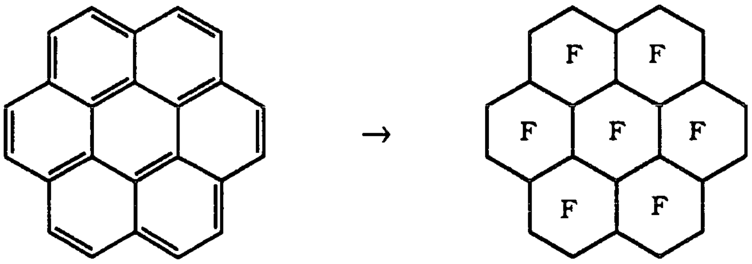
Fluorination of aromatic compounds

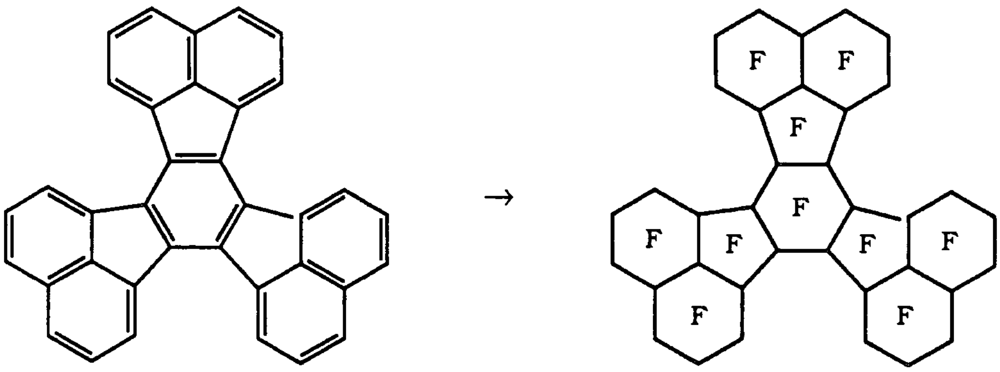
Reactions 8 to 12 were all performed at 20°C.[61]

8. 

9. 

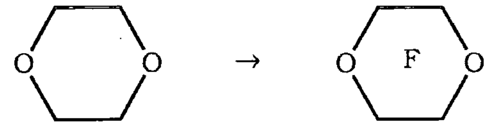
10. 

11. 

12. 

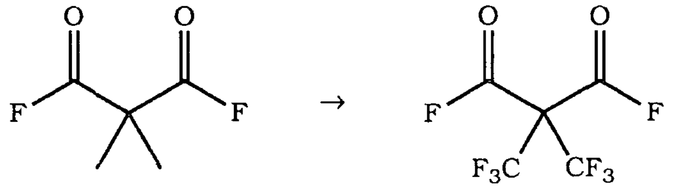
13. $CH_3OCH_2CH_2OCH_3$ → $CF_3OCF_2CF_2OCF_3$ (21%)

14. $CH_3O(CH_2CH_2O)_2CH_3$ → $CF_3O(CF_2CF_2O)_2CF_3$ (16%)

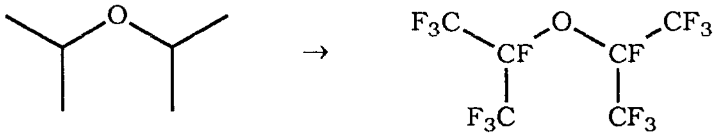
15.


(40%)

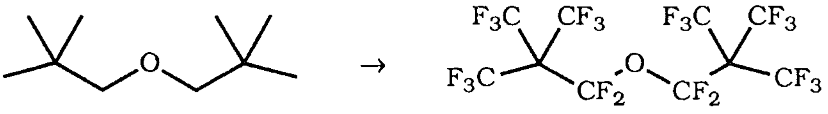
16. $C_2H_5OCOCH_3$ → $C_2F_5OCOCF_3$ (5%)
$CF_3CFHOCOCF_3$ (20%)

17.


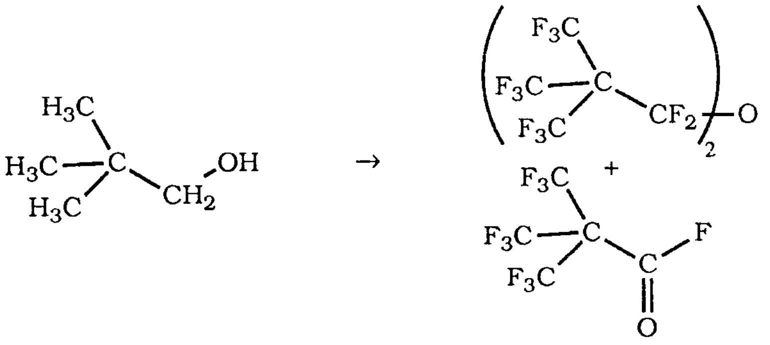
(14%)

18.


(25%)

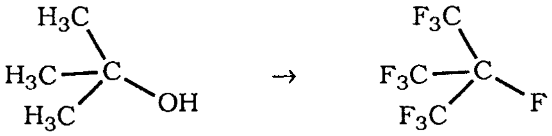
19.


(50%)

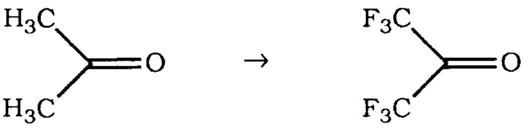
20.


(58%)

(14.2%)

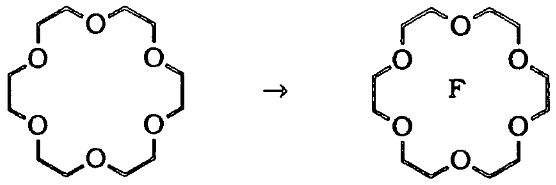
21.


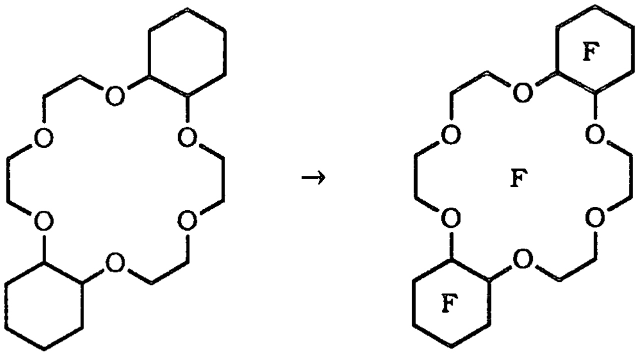
(44.5)

22.


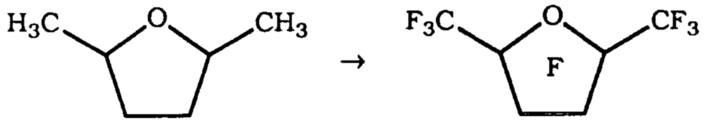
(38%)

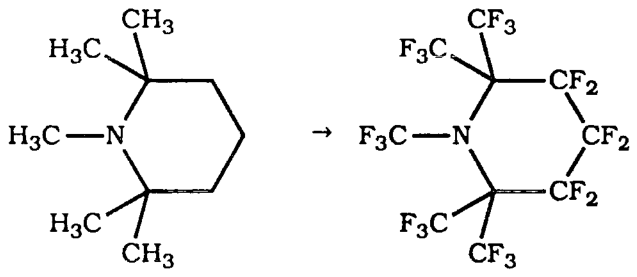
The ethers, esters, and acid fluorides in reactions 13 - 19 were all fluorinated at -78°C, and illustrate how well these functional groups remain intact.[69,70] Reactions 20 and 21 were fluorinated at -120°C to room temperature.[71] Acetone (reaction 22) was fluorinated on a bed of sodium fluoride,[72] that will have removed HF from the system. The following crown ethers were also fluorinated on a bed of sodium fluoride, at -78°C to -40°C.[73,74]

23.

(33.5%)

24.

(20.5%)

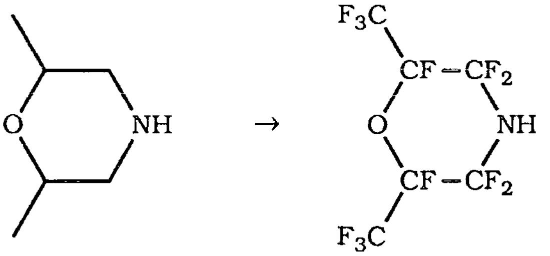
Fluorination of other heterocyclic compounds

25.

(50.2%)

26.

(19.5)

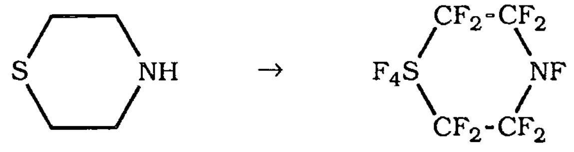
A variety of ethers and amines, such as the two above, were fluorinated for potential use in artificial oxygen carriers. The cyclic ether was fluorinated at -120°C up to room temperature and the amine at -78 to room temperature. The amine, being relatively involatile, was mixed with sodium fluoride,[75] as were the following heterocycles, which were fluorinate at -78°C to -25°C (reactions 27 and 28) and -78°C to -10°C (reaction 29).[76]

27.



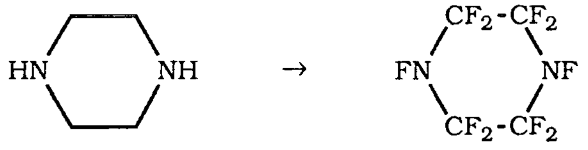
(95%)

28.



(80%)

29.



(86%)

Low molecular weight PFPEs

The fluorination of poly(ethylene oxide) (**24**) was performed at room temperature and higher to promote fragmentation, producing the low molecular weight materials indicated.[77,78] Fluorine concentrations were increased from 2.4% to 28% at ambient temperatures over 12 days, the temperature was then raised to 90 - 110°C over the next 4 days. 15 compounds were identified, of the general structure shown, the yield over all 15 compounds was 6.5%.

30. $(CH_2CH_2O)_n$ → $R_f(OCF_2CF_2)_mOR_f$

(24)

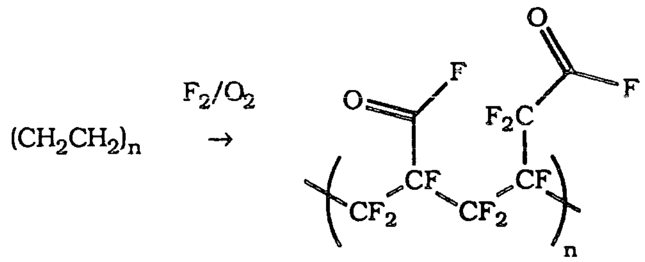
$R_f = CF_3, C_2F_5,$

n large, m = 1 - 6

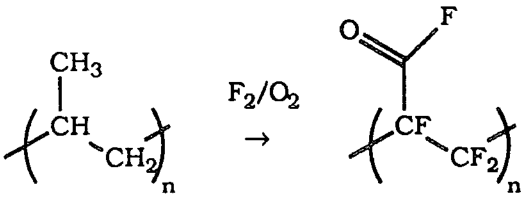
20 to 110°C

"Oxyfluorination"

By using a stream of oxygen and fluorine several functionalised perfluorinated polymers were synthesised, a process described as "oxyfluorination". These NAFION-like materials have possible applications such as catalyst supports and membranes or separators for chloro alkali cells and batteries.[79]



31.



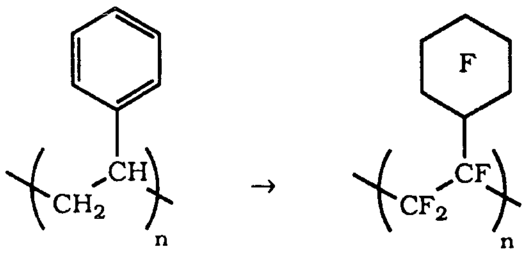
32.

Fluorination of polymers

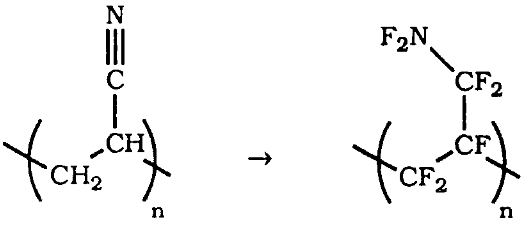
Some polymers were fluorinated. The starting materials were ground to fine powders, better than 100 mesh (less than 150 micron diameter), to allow fluorine gas to permeate all the way through the material. The schemes shown are idealised, it was accepted that some degree of cross linking occurred.[61] Note in reaction 38 the conversion of the hydroxy-group to a carbon-fluorine bond that was also seen in reaction 21, no explanation of this process was given. Reactions 33 and 34 were also performed on sodium fluoride, with yields around 80%.[80]

33. $(CH_2CH_2)_n \rightarrow (CF_2CF_2)_n$

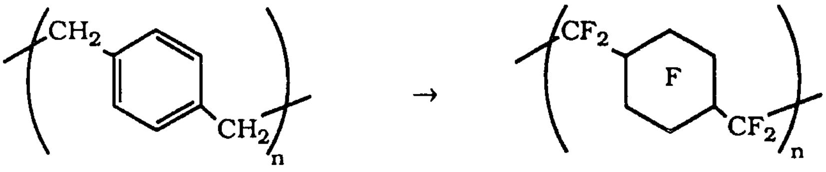
34. $(CH_2CHCH_3)_n \rightarrow (CF_2CFCF_3)_n$



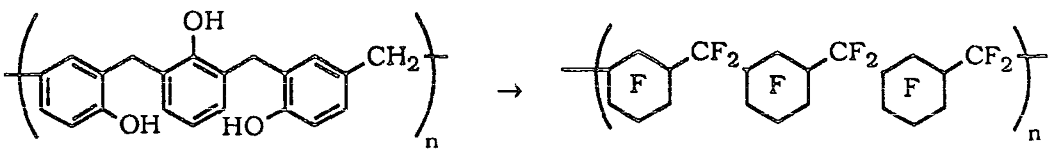
35.

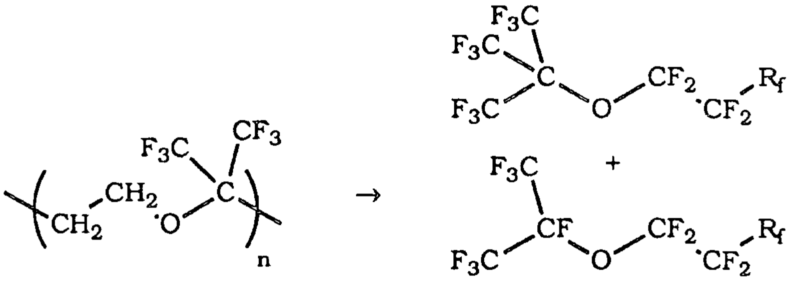


36.



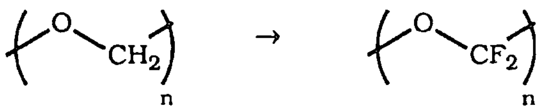
37.

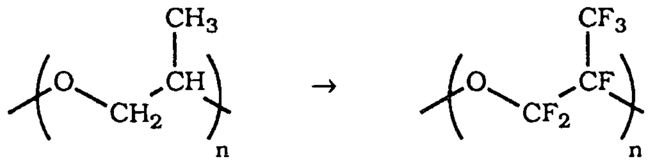
38. 

39. 

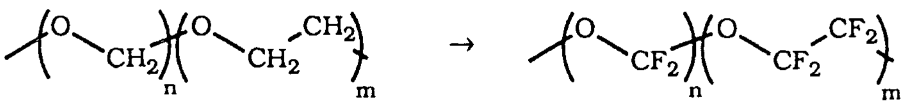
(25)

Rf = CF(CF3)2,
C(CF3)2OCF2CF3,
C(CF3)2OCF2CF2CF(CF3)2.

40. 

41. 

The polyfluoropolyether starting material (**25**) of reaction 39 was made by γ-ray induced copolymerisation of hexafluoroacetone and ethene. Fluorination was performed in two stages, the first at low temperature (-50°C) to incorporate a significant amount of fluorine, then at higher temperature, up to 75°C, to promote fragmentation.[81] Reactions 40 and 41 are important as they produce PFPEs.[82]

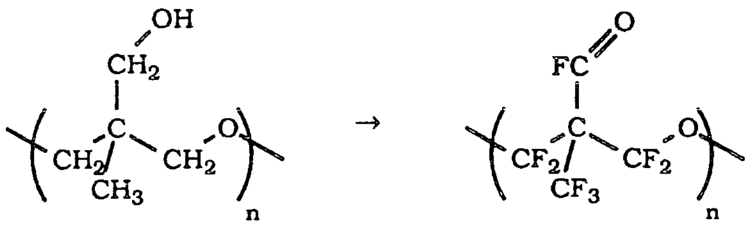
42. 

(**26**)

(37%)

This polyether (**26**) was fluorinated at room temperature up to 100°C on sodium fluoride. The value of m over n ranged between 0.04 and 0.14.[83] The reaction was also performed on poly(1,3-dioxolane), *i.e.*, with n equal to m. Like the products of reactions 31 and 32, that of reaction 43 is potentially useful in membranes and separators and as catalyst supports, it was fluorinated at room temperature to 60°C and subsequently converted to the free acid in boiling sodium hydroxide solution.[71]

43.

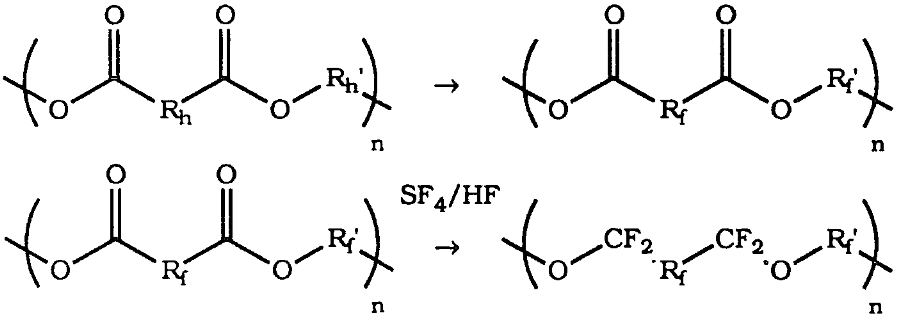


(87%)

Fluorination of polyesters to synthesise PFPEs

A general method of producing PFPEs from any polyester starting material was proposed. The polyester is fluorinated at room temperature using the normal technique. The carbonyl-groups, which survive direct fluorination, are converted to difluoromethylene groups by sulphur tetrafluoride. It was also suggested that a slight deficiency of sulphur tetrafluoride could be used, leaving a few carbonyl groups intact. These could then be fragmented at the ester linkage with elemental fluorine at 70-150°C, to give a range of lower molecular weight materials. In principle this methodology could produce a range of PFPEs, limited only by the availability of polyester precursors. The range of polyesters greatly exceeds that of polyethers.[84]

44.



i. $R_h = CH_2CH_2$, $R_h' = CH_2C(CH_3)_2CH_2$
$R_f = CF_2CF_2$, $R_f' = CF_2C(CF_3)_2CF_2$

ii. R_h, $R_h' = CH_2CH_2CH_2CH_2$
R_f, $R_f' = CF_2CF_2CF_2CF_2$

It can be seen that a vast range of materials can be fluorinated, though the yields range from 80-90% to less than 10%. However the equipment required is rather specialised and the reactions are fairly prolonged. The conditions used for reaction 22, the fluorination of acetone, one of the most recently published, are outlined in table 2.2 and show a total reaction time of 228 hours.[72] Furthermore the technique is inherently a batch process and so cannot be seriously considered for industrial scale up.

Helium/ ml min^{-1}	Fluorine/ ml min^{-1}	Temp/ °C	Time/ hours
20	1	-100	18
20	2	-100	18
20	3	-100	24
20	4	-100	24
10	4	-100	24
0	4	-100	24
0	4	-90	18
0	4	-80	18
0	4	-60	18
0	4	-40	18
60	0	25	24

Reaction conditions for the fluorination of acetone by the LaMar technique

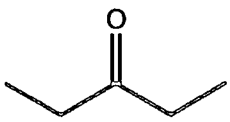
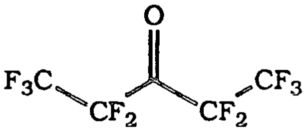
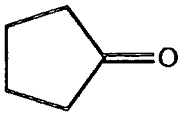
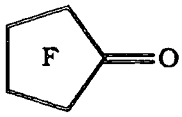
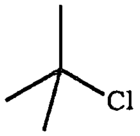
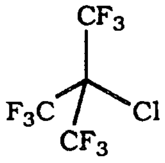
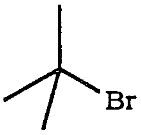
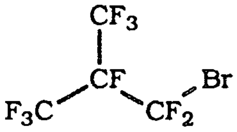
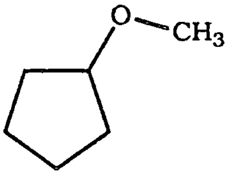
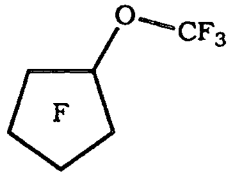
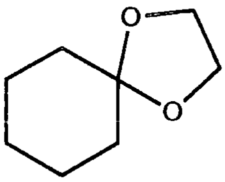
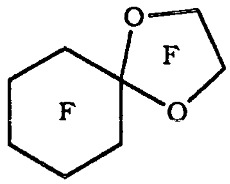
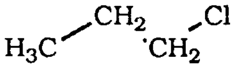
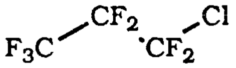
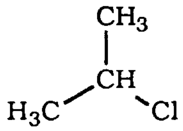
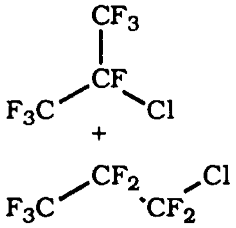
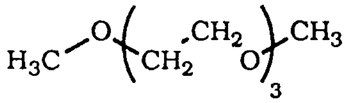
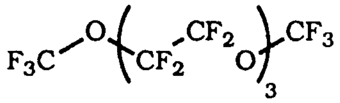
Table 2.2

2.42 Aerosol direct fluorination

Adcock *et al.* adsorb the substrate on to a sodium fluoride aerosol before reaction with fluorine.[85-88] This aerosol then passes down a reactor column while fluorine diffuses in through the reactor walls. A typical experiment involves heating sodium fluoride to around 1000° in a stream of helium to generate the aerosol, which has a particle size of about 17Å. The starting material is introduced into the reactor *via* a syringe and assorbed or condensed on the aerosol particles at about -196°. The aerosol is carried in the helium stream into the first reactor zone which is maintained at low temperature (-78° to -40°), fluorine is introduced through the porous reactor walls diluted 2 - 5% in helium. As the aerosol is carried down the reactor it passes through a series of other zones where the temperature and fluorine concentration are increased. Finally UV irradiation is used to achieve perfluorination. Virtually no fragmentation is observed and the products are almost completely perfluorinated.

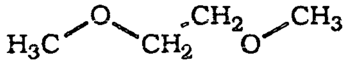
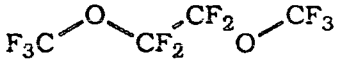
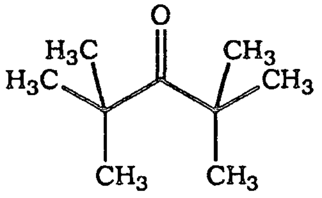
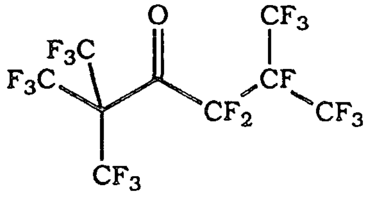
There are a number of reasons that explain the success of aerosol direct fluorination. The sodium fluoride in the aerosol particles absorbs HF and may also lead to interactions with fluorine molecules enhancing reaction. The sodium fluoride also serves to hold the substrate immobile, which will greatly reduce possible oligomerisation reaction (*i.e.*, the second termination reaction) and improve the chances of recombination after fragmentation. The substrate has a very high surface area, and it is all equally exposed so fluorination will tend to progress at a similar extent for all the substrate - no insufficiently fluorinated substrate should pass into a reactor zone too fierce for it. The sodium fluoride also provides a heat sink.

A range of perfluorocarbons and perfluorocarbon derivatives has been synthesised using this technique, some examples of which are shown in table 2.3.

	Substrate	Product	Yield
1.			(13%)[89]
2.			(24%)[89]
3.			(74%)[90]
4.			(63%)[90]
5.			(57%)[91]
6.			(14%)[91]
7.	 $H_3C-CH_2-CH_2-Cl$	 $F_3C-CF_2-CF_2-Cl$	(63%)[92]
8.	 $H_3C-CH(CH_3)-Cl$	 $F_3C-CF(CF_3)-Cl$ + $F_3C-CF_2-CF_2-Cl$	(49%)[92] (2:1)
9.	 $H_3C-O(CH_2CH_2O)_3-CH_3$	 $F_3C-O(CF_2CF_2O)_3-CF_3$	(30%)[93]

Reactions performed by aerosol direct fluorination

Table 2.3

	Substrate	Product	Yield
10.			(36%)[93]
11.			(9%)[94]
12.	$C(OCH_3)_4$	$C(OCF_3)_4$	(8%)[95]

Reactions performed by aerosol direct fluorination

Table 2.3 (continued)

The yield for reaction 8 is combined for the two products. Data was presented suggesting that this rearrangement, and that of reaction 4, is *via* a carbo-cation. This would imply an electrophilic fluorination process, rather than free radical, though a combination of the two is, perhaps, the more likely situation.[90] Whilst aerosol direct fluorination is a useful and versatile technique it is difficult to envisage it being used on a large scale.

2.43 Liquid phase fluorinations

Recently articles and patents have appeared on the subject of liquid phase fluorination. Lagow and co-workers have patented an alternative to the LaMar fluorination technique, performed in the liquid phase.[96] The patent describes a general process using any perhalogenated chlorofluorocarbon, chlorofluoroether or perfluorocarbon as a solvent, though the examples quoted for the majority used either 1,1,2-trichlorotrifluoroethane or (when fluorinating low molecular weight materials) the perfluorinated product. Reaction proceeds in a stirred reactor maintained at a constant temperature between -10°C and 50°C. Fluorine, diluted in an inert gas, and the substrate are admitted separately in a controlled manner. In some reactions, notably with polyethers, sodium fluoride was added as an HF scavenger. Two examples are shown in scheme 2.5. In the reaction with poly(ethylene glycol) (27), 252g of starting material, with an average molecular weight of 1000, was converted to several fractions of varied molecular weights, totalling 535g.

A further point of interest is that the patent discusses the use of benzene as a free radical chain initiator, used in the later stages of reaction to promote the formation of fluorine radicals as an alternative to methods like UV irradiation. Fluorine gas will tend to react first with the small amount of benzene present, the substrate being fairly inert towards fluorine molecules by this time. Reaction will proceed with the benzene to produce fluorine radicals, which are sufficiently reactive to interact with the substrate. The reaction chain can then continue normally.

$CH_3CO(CH_2)_5CH_3 \rightarrow CF_3CO(CF_2)_5CF_3$ (86.8%)

$HO(CH_2CH_2O)_nH \rightarrow CF_3O(CF_2CF_2O)_mCF_3$

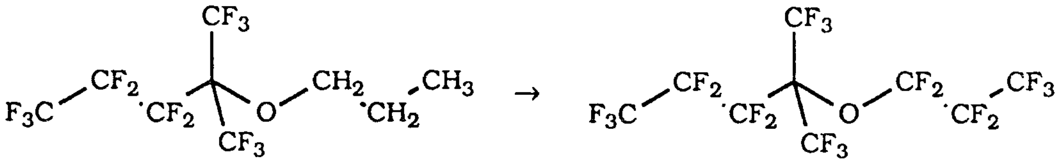
(27)

Scheme 2.5

A technique has recently been described where, rather than using very dilute fluorine, the substrate concentration is kept at a minimum. A paper by Scherer *et al.* gives conditions for the synthesis of perfluoro(heptyl propyl ether) (**28**), perfluoro(2-propoxy-2-methylpentane) (**29**) and other ethers, scheme 2.6.[97] The workers performed the fluorination in perfluoroalkanes, using poly-fluorinated starting materials (to achieve miscibility) at high dilution and so ensuring that the reaction mixture is unlikely to undergo oligomerisation. Excess energy is removed by the solvent. Undiluted fluorine is introduced into the reaction vessel to give a saturated solution in the perfluoroalkane (estimated at 0.02M at 25°C spectrophotometrically) and UV light is used to provide a greater number of fluorine radicals. Using substrates already containing fluorine, the molecules are already sufficiently deactivated with respect to fluorination that fragmentation is obviated.

$H(CF_2)_6CH_2OCH_2CH_2CH_3 \rightarrow F(CF_2)_7OCF_2CF_2CF_3$ (55%)

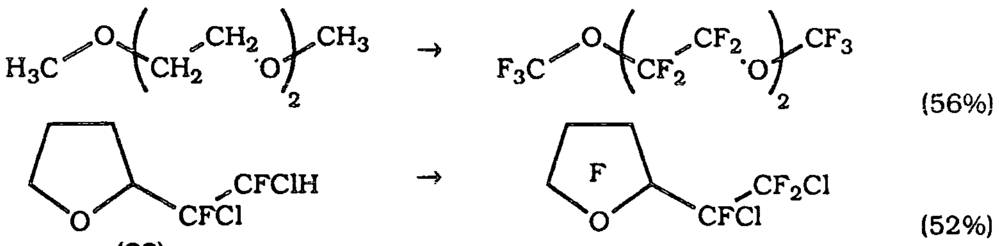
(28)



(29) (60%)

Scheme 2.6

In Italy another group has fluorinated some ethers and also adducts of 1,2-dichlorodifluoroethane with oxolane (**30**) and 1,4-dioxane, using a PFPE (Fomblin) as the medium mixed with potassium fluoride, scheme 2.7.[98,99] The substrate was admitted into the preheated reaction vessel (100°C to 120°C), together with fluorine diluted 1:1 in nitrogen. The perfluorinated products were collected in a cold trap, and separated from polyfluorinated materials by distillation. The technique works by diluting the substrate in an inert and viscous material, limiting the contact with fluorine. Potassium fluoride will have removed HF.



(30)

Scheme 2.7

Nappa and Sievert have fluorinated some ethers in 1,1,2-trichlorotrifluoroethane, using fluorine diluted in nitrogen, 5% rising to 50%, at -25°C or -15°C, scheme 2.8.[100,101] The reactions were irradiated with UV light once the fluorine concentration reached about 30%. The success of the reaction can be attributed to four effects, already discussed in other systems namely the use of substrates already containing fluorine, dilution of the substrate, low fluorine concentration and low temperature. Good yields were obtained.

$C(CH_2OCF_2CF_2H)_4 \rightarrow C(CF_2OCF_2CF_3)_4$ (78%)

$HCF_2CF_2OCH_2CH_2OCF_2CF_2H \rightarrow CF_3CF_2OCF_2CF_2OCF_2CF_3$ (85%)

Scheme 2.8

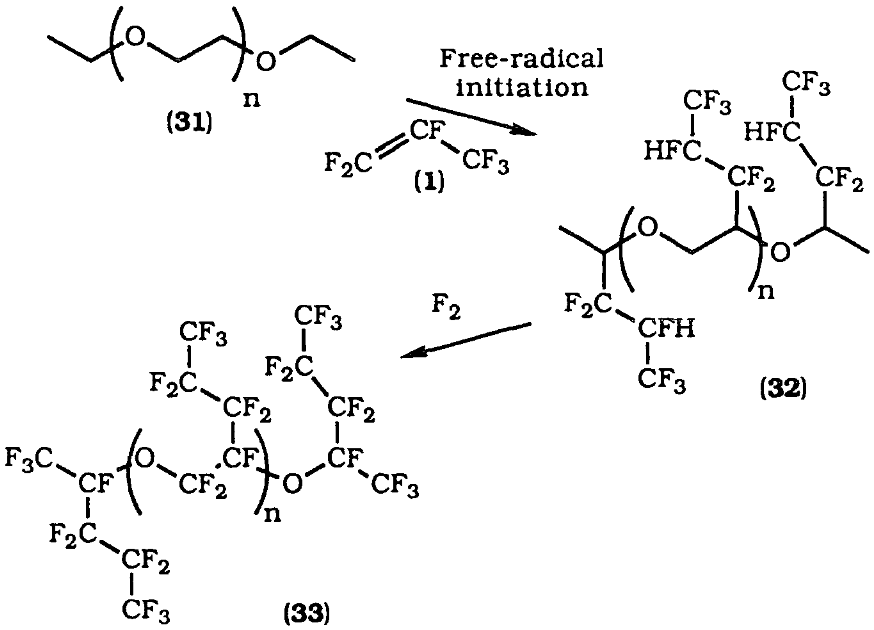
A Japanese patent has recently been published in which liquid substrates were adsorbed onto nickel fluoride in a perfluorotripentylamine medium.[102] Heptane was successfully fluorinated with a yield of 76%, compared with 9% when a similar reaction was performed without nickel fluoride. The degree of moderation provided by the nickel fluoride is illustrated by the reaction conditions; 33% fluorine in nitrogen at 125°C.

CHAPTER THREE

FREE RADICAL ADDITIONS OF ETHERS TO HFP

3.1 Introduction

It was believed that a viable alternative to the routes to PFPEs already discussed would be a two step process, the first forming a polyfluorinated material from a polyether, such as diethyl poly(ethylene glycol) (DEPEG) (**31**), by the free radical addition of fluoroalkenes like HFP (**1**), and the second step in which the polyfluorinated material (**32**) was further fluorinated by elemental fluorine at room temperature, as idealised in scheme 3.1. It has already been demonstrated that this approach is highly successful for low molecular weight ethers.[103,104]



Scheme 3.1

This technique has a number of advantages. Firstly, as PEGs are commercially available in narrow molecular weight ranges, a range of materials with similarly narrow molecular weight distributions could potentially be synthesised. Also these materials (**33**) should be of particularly high stability towards metals, having both two carbon units between oxygens, and pendant perfluoroalkyl groups all along the polymer (the oxygens therefore having little or no donating properties similar to Krytox). Furthermore, a wide range of materials can be envisaged in which the nature, and number, of the perfluoroalkyl side chain is altered, such as heptfluorocyclobutyl or heptafluoroprop-2-oxy.

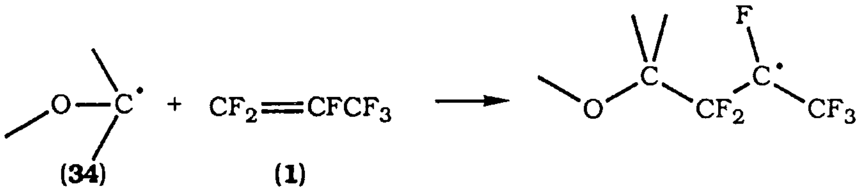
The first step is therefore the free radical addition of the polyether to a fluoroalkene. This should be viewed in the context of an on-going project within this laboratory, investigating the use of the carbon-hydrogen bond as a functional group.

3.11 Free Radical Reactions

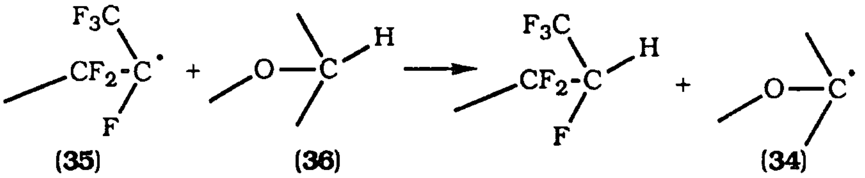
A free radical is a species with an unpaired electron which is therefore very reactive. In general they are very short lived species, because, unlike ions, radicals are not as readily stabilised by solvents and so tend to be of higher energy[105] (though solvent effects can be important[106]). The free radical reaction involves formation of a radical (initiation), subsequent chemical transformations which occur due to radicals present (propagation) and loss of the radical (termination).

3.12 Free Radical Additions to Fluoroalkenes

A free radical reaction chain can easily be several thousand steps long, consisting of one initiation step, one termination step and a very large number of propagation steps. Clearly therefore the propagation steps will be most important in determining reactivity, selectivity and orientation. These effects are determined by a number of factors, such as polarity, stereochemistry and stabilisation, and numerous reviews have been published concerning them.[107-109] Only a brief overview will therefore be given, concentrating mainly on the specific case of the free radical addition of an ether to HFP (**1**). The two important steps for this reaction are attack of an oxygen-stabilised carbon radical (**34**) on a double bond of a fluoroalkene, scheme 3.2, and abstraction of a hydrogen by a fluorine stabilised carbon radical (**35**), scheme 3.3.



Scheme 3.2



Scheme 3.3

The first of these steps is the reaction of the nucleophilic radical (**34**), being stabilised by donation from the oxygen lone pair. The nature of the stabilisation can be explained by both valence bond, figure 3.1, and the molecular orbital theory, figure 3.2.

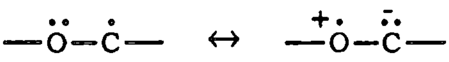


Figure 3.1

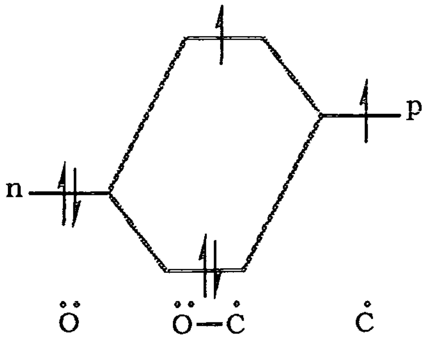


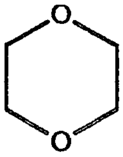
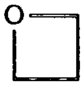
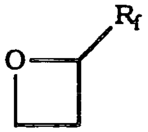
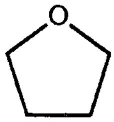
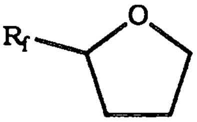
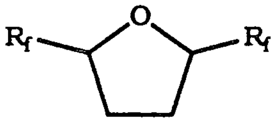
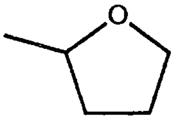
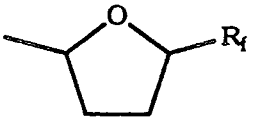
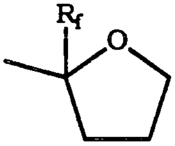
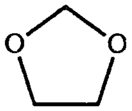
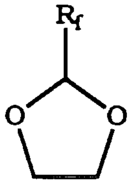
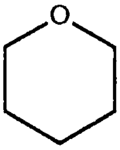
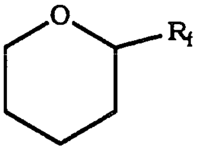
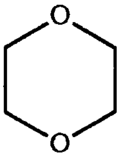
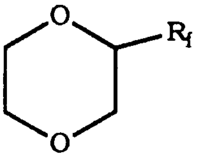
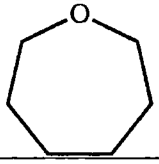
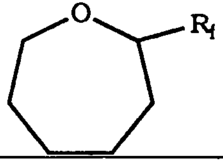
Figure 3.2

Attack occurs at the terminal difluoromethylene. This can be rationalised on the grounds that it is the most electron poor site and the least sterically hindered site. It also seems likely that the radical formed (**35**) will be more stable, being adjacent to fluorine, and the difluoromethylene and the trifluoromethyl moieties. The fluorine atom on the carbon radical will provide a similar stabilisation to oxygen in figure 3.1. The trifluoromethyl and difluoromethylene groups will cause electron withdrawal from the radical site, and so would be expected to stabilise the canonical form on the right of figure 3.1, similar to the 'capto-dative' effect.[110]

There is some evidence that fluorines both α and β to a carbon centred radical may have a destabilising effect. Pasto and coworkers have performed calculations which have shown that successive substitution of hydrogen by fluorine on or adjacent to a carbon radical leads first to more stabilised radical, but with further substitution to a destabilised radical.[111] This has been confirmed experimentally, to some extent ,by the decomposition of *tert*-butoxy radicals fluorinated or trifluoromethylated at one carbon;[112] trifluoromethyl and 2,2,2-trifluoroethyl radicals forming a lot less readily than methyl radicals. Nevertheless, free radical addition to HFP does proceed, implying the destabilisation is negligible if there at all.

HFP does not homopolymerise, so it can be predicted that telomerisation will not occur, either for steric or electronic reasons. Instead, attack, in the form of hydrogen abstraction, occurs on the ether (**36**). This will be at the carbon adjacent to oxygen, which will tend to be more nucleophilic and where the most stable radical will form as already discussed.

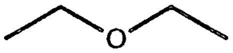
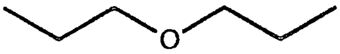
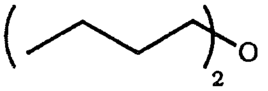
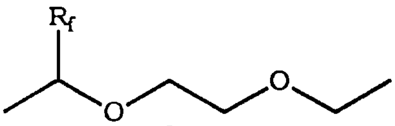
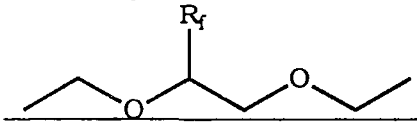
Table 3.1 reviews the additions of cyclic ethers to HFP reported, while table 3.2 summarises the additions of acyclic ethers and diethers. Some of the important results from these reactions are discussed in later sections of this chapter.

	Initiation method	Product	Yields, notes
	γ-rays	 (mainly)	16%[113]
	γ-rays		65%[114]
	γ-rays DBPO	 	Mixture ranging from 95%/0% to 5%/90% [113-117]
	γ-rays	 	31% and 64%,[118] combined 96%[114]
	DBPO		90%[116]
	γ-rays/ thermal (300°C)/ UV		95%[113]/ 10%[119]/ 82%[120]
	γ-rays/ UV		80%-90%[113,114]/ 95%[120]
	γ-rays		70%[113]

$R_f = CF_2CFHCF_3$

Addition of cyclic ethers to HFP

Table 3.1

Acyclic ether	Initiation method	Products, yields, notes
	γ-rays/ thermal (280°C)/ UV	Monoadduct (68%)[114]/ Monoadduct (10%)[119]/ Monoadduct (65%)[120]
	γ-rays	Mixture of monoadduct and diadduct ranging from 44%/56% to 35%/57% [114,117,121]
	γ-rays	Monoadduct (12%) and diadduct (28%)[114]
	γ-rays	Monoadduct (16%), diadduct (28%) and triadduct (26%)[114]
	γ-rays	Monoadduct, R_f at methyl (30%) R_f at ethylene (60%)[121]
	γ-rays TBPO	Monoadduct (62%) and diadduct (38%)[121]
	γ-rays	Diadduct (i.e., with two R_f groups in total) (21%)[121]
	γ-rays	Diadduct (2%)[121]

$R_f = CF_2CFHCF_3$

Addition of acyclic ethers to HFP

Table 3.2

3.2 Different Techniques of Initiation

An investigation into different methods of initiation was undertaken. Initiation involves the formation of a free radical in one of the substrates, starting the chain reaction. This can either be performed thermally or by irradiation, typically with UV, visible light or γ-rays, causing a very small number of the substrate molecules to undergo homolytic cleavage, scheme 3.4. Alternatively chemical initiation can be used, which involves some secondary material, an initiator, undergoing homolytic cleavage, scheme 3.5. The radical produced from the initiator reacts with the substrate to form the desired radical, as before. Oxidation and reduction processes, including those in electrochemical reactions, can also produce radicals. This is important in living systems, but is beyond the scope of this discussion.[105]

$$\text{X-Y} \rightarrow \text{X}^{\circ} + \text{Y}^{\circ}$$

Scheme 3.4

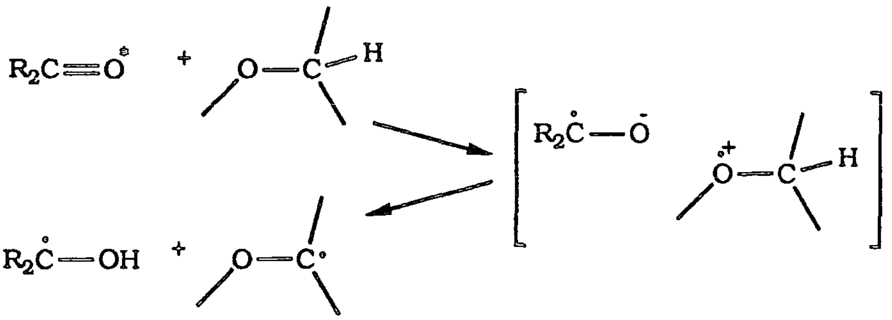
$$\begin{aligned} \text{a-b} &\rightarrow \text{a}^{\circ} + \text{b}^{\circ} \\ \text{a}^{\circ} + \text{X-Y} &\rightarrow \text{a-X} + \text{Y}^{\circ} \end{aligned}$$

Scheme 3.5

As can be seen from tables 3.1 and 3.2 the majority of work in this area has used γ–initiation. This has several advantages to it, the most important being the fact that it can be used over a wide temperature range[122])unlike peroxides which are resticted to a very narrow temperature band). Thermal initiation has not generally been used as at the sort of temperatures required to break a bond in these system the compounds are likely to decompose. It is only really suitable for substrates where a particularly weak bond is present. Peroxides (and other chemical initiatators) allow a similar initiation process at lower temperatures. Tables 3.1 and 3.2 show examples using *tert*-butyl peroxide (TBPO) and dibenzoyl peroxide (DBPO), which would be performed at about 140°C and 80°C respectively.[123] Peroxide initiation has a major advantage over γ–irradiation in that the facilities required are more generally available. However it is a lot less flexible, reaction temperatures are determined by the peroxide used, and the decomposition products of the peroxides will remain in the system. With a specific amount of peroxide in the system, the number of initiating radicals is necessarily finite

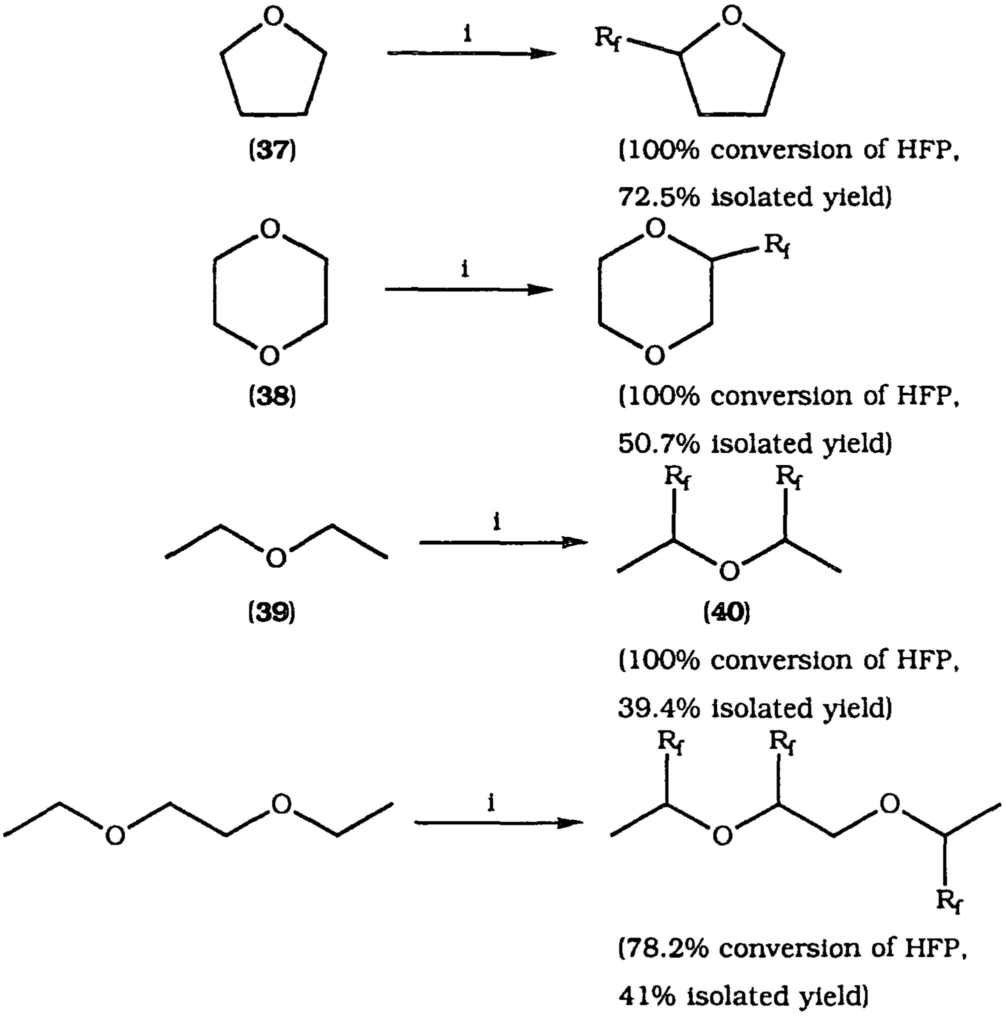
UV irradiation has been used infrequently in synthesis, despite its potential simplicity. UV initiated reactions have the advantages that they can be performed at a variety of temperatures, with commonly available equipment, to produce more energetic radicals (at the start of the reaction chain). There is also greater flexibility in the time scale of the reaction than is possible when using peroxides.

Other workers have studied hydrogen abstraction by triplet state benzophenone in amines,[124] reaction is believed to proceed through a charge transfer complex, as indicated in scheme 3.6. HFP, as well as most common organic compounds and materials, is soluble in acetone and it seemed reasonable to suppose that reactions could be performed using acetone as both a photosensitiser and solvent for most of the work in this project.



Scheme 3.6

A series of reactions was performed, therefore, using UV light for initiation, on some low molecular weight ethers, for comparison with other techniques, scheme 3.7. The ethers were selected as model compounds for DEPEG and, in the case of oxolane (37), PTHF. All reactions were irradiated for three days in acetone, from a medium pressure mercury lamp (1000W).High yielding reactions were observed in all cases.



(37) (100% conversion of HFP, 72.5% isolated yield)

(38) (100% conversion of HFP, 50.7% isolated yield)

(39) (40) (100% conversion of HFP, 39.4% isolated yield)

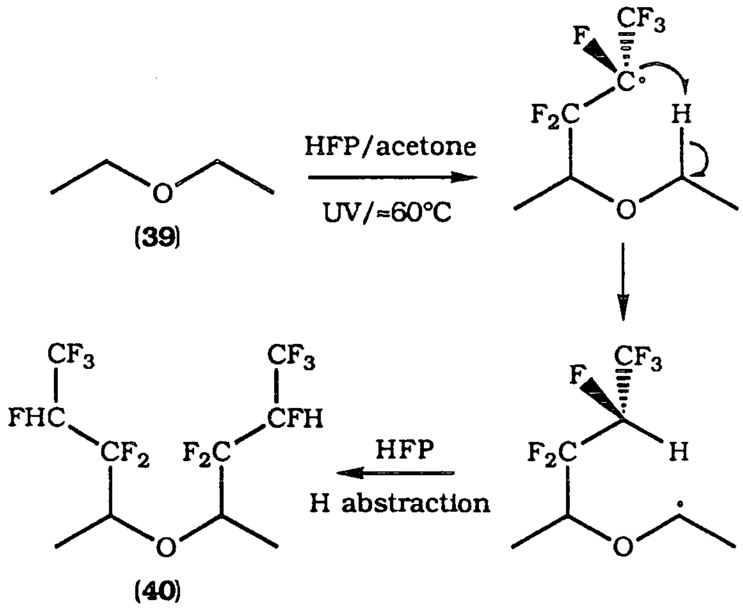
(78.2% conversion of HFP, 41% isolated yield)

$R_f = CF_2CFHCF_3$

i = HFP/acetone/UV/≈60°C

Scheme 3.7

The difference between conversion figures and yield figures is due to the presence of higher or lower adducts in the reaction mixture. In the diethyl ether (**39**) reaction the diadduct (**40**) predominates in the product mixture. This has been attributed to an intramolecular hydrogen abstraction process,[125] which is particularly favourable involving as it does a six-membered ring, scheme 3.8. This process is discussed more fully at the end of the chapter.



Scheme 3.8

UV light interacts a lot more readily with organic materials than γ-rays, the majority of which will pass straight through the reaction mixture. The number of radical chains started by peroxides is limited by the quantity of peroxide in the reaction mixture. The high yields of the UV reactions may thus be due in part to a greater flux of radicals. A second factor may be the temperature, higher than that at which γ-initiated reactions tend to be performed, improving the conversions, but not high enough to promote side reactions, such as decomposition. The radicals formed under UV irradiation will be of high energy, so another possible factor, in the early steps of the reaction chain, may be the higher energy of the radical., due to the initial high energy state promoted by the UV light. This energy will be dissipated fairly quickly, but may be associated with the radical centre for long enough to influence the reaction to some extent.

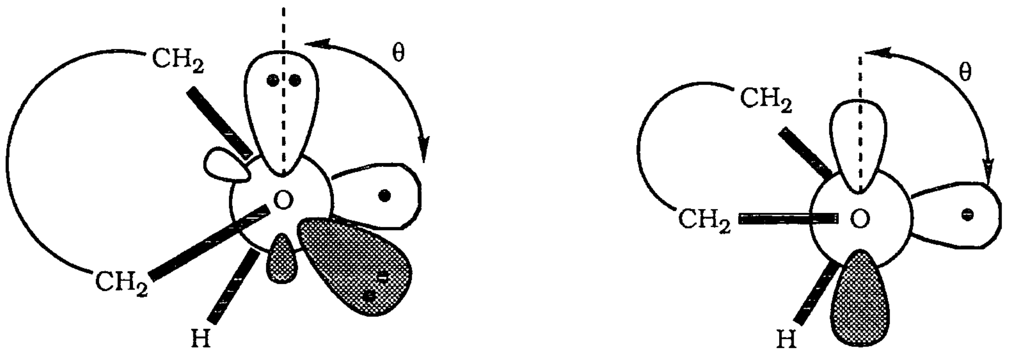
The use of acetone might actually stabilise the radicals, effectively solvating them, lowering their energy. Reaction chain lengths are increased and conversions improved. The use of acetone in peroxide and γ-initiated reactions is discussed in the next chapter.

3.3 Stabilisation of Radicals Adjacent to Oxygen

The degree of stability of a radical next to oxygen depends on a number of effects. A comparison of the reactivity of various cyclic ethers has shown the importance of molecular conformation.[113] A reactivity series was derived, supported by studies on the ease of hydrogen atom abstraction:[116]

Oxolane > Oxepane > Oxetane > Oxane

The ordering was explained by considering the geometry of the radical formed. A more stable radical will result if its conformation favours the donation of electron density from the oxygen lone pair to the radical centre. It has been shown that the oxygen lone pairs are inequivalent, their nature being intermediate between two sp^3-orbitals and one lone pair in an s-orbital, the other in a p-orbital, figure 3.3. As an approximation they are frequently assumed to resemble the former.



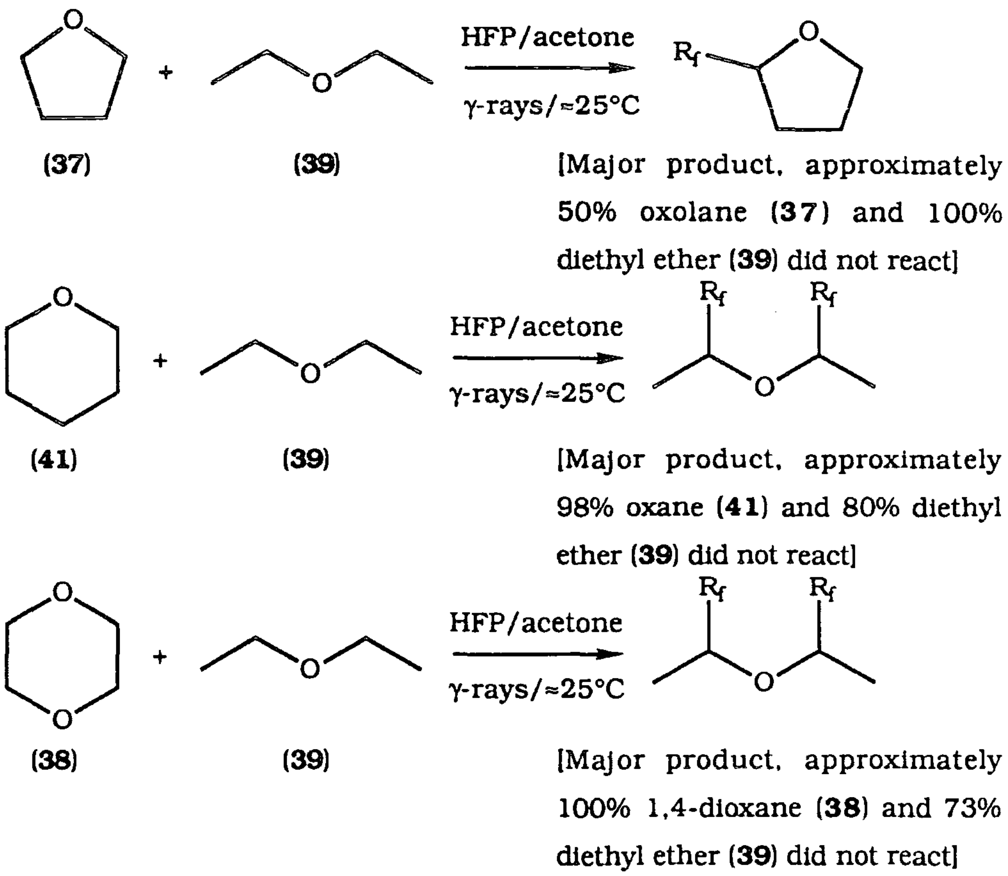
Two sp^3-type lone pairs

One p-type lone pair, one s-type (not shown)

Figure 3.3

For stabilisation to be maximised the dihedral angle, θ, between the lone pair and the abstracting hydrogen (*i.e.*, the hydrogen on the far right of each figure) must be decreased, to allow better overlap of a lone pair orbital of the oxygen and the SOMO of the radical centre. Thus radical formation is expedited in systems where the three carbon atoms and oxygen atom shown are approximately coplanar, such as is the case with oxolane.

An investigation was undertaken to compare the reactivity of cyclic and acyclic ethers. Competition reactions were carried out comparing an acyclic ether, diethyl ether (**39**), with some cyclic ethers, scheme 3.9. Equimolar amounts of the ethers were used, and an overall one sixth deficiency of HFP. γ-Initiation was used as the lower temperature would give greater selectivity.



(37) **(39)** [Major product, approximately 50% oxolane (**37**) and 100% diethyl ether (**39**) did not react]

(41) **(39)** [Major product, approximately 98% oxane (**41**) and 80% diethyl ether (**39**) did not react]

(38) **(39)** [Major product, approximately 100% 1,4-dioxane (**38**) and 73% diethyl ether (**39**) did not react]

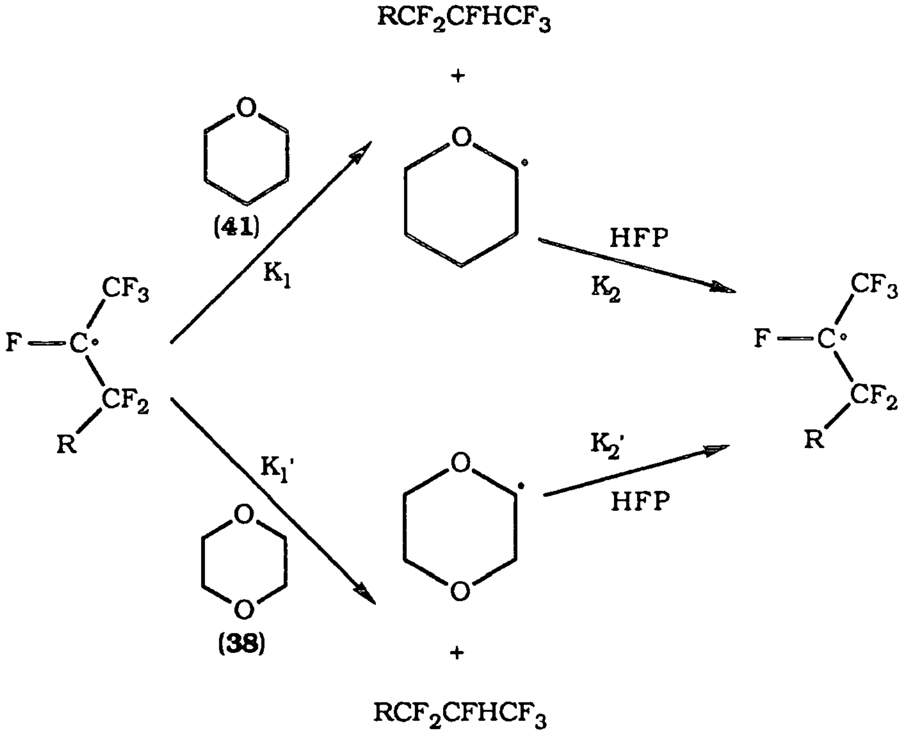
Scheme 3.9

It was established that diethyl ether (**39**) is more reactive than oxane (**41**) and 1,4-dioxane (**38**), less reactive than oxolane (**37**). This can also be rationalised using the diagrams of figure 3.3. In the diethyl ether system the ether is relatively free to form any conformation, *i.e.*, θ can vary freely. It is not held in a beneficial conformation, so is less reactive than oxolane, but is more free to enter that conformation so is more reactive than oxane and 1,4-dioxane. As will be discussed in the next section, the lower reactivity of 1,4-dioxane may also be due to the presence of the second oxygen.

3.4 Additions through Multiple Oxygen Stabilised Radical Centres

Additions of ethers containing more than one oxygen to HFP occur less readily than additions of similar monoethers.[118] This will clearly be important in the polymeric systems discussed at the beginning of the chapter. Competition reactions between 1,4-dioxane and oxane show oxane to be more reactive. Also experiments have been performed looking at the ease of abstraction of hydrogen atoms from ethers by two groups, using the decomposition of the *tert*-butoxy radical as a 'radical clock,' which support these findings.[113,126]

The case of a competition reaction between oxane (**41**) and 1,4-dioxane (**38**) is illustrated in scheme 3.10. With an appreciable amount of HFP present it can be assumed that all oxanyl and 1,4-dioxanyl radicals react, so K_2 and K_2' are not important.



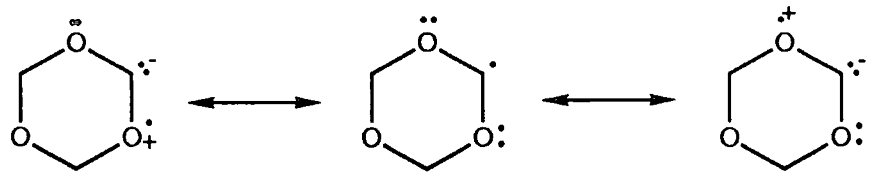
R = oxanyl or 1,4-dioxanyl

Scheme 3.10

The competing processes are K_1 and K_1'. While the degree of stabilisation is likely to be greater for 1,4-dioxane, nevertheless it is oxane which reacts preferentially. Thus the reactivity can only be attributed to electronic effects, the site on 1,4-dioxane is significantly less nucleophilic than that on oxane due to the electron withdrawing effect of the second oxygen.

3.41 The addition of 1,3,5-trioxane

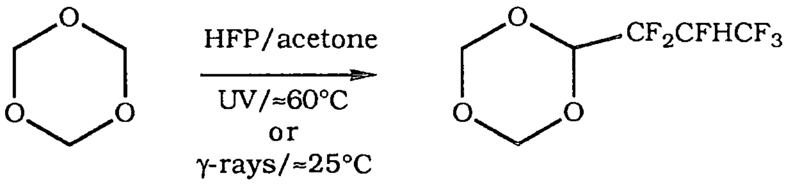
Attempted reactions with 1,3,5-trioxane (**42**) have in the past failed.[113] The behavior of 1,3,5-trioxane may be accounted for in either of two ways. It may be that the radical which forms on the 1,3,5-trioxane is particularly stable, with lone pair donation possible from two adjacent oxygens as indicated in figure 3.4, or the electron withdrawal may be so great as to effectively deactivate the substrate towards hydrogen abstraction.



(42)

Figure 3.4

Nevertheless, it was thought that the use of UV initiation would facilitate the reaction between 1,3,5-trioxane and HFP. It was thought that by using a greater flux of radicals, initially of higher energy, coupled with a higher reaction temperature, reasonable yields could be obtained. As a comparison, a second reaction was also performed, using γ-initiation over an extended time period, 29 days, scheme 3.11. Table 3.3 summarises the results.



(42)

Scheme 3.11

Initiation method	Duration/d	Equivalents of HFP reacted
γ-rays	29	0.4
UV	3	1.1

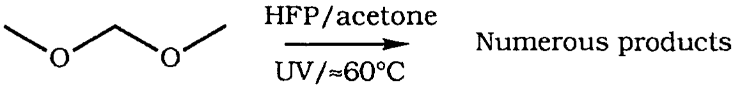
Addition of 1,3,5-trioxane (**42**) to HFP in acetone

Table 3.3

The γ-initiated reaction shows just how unreactive 1,3,5-trioxane is, four days would be a more usual irradiation period. The second reaction illustrates the scope of UV initiation, a greatly reduced reaction time, and a much higher degree of incorporation of HFP. It seems unlikely that this wide difference in reaction can simply be due to the quantity of radicals formed; it can be assumed that over 29 days of irradiation a large number of radicals are certain to form. For a difference in temperature of 35° to have such a dramatic effect is doubtful. This leads to the conclusion that the high energy state of the radical in the UV initiated reactions is responsible for the enhanced reaction, and that this energy is being transferred along the reaction chain. This would necessarily imply a very short reaction chain length as the energy will, of course, soon be dissipated.

3.42 The addition of dimethoxy methane

The addition of dimethoxy methane (**43**) was also attempted. The presence of only two oxygens in this system will have a less detrimental effect on the reaction, and this is substantiated by studies on hydrogen abstraction by butoxy radicals.[113,127]



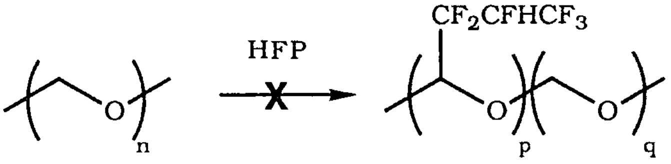
(43)

Scheme 3.12

Upon work up GLC analysis of the volatile components (the bulk of the products) showed the presence of a great number of products (in excess of 25). It has been reported that dimethoxy methane can decompose after hydrogen abstraction,[128] to give formaldehyde, methyl formate and methyl radicals. The methyl radicals may attack HFP, the formaldehyde may polymerise and any of these products may have HFP incorporated. It can be seen that several products can result, and further analysis was not attempted.

3.43 The attempted addition of para-*formaldehyde*

Given the success of reacting HFP with 1,3,5-trioxane (**42**), it was hoped that *para*-formaldehyde (**44**) would also undergo free radical addition to HFP. The decomposion of dimethoxy methane (**43**) under these conditions was mainly from the terminal groups,[128] resulting principally in volatile components. It was hoped that all such materials could be removed under vacuum to leave the bulk of the polymer still intact, with the polyfluoroalkyl groups attached. Having a single, simple repeating unit, it was envisaged that the product (**45**) would be fairly simple in composition, as is suggested in scheme 3.13. Two attempts were made, in acetone and trifluoroethanol respectively, without success. This can almost certainly be attributed to the insolubility of the polyether in either solvent, the previous two experiments would certainly insubstantiate any other rationale. No other suitable solvent was identified.



(44) **(45)**

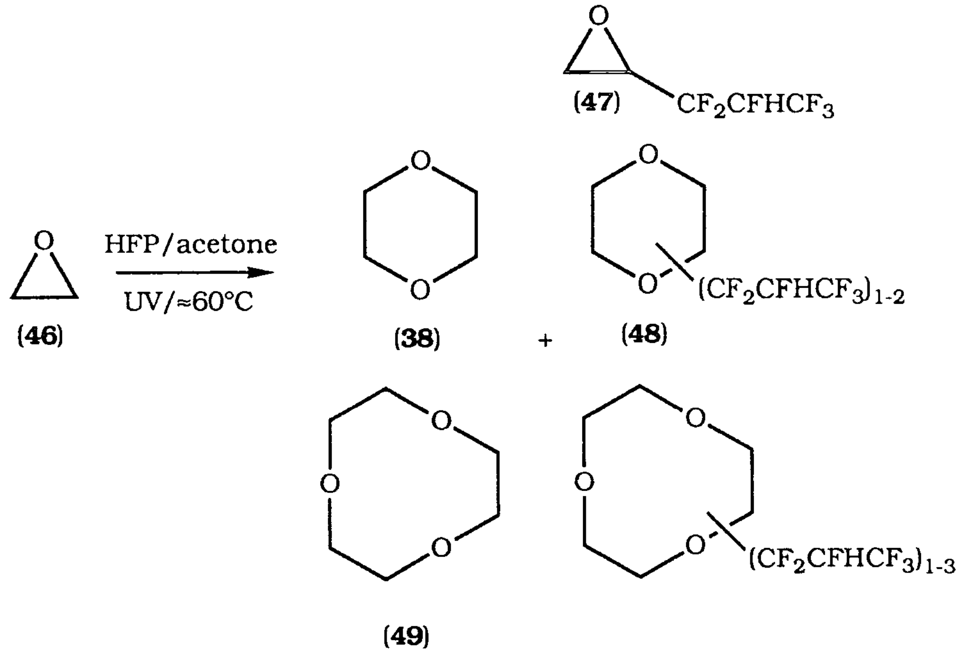
Scheme 3.13

3.5 Additions to Strained Rings

Previously the addition of HFP to oxirane (**46**) has been reported as unsuccessful; instead of the simple addition product forming, the substrate ring-opened and dimerised, and also added to HFP to give (2*H*-hexafluoropropyl)-1,4-dioxane. The reasons for this process are clearly the release of ring strain. The addition of oxetane to HFP has however been reported in good yield. A comparison of these two reactions, performed under UV conditions, was believed worthwhile.

3.51 The attempted addition of oxirane

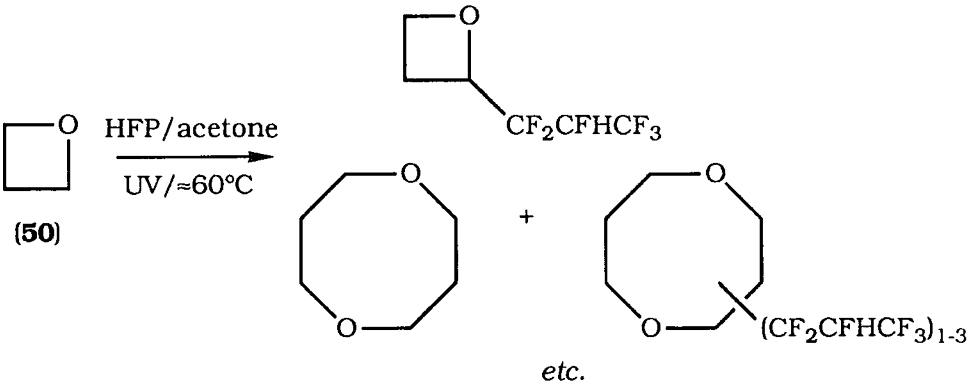
Analysis of the resultant mixture from the reaction between oxirane (**46**) and HFP showed the presence of many products. GLC/MS analysis of the volatile components showed the presence of some 1:1 adduct (**47**), 1,4-dioxane (**38**) (*i.e.*, the dimer of oxirane), the mono- and di-adducts of 1,4-dioxane (**48**) and 9-crown-3 (**49**) (the trimer of oxirane), all in fairly low overall yield (no product greater than 10%), scheme 3.14. NMR analysis of the involatile residue suggested that this was composed of higher oligomers of oxirane, with varying amounts of HFP incorporated. The overall conversion of HFP was high (≈100%), but this was not surprising when the high conversion in the reaction of 1,4-dioxane is considered.



Scheme 3.14

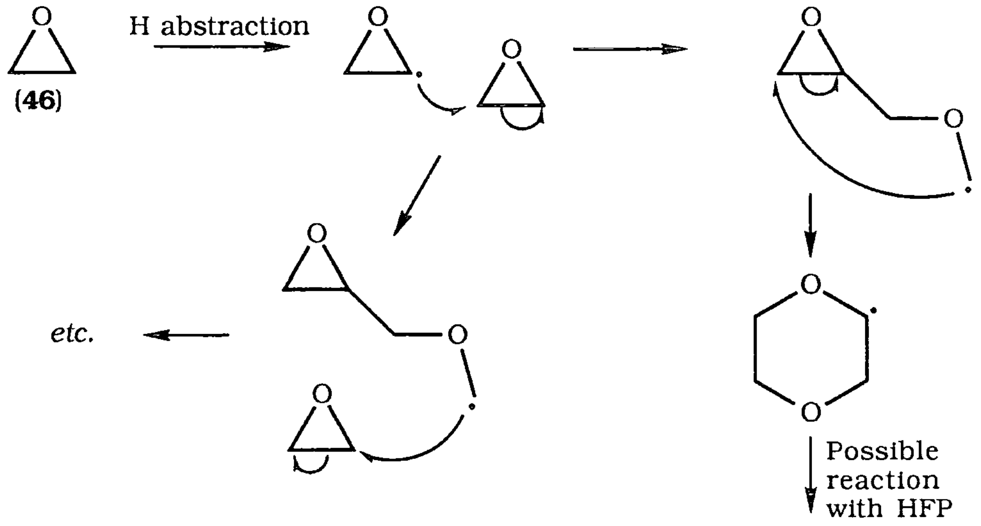
3.52 The attempted addition of oxetane

The reaction between oxetane (**50**)and HFP behaved similarly, GLC/MS of the volatile components showed an analogous mixture of dimers and trimers, with numbers of fluoroalkyl groups attached, scheme 3.15.



Scheme 3.15

The same reaction performed with γ-irradiation had a reported 65% yield.[118] It is believed that a similar ring opening process was occurring in both these reactions, facilitated by ring strain. This was enhanced by the higher temperatures at which the reactions were performed. Neither ethers are chromophores, and so direct interaction with the UV light is not possible. A more likely rational is the free radical, ring opening polymerization of scheme 3.16. A similar process can be envisaged for oxetane. This is supported by competition reactions, which have shown oxetane to be more reactive than oxane (*i.e.*, easier to abstract a hydrogen from).



Scheme 3.16

3.8 Characterisation of Model Compounds

Materials that result from the addition of polyethers to HFP are a complex mixture of isomeric compounds, which figure 3.5 only hints at. Inevitably, they will vary to some degree in the length of the polymer backbone (*i.e.*, the value of p plus q), more significantly in the number of fluoroalkyl groups (p plus 2) and the distribution of those groups. NMR presented itself as the most suitable technique for the determination of these factors. A study on the low molecular weight compounds was therefore undertaken.

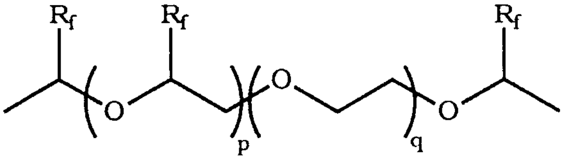
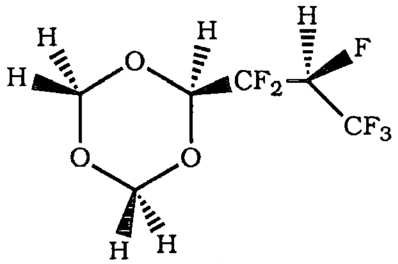


Figure 3.5

The addition of an ether to HFP generally leads to the formation of two new chiral centres. The simple monoaddition product will usually therefore comprise two additional diastereoisomers.[116] Although most resonances of many of the simple adducts of ethers to HFP have already been established, most of the resonances of specific diasteromers have never been assigned, and only a few larger coupling constants have been determined. Using high field NMR (400 and 500 Hz) it was hoped that a far higher degree of analysis could be obtained.

3.81 The monoadduct of 1,3,5-trioxane to HFP

The product of the reaction of 1,3,5-trioxane and HFP (**51**), figure 3.6, is unusual in that only one chiral centre is present, and so no diastereoisomers form (though of course two enantiomers form). With only one set of resonances, the splitting patterns could more easily be interpreted, and once these were understood similar patterns in other adducts could be identified, primarily those associated with the the 2*H*-hexafluoropropyl side group.

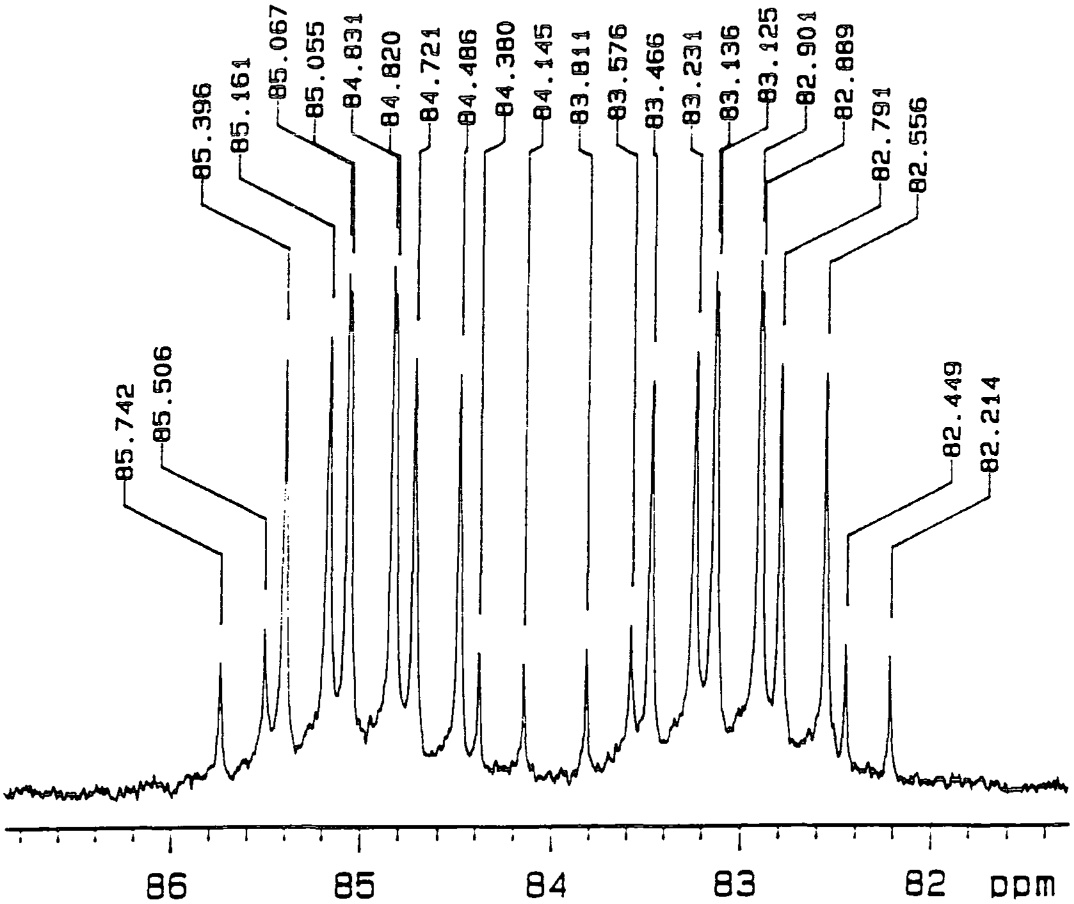


(51)

Figure 3.6

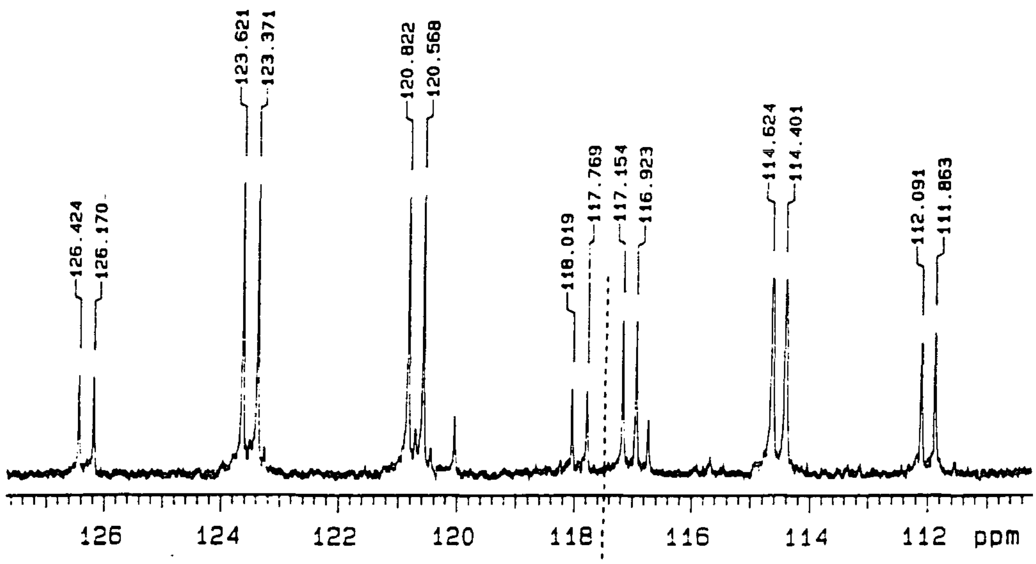
A look at the broad band proton decoupled carbon spectrum of (2*H*-hexafluoropropyl)-1,3,5-trioxane shows several interesting splitting patterns, the most impressive being at about 84 ppm, due to the CFH carbon, figure 3.7. A large $^{1}J_{CF}$ coupling of 194.2 Hz is due to the adjacent fluorine, splitting the peaks into two groups. The other five fluorines cause a doublet of quartet of doublets, all the coupling constants being around 30 Hz. The CF_3 fluorines are all equivalent and so cause the quartet. The other two fluorines are not equivalent, being diastereotopic, and in the ^{19}F spectrum can be seen as two distinct resonances.

Between 111 and 127 ppm the peaks due to the other carbons in the side chain can be seen, figure 3.8. Centred at about 122 ppm is the CF_3 carbon resonance, a quartet due to the three attached fluorines, further split as a doublet by the CFH fluorine. The resonances centred at approximately 114 ppm arise from the CF_2 carbon resonance. As has already been stated, the two fluorines are inequivalent, and so the pattern here is an overlapping doublet of doublets, with very similar coupling constants. Again this is further split by the CFH fluorine.



13C NMR spectrum, CHF carbon

Figure 3.7



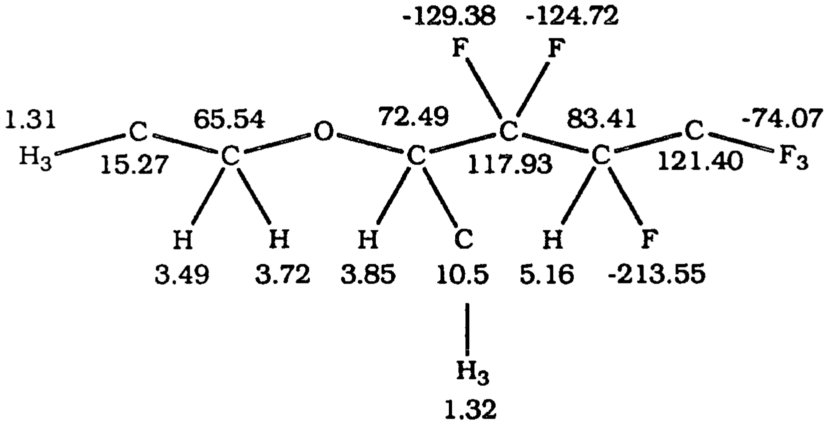
^{13}C NMR spectrum, CF_3 (left of dotted line) and CF_2 (right) carbons

Figure 3.8

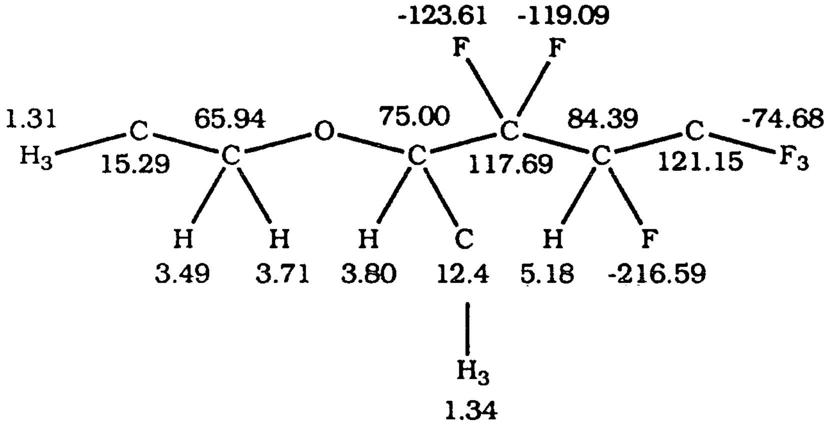
Two peaks at 94 ppm show that the two methylenes are not equivalent, being diastereotopic, and this is further seen in the ^{1}H spectrum, which shows two AB systems around 5.3.

3.82 The monoadduct of diethyl ether to HFP

Determination of which peak resulted from which diasteroisomer could readily be done by comparing the integrations of both signals in the ^{13}C and ^{19}F spectra, though there was too much overlap in the ^{1}H spectrum to allow unambiguous assignments. It was necessary, therefore, to employ other techniques. A 2D $^{1}H^{13}C$ HETCOR spectrum was run, appendix 2.1 and 2.2, correlating ^{13}C resonances to proton resonances, allowing identification of the latter. Resonances were completely assigned, as indicated in figure 3.9.



Major isomer



Minor isomer

NMR data for proton, carbon and fluorine nuclei

Numbers refer to the chemical shift of the associated nuclei in ppm

Figure 3.9

Coupling constants could be assigned and correlated for most ^{1}H and ^{13}C resonances, and some ^{19}F resonances, partly based on the patterns seen in the (2*H*-hexafluoropropyl)-1,3,5-trioxane spectra. The complete set of results are presented in tabular form in appendix 1.

The imbalance in the proportion of isomers, which allowed the full assignment of resonances is surprisingly large, about 43:57, and this is typical of all the monoadducts which exhibit diastereoisomerism. There is clearly some degree of stereo control at the hydrogen abstraction step.

Much work has been performed attempting to show that radicals can maintain their stereo chemistry in certain cases,[129] but in general, and especially at the temperatures at which these reactions were performed, this is very unlikely to be the case, rather the radical will be a rapidly inverting tetrahedral conformation or planar.

Rather, it must be the effect of the first chiral centre, making attack from one direction preferable over another. What is surprising is the size of the effect, when the distance of the chiral centre from the radical is considered.

Courtieu *et al.* have looked in detail at the adduct of oxolane to HFP.[116] Looking at the coupling constants they claim to have established which is the RS or SR isomer, and which is the RR or SS isomer. Assuming that the resonances in the side chain follow a similar pattern in all the simple diastereoisomeric monoadducts (and inspection of the spectra supports this supposition), the major isomer can thus be tentively attributed to an RS or SR configuration, the minor isomer to the RR or SS.

3.83 The monoadduct of 1,4-dioxane to HFP

Resonances from nuclei on the 2*H*-hexafluoropropyl side chain were similar to those of the diethyl ether adduct, and could easily be assigned. The resonances of the carbons on the ring could also mostly be attributed. However, in this and many other adducts with cyclic ethers all the protons are inequivalent. This causes some very complex coupling in the ^{1}H spectra, and as most signals occurred at around 0.3 ppm the spectrum was decidely complicated.

In an attempt to assign these peaks with any certainty, 2D^{13}C^{1}H HETCOR and COSY NMR spectra were used, see appendix 2.3 and 2.4.

The seven peaks which lie between 70 and 76 ppm in the ^{13}C spectrum can be assigned to the carbon and proton adjacent to the fluoroalkyl group. Notice that this signal is split, firstly because there are the two isomers, but further due to fluorine splitting from the adjacent fluoroalkyl group.

Going left across the spectrum, the next set of peaks is at 66.9 ppm on the carbon axis. This relates to one of the two sets of carbon and two protons at either the 5- or 6-position on the ring. One proton gives a signal at 3.84 ppm, the other gives two signals, one for each isomer, at 3.72 and 3.76 ppm and these can be matched with the carbon resonances at 66.91 and 66.94 ppm respectively. The next grouping at 66.1 ppm on the carbon axis will be due to the carbon and protons at other position. In this case no differences are observed between the two diastereo-isomers, implying it is further removed from the chiral centres, suggesting that this is at the 5-position. The protons resonate at 3.70 and 3.61 ppm.

Finally the carbon and protons at the 3-position are seen. The nucleii are sufficiently close to a chiral centre to show major splitting, giving pairs of peaks at 64.3 and 63.6 ppm. The two peaks connected with each carbon is due to the two protons on each, one *cis*- and one *trans*- to the polyfluoroalkyl group.

Assignment of protons around one carbon could be performed, to some extent, by examination of a COSY spectrum. By looking at the magnitude of the peaks off the diagonal an idea can, to some extent, be obtained of the magnitude of the splitting between the concerned nucleii. It must be noted, however, that other factors can be significant and the following assignments can only be regarded as tentative. By considering the dihedral angle between protons and the likely splitting therefore arising it is probable that the peaks at 3.61 ppm and 3.73 ppm are due to protons lying on the same side of the molecule. Further it seems probable that the proton giving a peak at 3.67 ppm lies on the same side of the molecule as the fluoroalkyl group.

This allowed an almost complete assignment of peaks, the only ambiguity being the arrangement of protons in the 5- and 6-position, which lie *cis*- and which lie *trans*- to the fluoroalkyl group.

3.84 The diadduct of diethyl ether to HFP

The introduction of four chiral centres in the diethyl ether system gives rise to a total of 10 stereoisomers (a plane of symmetry causes there to be less than 16), including 4 pairs of enantiomers. In the NMR spectra we will see 6 different sets of resonances therefore. Of these six isomers 2 will have a σ-plane (RRRR* and RSSR) and two an inversion centre (RSRS and RRSS), so the halves of each molecule will be magnetically equivalent. The remaining two (RRRS and RSRR) will gives two sets of resonances, one from each half of the molecule. Overall eight distinct sets of resonances should be observed.

---

* NOTE: Configuations are given in the order; CHF of the first alkyl group, CHR$_f$ of the first fluoroalkyl group, CHR$_f$ of the second fluoroalkyl group, CHF of the second alkyl group, and are not therefore in the order in which they form. Only those isomers starting R are mentioned, obviously those starting with an S configuration will also be present as enantiomers and so identical to NMR spectroscopy.

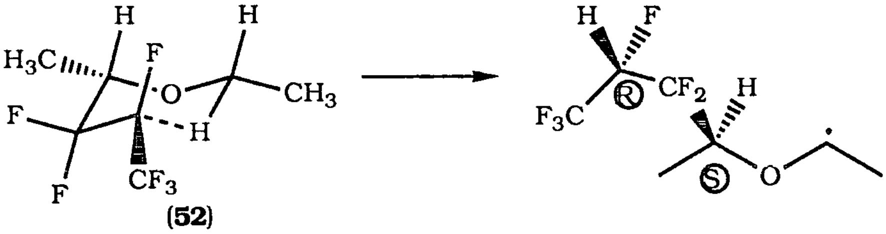
In the ^{19}F spectrum these eight sets of resonances are clearest in the CF_2 region (see appendix, 2.5). Eight distinct AB systems can be identified and matched with each other with the aid of a ^{19}F COSY spectrum (see appendix, 2.6). These AB systems fall into two groups, four sets in each, one group arising from isomers with RS configurations in that half of the molecule, one from RR configurations. Small variations in chemical shifts arose from chiral centres further away. This allowed the proportion of each isomer to be gauged, leading to some conclusions on the stereochemistry of diadduct formation. It was observed that these proportions vary to a major extent, implying that already formed chiral centres are having a major influence on the formation of new ones.

In the ^{13}C spectrum, the carbon nucleii orginating from the ethyl ether molecule also could be readily resolved, and the size of each isomer similarly measured. These data appear in table 3.4, at the end of this section.

So what are the factors that influence one isomer forming over another? The chiral centres of a diadduct will form in four steps:

(a) As both diethyl ether and HFP are achiral the first step, the ether derived radical attacking HFP, will form two enantiomers in exactly equal proportions.

(b) Secondly, the radical on the hexafluoropropyl chain intramolecularly abstracts hydrogen. Looking at the transition states for this process, scheme 3.17, shows how the stereo chemistry of the first chiral centre may influence the formation of the new one.



Scheme 3.17

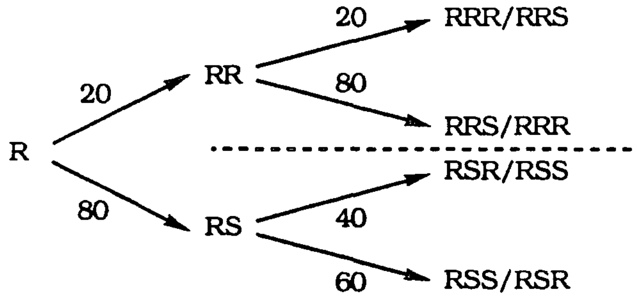
The most favoured process will involve a six membered ring transition state (**52**) where the two methyl groups and the trifluoromethyl group are equatorial. An S configuration at the original chiral centre will tend to give an R configuration at the new site and *vice versa*. In the CF_2 region of the ^{19}F NMR spectrum the proportion of peaks on the up field side was 67% of the total, instead of 57% in the monadduct. On the basis of the previous argument these resonances would be due to the RS isomers, while the RR isomers lie down field. This agrees with the finding of Courtieu *et al.* (see earlier).[116]

(c) The third chiral centre forms when the 1-(2,2,3,4,4,4-hexafluoro-1-methylbutoxy)ethyl radical attacks HFP. Here again NMR suggests that the previously formed chiral centres influence the formation of the new one to some extent, though not as great. What influences the stereochemistry is unclear. It may be that the radical formed at step (b) is so reactive that addition to the second HFP occurs virtually straight away, and the stereochemistry is determined by conformation of step (b). Such processes, where the stereochemistry at a radical centre is maintained, have been proposed,[129] though the arguments have never been that convincing. One point in favour of this theory is the reactivity of the radical - as is shown by the very low reactivity of the monoadduct to further addition. Alternatively, there may be some constraint imposed on the structure of radical, leading to one stereochemistry over another, though as to what this might be can only be speculated.

(d) The final chiral centre forms when the second hydrogen abstraction occurs. This step will be more or less identical to the intermolecular hydrogen abstraction step observed in mono-adduct formation, with only minimal influence from the further removed chiral centres. The proportion of isomers can therefore be predicted as being about the same, approximately 43:57.

A look at the exact ratios of the isomers can give an idea of how much stereo control there is. The RSRR+RRSR and RRRS+RSSS isomers will occur in both halves of the spectrum and can be matched to each other. The RRRR and RRSS isomers can then be identified together (the remainder of down field peaks), and similarly the RSRS and RSSR isomers (the remainder of up field peaks). Comparing the size of these peaks gives the probability of one isomer forming over another as the third chiral centre forms, when the ether derived radical attacks the second HFP molecule. Comparing the RRRR and RRSS resonances with the RSRS and RSSR resonances gives information for the formation of the second chiral centre, the intramolecular hydrogen abstraction.

This led to the conclusion that at the formation of the second chiral centre, in the diadduct reaction, the probability of an RS or SR configuration forming is 80%. Given an RS or SR configuration, at the next step there is a 60% chance of one configuration forming over another. Otherwise, with RR or SS configuaration already present, the ratio at the next step is 20:80. This is summarised in figure 3.10.



Degree of stereocontrol at the formation of the second and third chiral centres

Figure 3.10

Assignment of resonances to the eight isomers was therefore possible, with only limited ambiguity in the CF_2 region of the ^{19}F spectrum and the CH_3 and CHR_f of the ^{13}C spectrum, as shown in table 3.4. Calculated values for the proportions of each isomer are also given, for reference only.

	^{13}C				^{19}F		
Assignment	CH_3		CHR_f		CF_2		Calc.
	Shift/ ppm	Integration	Shift/ ppm	Integration	Shift/ ppm	Integration	
RSSR/ RSRS	9.5	25.4%	70.0	24.5%	-129.20 -124.28	32.1%	27%
RRRS/ RRSR	10.3	13.8%	72.8	16.0%	-128.00 -123.88	12.0%	15%
RRSR/ RRRS	11.8	10.7%	73.9	24%	-128.61 -123.68	4.0%	8%
RSRS/ RSSR	12.4	17.8%	74.3		-126.59 -123.19	19.6%	18%
RRRS/ RRSR	12.2	13.8%	72.8	15%	-123.62 -117.94	15.1%	15%
RRRR/ RRSS	13.3	6.3%	75.0	9%	-123.12 -119.24	6.3%	7%
RRSS/ RRRR	14.2	1.8%	75.8	1.9%	-123.10 -118.15	3.2%	2%
RRSR/ RRRS	15.0	10.3%	76.6	9.8%	-122.39 -119.04	7.7%	8%

Ratio of isomers from NMR integrations of di(2,2,3,4,4,4-hexafluoro-1-methylbutyl) ether

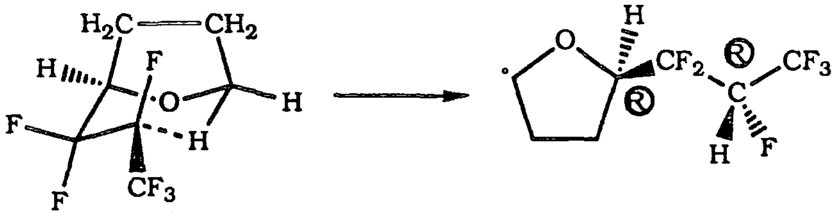
Table 3.4

The addition of diethyl ether to HFP was also performed under γ-irradiation to afford the diadduct, with a view to establishing the temperature dependance of the stereo control (the reaction being performed at about 25°C, rather than 60°C). Integration of the relevant peaks showed no significant variation in the proportion of isomers.

3.85 The diadduct of oxolane to HFP

In additions to cyclic ethers, intermolecular hydrogen abstraction becomes more likely as the alternative six membered ring transition state for intramolecular hydrogen abstraction is distorted. However, diadducts do form, and the very low reactivity of the monoadducts[113] implies that here too, intramolecular hydrogen abstraction is the primary mechanism.

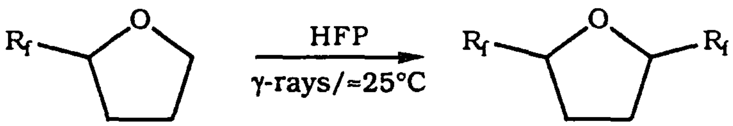
The ^{19}F NMR spectrum of 2,5-di(2*H*-hexfluoropropyl)oxolane (55) was studied. Again, six magnetically inequivalent stereoisomers are possible for the diadduct. As before the first step is trivial but the second step of an intramolecular process with the six-membered ring, is shown in scheme 3.18.



(53)

Scheme 3.18

In this transition state (53) the oxolane ring constrains the six membered ring so that the methylenes are axial only, forcing the bulky trifluoromethyl group to adopt an equatorial conformation. In this case, then, an R configuration at the first chiral centre will generally lead to an R configuration at the new site (i.e., the reverse of the trend seen in diethyl ether), and it would be predicted that these isomers will be far in excess of the others. However this sort of imbalance, between RR+SS and RS+SR configurations in the side chain, is not seen. Instead the proportion of RR+SS to RS+SR is virtually identical to that in the monoadduct, 47% in both cases. It can therefore be said with some confidence that *hydrogen abstraction in the diadduct is almost entirely intermolecular.* To confirm the possibility of a step-wise mechanism HFP was reacted with (2*H*-hexfluoropropyl)oxolane (54) under γ-irradiation, scheme 3.19.



(54) $R_f = CF_2CFHCF_3$ (55)

[55% conversion of (2*H*-hexfluoropropyl)oxolane]

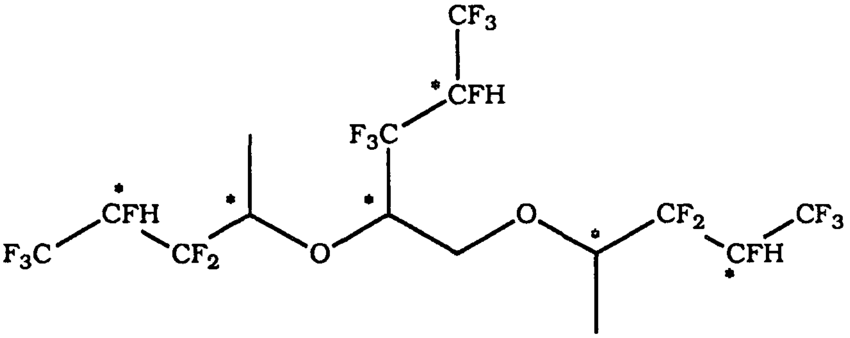
Scheme 3.19

However, there is a sizable variation in the proportions of the isomers, and this can only be due to the stereo control as the third chiral centre forms. Unlike the diethyl ether case, the fluoroalkyl group, R_f, is held in the one position which presumably accounts for the far greater stereo control in this step. Whether the radical is tetrahedral or planar, *trans*-attack will occur preferencially, leading to RR or SS configurations of the chiral centres on the ring. NMR suggests that approximately 75% of the molecules are of this configuration. The fourth chiral centre will form as before.

Unlike the case for diethyl ether, assignment of configuration of the isomers is mostly not possible. However, it can be assumed that the RR isomer halves will be seen in approximately the same region as in the diethyl ether, and similarly the RS isomer halves (similarities between the spectra of the monoadducts justifies this assumption). Also the RRRS and RRSR isomers can be identified from the rest (though not from each other) as they will have resonances in both regions. Each signal can therefore be assigned to one of two possible configurations (see appendix).

3.86 The triadduct of 1,2-diethoxy ethane to HFP

In this triadduct (**56**) there are 6 chiral centres, and no symmetry. 64 isomers will therefore result, 32 pairs of enantiomers. Furthermore, in each isomer there will be three CF_3, CFH, CF_2 and CHR_f environments in each. A total of 96 magnetically different sets of resonances will be seen. With this in mind, it must be accepted that the degree of elucidation possible will be significantly reduced.



(**56**)

Figure 3.11

The CF_3 carbons and fluorines will, perhaps, be best resolved as they will tend to be quite similar. Six groups of isomers would be expected, due to CF_3 environments on each of the three side chains, each having an RS or SR configuration or RR or SS configuration (further chiral centres having minimal effect on the chemical shifts). In the ^{19}F spectrum four groups are found, two particularly large, each presumably due to two overlapping groups. The resolution in the ^{13}C spectra is sufficiently good to.identify five quartets of doublets, the sixth hidden beneath one of these.

Looking further at the ^{19}F spectrum, the CFH fluorine is seen as a collection of broad peaks between -210.5 and -215.0. No further analsis was possible. Between -120 and -136 are potentially 96 AB systems, due to the CF_2 fluorines. These fell in three groups: -120.7 to -125.4 ppm, the downfield fluorine of an RR or SS configuration side group; -125.4 to -129.8 ppm, the upfield fluorine, overlapping with the downfield fluorine of an RS or SR sidegroup; -129.8 to -135.2 ppm, the upfield fluorine of the latter. Resolution within these groups was not possible due to the number of peaks present.

Integration of the CF_2 region of the ^{19}F spectrum showed the ratio of RS and SR side chains to RR and SS to be about 52.5:47.5. This compares with 59:41 in the monoadduct, and suggests that rather than an intramolecular hydrogen abstraction process leading to greater stereocontrol, there is actually less. However, the addition of a fluoroalkyl group to the middle of the polyether is an unknown quantity, and it is possible that the reverse effect is seen; RR and SS configurations favoured over RS and SR. It does seem likely, though, that intramolecular hydrogen abstraction is a lot less common in this system than in the diethyl ether case.

In the ^{13}C spectrum triplets appear at around 118.5 ppm. These are seen as two reasonably well defined sets, each further split into doublets (as in the simpler adducts). The CFH carbon is seen as a doublet of multiplets at 84 ppm. Between 70 and 80 ppm are the CHR_f carbons, three broad multiplets at 74.5, 76.5 and 78.0, and two overlapping doublet of doublets at 70.5. With a variation of 3 ppm between the RS and RR isomers of the monoadduct, assignment of the multiplets is not possible. However, by comparison with the diethyl ether monoadduct, it is likely that the peaks at 70.5 are due to an RSSR or SRRS configuration of adjacent side groups, figure 3.12, not quite identical as one is next to a methyl one next to $-CH_2OR$ (chirality of R is assumed to be having a minimal effect).

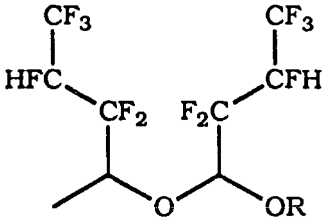


Figure 3.12

The methylene carbons occur as a series of peaks between 67 and 70 ppm. The methyl peaks, between 10 and 16 ppm, were numerous. By comparison with the monoadduct of 1,2-diethoxy ethane, the peaks at 11.3 and at 12.7 or 13.4 ppm can be tentatively assigned to the $CH_3CHR_fOCH_2$- methyl, RS and RR configurations respectively. The other methyls, closer to further chiral centres, make up the numerous smaller peaks, similar to those seen in the diethyl ether diadduct.

The 1H spectrum showed the methyls at 1.4 ppm, the CFH protons at 5.0 ppm (too broad to see as a doublet) and the rest at 3.5 to 4.4 ppm, irresolvable.

3.87 Conclusions

Although the monoadducts are relatively straight forward to interpret, it can readily be seen that the complexity of the spectra increases dramatically with the addition of further fluoroalkyl groups. Nevertheless, information can be derived from these more complex spectra, leading to interesting conclusions about the addition process.

Comparing formation of the diadducts of diethyl ether and oxolane two different mechanisms are observed. Reaction with diethyl ether goes more or less exclusively intramolecularly, where the six membered ring transition state is particularly favoured. However, reaction with oxolane proceeds though an intermolecular step-wise process. Here, diadduct formation is only possible because the oxolane ring allows a relatively stable 5-(2*H*-hexfluoropropyl)oxolanyl radical (compared with other radicals with 2*H*-hexfluoropropyl groups attached). While preventing intramolecular hydrogen abstraction, the ring promotes diadduct formation through an intermolecular process.

Can the stereochemistry of the monoadducts be similarly explained? The imbalance in the diastereoisomers observed with the acyclic ethers may party be due to an intramolecular process identical to (b) earlier. A small, but significant proportion of these resultant radicals undergo *inter*molecular hydrogen abstraction from a second diethyl ether molecular, rather than attack at HFP, giving monoadduct; the same stereocontrol will apply as in the diadduct. This cannot be the mechanism of formation for the majority of the monoadduct - otherwise the selectivity would be greater than that of the diadduct - but it may account for the greater stereocontrol in the diethyl ether monoadduct, compared with the oxolane monoadduct. Also, if the intramolecular process is all but impossible for the oxolane system, there must be some other form of stereocontrol, and it would seem likely that this would apply to the other ethers too.

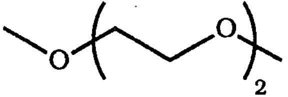
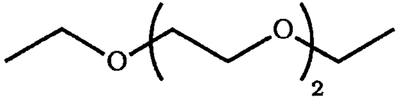
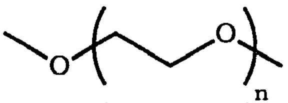
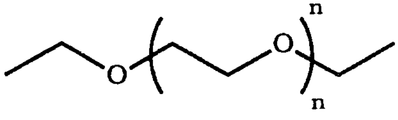
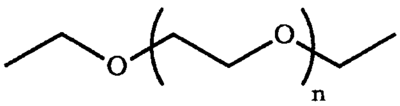
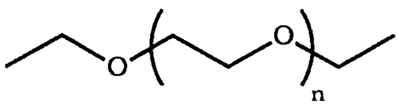
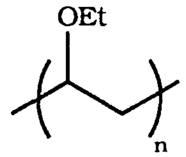
This has certain implications for additions to polyethers. Presumably they will behave similar to diethyl ether, and most of the HFP addition will occur in a step-wise, intramolecular process. It would also seem likely that, once a polyadduct has been made, further addition of HFP will become somewhat more difficult, without the radical-stabilising influences of a five membered ring.

CHAPTER FOUR

FREE RADICAL ADDITIONS OF POLYETHERS TO HFP

4.1 Introduction

The synthesis of high molecular weight PFPEs by the route described earlier will involve the free radical addition of polyethers to fluoroalkenes. Some work has already been performed in this area, and is summarised in table 4.1.

	Polyether	Initiator	Products, yields, notes
1.		DBPO	Monoadduct (99%), reaction performed in benzene.[130]
2.		γ-rays	Monoadduct (24%), diadduct (33%), triadduct (34%) and tetraadduct (8%), all mixtures of isomers.[121]
3.		DBPO	Monoadduct (75%).[130]
4.		TBPO	(n≈8, DEPEG 400*) Mixture of adducts, approximately 6 molar equivalents of HFP incorporated (95%).[103,121]
5.		TBPO	(n≈13, DEPEG 600) Mixture of adducts, approximately 11 molar equivalents of HFP incorporated (84%).[103]
6.		TBPO	(n≈45, DEPEG 2000) Mixture of adducts, approximately 20 molar equivalents of HFP incorporated (80%).[103]
7.	$HO(CH_2CH_2CH_2CH_2O)_nH$	TBPO	(n≈9, DEPTHF 650) Mixture of adducts, approximately 5 or 6 molar equivalents of HFP incorporated.[131]
8.		γ-rays/ acetone	(High polymer) Material with approximately $\frac{n}{4}$ equivalents of HFP incorporated.[132]

Addition of polyethers to HFP

Table 4.1

As will be seen in a later chapter, a large degree of incorporation is necessary if a polyether is to be successfully fluorinated by our techniques, and this is born out by the

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* Molecular weight designations are derived from the commercially available dihydroxy materials.

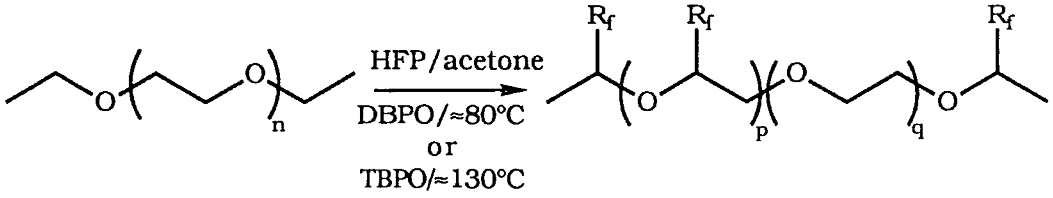
exploratory work on this project by Telford.[121] The products of reactions 1 to 3 and 6 to 8 would be very unlikely to survive the fluorination process. The products of reaction 4 and 5 both have a large proportion of fluorine in them, and that of reaction 4 has been fluorinated. However, even in these cases fluorination could be performed faster and with less risk of decomposition if more HFP was incorporated.

4.11 Use of ethyl terminated polyethers

Previous work[121] has shown that there is a reactivity order; ethyl groups being more reactive than ethylene groups, which are in turn more reactive than methyl groups. Using diethylated polyethers a greater number of polyfluoroalkyl groups will tend to be directed towards the chain ends. This will be beneficial, as these parts of the polymer tend to be more exposed, and therefore more vulnerable to fluorination. It is therefore especially important to achieve incorporation at these points. Reactions 4 to 6, table 4.1, were performed on DEPEG of various molecular weights, and most of the work discussed in this chapter will similarly be based on these materials.

4.2 The Effects of Solvent

Most of the reactions of table 4.1 were performed in the absence of solvent, but, as was discussed in chapter 3, solvents can greatly facilitate free radical additions. DEPEG 600, DEPEG 2000 and PTHF 1000 are all solids at room temperature, so clearly reactions under this condition (specifically γ-initiated reactions) will be particularly poor. Even above the melting point the miscibility of fluoroalkenes in polyethers is not high. Some experiments were performed, repeating the work of Telford,[103] using acetone as a solvent, scheme 4.1.



(57) $R_f = CF_2CFHCF_3$ **(58)**

n ≈ 8* **(57a)**, 13 **(57b)**, 43 **(57c)**

Scheme 4.1

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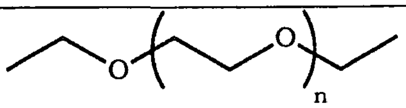
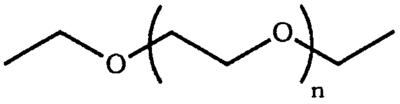
* Molecular weights of starting materials were estimated from the ^1H NMR spectra, comparing the integration of CH_3- protons with -CH_2- protons. Some values were confirmed by gel permeation chromatography.

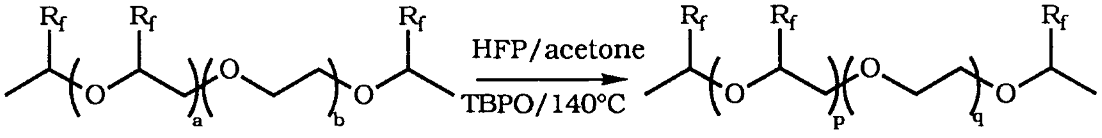
It can be seen that at best the incorporation equals the highest quoted without acetone, reaction 5, table 4.2.

Acyclic polyether	Initiation method	Equivalents of HFP incorporated* (p + 2)
 **(57b)**	DBPO	11 5 7
 **(57b)**	TBPO	6 5

Addition of polyethers to HFP using peroxide initiation in acetone

Table 4.2

Further reaction with HFP would obviously increase the number of fluoroalkyl groups present, scheme 4.2. This method was used for the same reaction as before, using TBPO as an initiator at 140°C. In the first instance 5 molar equivalents of HFP were incorporated into a sample of DEPEG 600 (**57**) the low conversion was due to a less than advantageous ratio of polyether to solvent and HFP, which resulted from performing the reaction on a significantly larger scale. Reacting this polyadduct (**58**) with more HFP incorporated 5 more equivalents of HFP. A third reaction raised the number of equivalents a further 2. This was a total of 12 molar equivalents of HFP incorporated over the three reactions, exceeding any previous results, though the material obtained (**59**) was a fairly dark brown. It was believed that fluorination of this material would proceed with ease.



(58) $a + b = p + q,\ a < p$ **(59)**

Scheme 4.2

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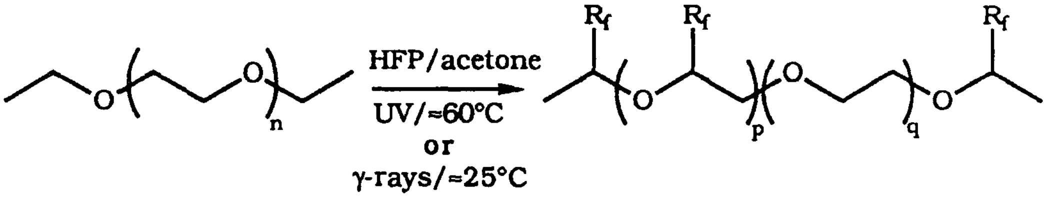
* Incorporation of HFP was derived from the masses of reactants and the mass of HFP recovered, and confirmed by comparison of ^1H and ^{19}F NMR spectra, using (trifluoromethyl)benzene as a reference.

A process could be envisaged where the reaction is carried out in one step, extra HFP and peroxide being added even as the materials react. Such a process may easily be possible on an industrial scale, and is the subject of on-going work in these laboratories.

4.3 A Comparison of Different Initiation Techniques

Table 4.1 shows that peroxide initiation is the most used technique for additions of polyethers to HFP. This is perhaps the most obvious choice as the reactions are performed at elevated temperatures, above the melting point of the polyether, aiding mixing between HFP and the polyether. The use of a solvent transcends this restriction allowing experiments to be performed with UV and γ-initiation, scheme 4.3.

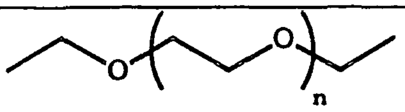
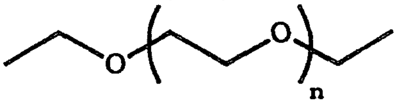
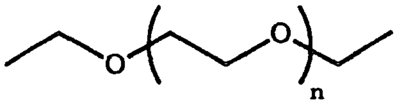
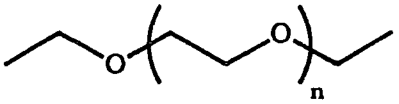
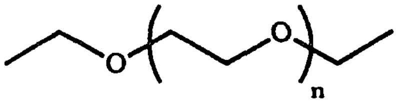
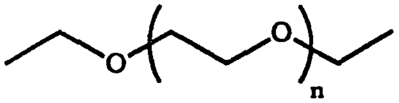


(57) $R_f = CF_2CFHCF_3$ **(58)**

Scheme 4.3

Table 4.3 sets out the results of these reactions. The mean number of equivalents of HFP incorporated can extend over quite a range, a function of the exact ratios of HFP to polyether and acetone. However, overall trends can be observed. Unsurprisingly, γ-initiated reactions tend to proceed further the more they are irradiated, though even after 12 days irradiation the conversion of HFP is not as good as can be achieved with peroxides. Nonetheless, the materials obtained were cleaner, as could be seen from the much paler colour and the NMR spectra (see section 4.31). This was presumably due to the lower temperature at which the reactions were performed.

The UV reactions in general surpassed both the peroxide and the γ-initiated reactions, and this is especially noticeable with the DEPEG 2000 adduct. They were a good deal quicker than the γ-initiated reactions. A further point to notice is that reaction proceeded equally well in Pyrex as in quartz, even though Pyrex will stop virtually all UV light of wavelengths above 298.5 nm. Indeed, the reactions were much cleaner when performed in Pyrex, more so than the materials obtained from γ-initiated reactions. It seems likely that the higher wavelength light effected side reactions, forming the coloured side products.

Polyether	Initiation method	Duration/d	Equivalents of HFP (p + 2)*
 (57a)	UV	3	6, 8
 (57b)	γ-rays	4	3, 4, 5, 6
		5	3, 3
		6	6
		7	5,6,6
		12	8
 (57b)	UV	3	11, 14, 14
 (57b)	UV (quartz reactor)	3	12
 (57c)	γ-rays	7	12, 14, 17
 (57c)	UV	3	35

Addition of polyethers to HFP using UV initiation in acetone
(1000W medium pressure mercury lamp, Pyrex reactor unless otherwise stated)
* Incorporation of HFP estimated from ^{1}H and ^{19}F
NMR with (trifluoromethyl)benzene as a reference
Table 4.3

It was believed that all the materials obtained from the UV reactions in Pyrex would have sufficient fluorine in them to withstand fluorination. They were all prepared in one step, unlike the highly fluorinated material produced using peroxide initiation, and all were clear and virtually colourless.

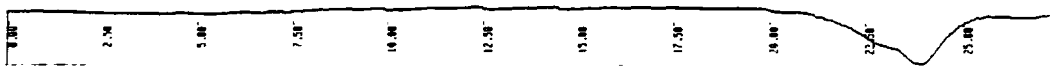
4.31 Polymer integrity

Anomalous peaks were observed in the ^{1}H NMR spectra of some of these polyadducts that at first suggested decomposition. The peaks occurred at about 0.9 ppm, and were particularly strong in adducts formed at higher temperatures, when peroxides were used, for example the reactions of table 4.2. It was originally thought that this was due to breakdown of the polymer chain, leading to the formation of extra ethoxy groups.

4.3.1 Molecular weight determination

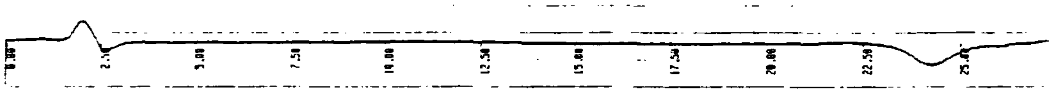
Methods for the accurate determination of molecular weights of polymers are not available, however gel permeation chromatography (GPC) is a frequently used technique, providing some insight.[133] GPC involves polymers dissolved in solvent passing through a swollen, cross-linked polymer (the gel). Lower molecular weight components tend to get trapped in the gel, and so are eluted after larger components.

Figures 4.3 and 4.4 show the chromatagrams from γ-ray and also TBPO initiated reactions. A refractive index (RI) detector was used, and, as the RI of the solvent (oxolane) was greater than the sample, the traces show troughs rather than peaks. No later eluting peaks or troughs were observed.



GPC trace of DEPEG 600/HFP adduct (**58b**) formed by γ-initiation*

Figure 4.3



GPC trace of DEPEG 600/HFP adduct (**58b**) formed by TBPO initiation

Figure 4.4

An idea of molecular weight (more correctly molecular volume) can be obtained by calibrating the machine with polyethylene. From this, a figure of about 1750 could be obtained for the approximate mean mass of both samples. This corresponds to DEPEG 600 with just over seven HFP units incorporated, while NMR analysis of the two materials [using (trifluoromethyl)benzene as a reference] suggested that 11 to 12 equivalents of HFP were incorporated. The discrepancy between these two figures arises from the branched nature of the materials, giving a lower molecular volume compared with polyethylene of the same mass. The fact that the two samples elute at the same time suggests they are of similar molecular weights to each other. This fact and the reasonably narrow molecular weight (seen in the width of the trough) suggests little or no decomposition is occurring. It is interesting to note that the material from the peroxide

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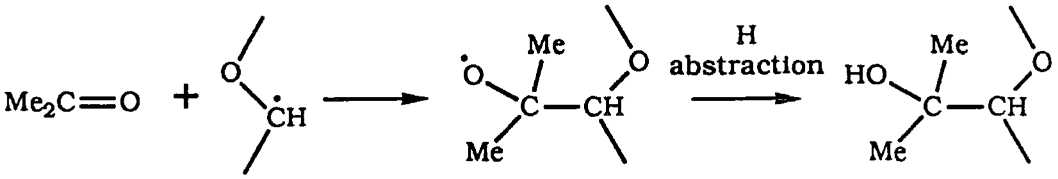
* GPC samples were run in oxolane, numbers along the bottom of each trace indicate retention times in minutes. The ripple at the start of the first chromatagram is probably due to a change of solvent before the traces were run and can be ignored.

initiatated reaction has the narrower distribution. Why γ-initiation should lead to a broader distribution is unclear.

4.312 Incorporation of acetone

Later reactions with UV initiation also showed these peaks in the NMR spectra, to a lesser extent, though the problem was much more prevalent with other fluoroalkenes (discussed in the next chapter). An experiment in which DEPEG 600 and acetone were irradiated with UV light (with no fluoroalkene present) showed that this effect involved only these two components. It is suggested that acetone is incorporated into the polyether backbone by the process of scheme 4.4. Paleta *et al.* have suggested a similar scheme.[134]



Scheme 4.4

A separate experiment, involving no polyether, in a quartz reactor, showed that a side reaction can also occur between acetone and HFP. This appeared to be a vapour phase reaction, as a gel-like material became deposited on the reactor wall, above the level of the liquid. This reaction could be obviated through the use of Pyrex reactors, and it seems likely that this is the material that caused the colouration in the reaction of table 4.3 performed in a quartz reactor.

In general, then, these side reactions could be minimised by performing the reactions at low temperature (*i.e.*, not using peroxides) and, in the case of UV initiation, using Pyrex reactors.

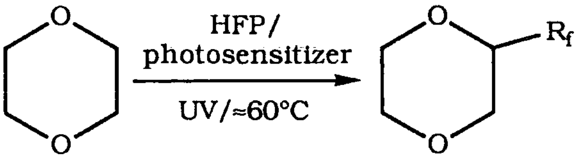
4.32 Alternative photosensitisers

A wide range of compounds absorb UV light beside acetone, many to a much greater extent. Would reaction proceed faster and cleaner with any of these? Sensitisers had to be chosen which would not react themselves, or inhibit reaction, and table 4.4 lists some possibilities.

Compound	λ/nm	ε	E_T/kJ mol^{-1}
Fluorene	263	$10^{4.6}$	284
m-Terphenyl	251.5	44 000	272
Naphthalene	220	133 000	225
Biphenyl	251.5	18 300	276
Anthracene	256	180 000	180
Benzene	183	46 000	351
Benzophenone	252	20 000	288
	(325)	(180)	
Acetone	188 (279)	900 (15)	326

UV absorption of various aromatic and carbonyl photosensitisers
Table 4.4[135,136]

The acetone sensitised reaction proceeded best in a Pyrex reactor, so it can be assumed that the important wavelength that acetone is absorbing at is 279 nm (which will tail appreciably into the Pyrex transparent wavelengths below 298.5 nm), with an extinction coefficient of only 15. As can be seen, this is comparatively low. It was believed that any of these alternative compounds would increase the conversion and rate of reaction. Comparative reactions were performed, in quartz reactors, irradiated for 3 days. 1,4-Dioxane (**38**) was used as the substrate, scheme 4.5; all the sensitisers were soluble in this medium with the exception of anthracene. Table 4.5 summarises the results.



(**38**) $R_f = CF_2CFHCF_3$

Scheme 4.5

Photosensitiser	% conversion of HFP
Fluorene	27
m-Terphenyl	21
Naphthalene	23
Biphenyl	3
Anthracene	39
Benzene	4
Benzophenone	54
Acetone	99
Acetone + benzene	66

Conversion of HFP in the addition of 1,4-dioxane (**38**) to HFP using various photosensitisers

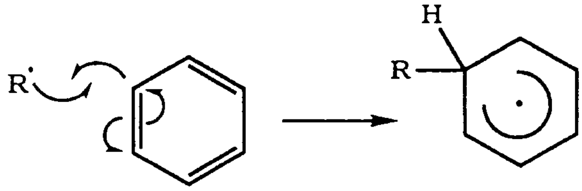
Table 4.5

In three cases reaction was observed directly involving the sensitiser. The fluorene and benzene reactions produced an insoluble material, and in another reaction the insoluble anthracene turned pale yellow, and this new material not being luminescent in UV light. This may account for the low conversions; the sensitiser is reacting with HFP or 1,4-dioxane, losing aromaticity (to some extent) and thus no longer absorbing UV light. Further reaction is thus prevented. A similar process may also be occurring in the other reactions, giving soluble, and hence not immediately apparent, side products.

Some analysis of these side products was attempted. The compounds from the fluorene and anthracene reactions both sublimed, and so were not polymeric. However, neither were soluble in any common solvents (water, acetonitrile, ethanol, acetone, chloroform, diethyl ether, benzene) so no NMR data was available. The compound from the fluorene reaction appeared to involve all three starting materials, 1,4-dioxane, HFP and fluorene, as *the absence of any one* stopped its formation. The mass spectrum of this 'cheesey' white solid was unclear, but suggested a mass of perhaps 482 or 488.

The second compound was a product of the reaction between 1,4-dioxane and anthracene only. The mass spectrum showed a very prominent peak, strongly suggesting a mass of 576, which, in conjunction with elemental analysis data, gave a molecular formula of $C_{44}H_{32}O$. IR spectroscopy showed only aromatic and aliphatic carbon-hydrogen bonds prominent. No further analysis was attempted.

Alternatively, it may be that the aromatic compounds are acting as inhibitors. They are excited by UV, and transfer energy to the substrates as desired. The propagating radical later reacts with the aromatic material; this will be a favoured process because of the great stabilisation possible in aromatic radicals, scheme 4.6. Once this radical forms, it will tend not to react further, and so the radical chain stops. The last reaction of table 4.5 supports this theory to some extent (like the acetone reaction this was performed in Pyrex). The conditions are exactly the same as for the previous, acetone initiated, reaction, but the conversion has been cut by a third by the additional presence of benzene.



Scheme 4.6

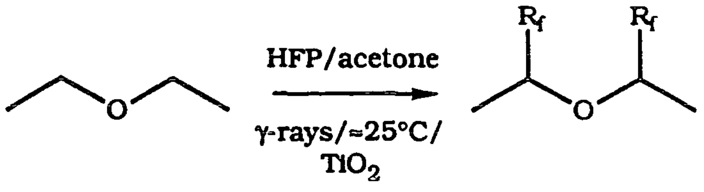
It seems unlikely that any aromatic photosensitiser will perform better than acetone. In additions to higher molecular weight ethers and polyethers there is also the problem of removal of large aromatic compounds, if the sensitiser cannot be removed by distillation or sublimation. Wherever possible, therefore, acetone has been used in later reactions.

4.33 Attempted use of a possible γ-ray sensitiser

Other workers in this laboratory have investigated the use of titanium dioxide as a sensitiser for γ-initiatated reactions. γ-Particles are of very high energy and will generally pass through organic compounds, which have only low atomic weight elements present (it is actually secondary electrons which initiate γ-irradiated reactions). The introduction of titanium into the system would, it was hoped, allow a significantly number of particles to be absorbed, and the rate of reaction considerably enhanced.

The reaction of diethyl ether (**39**) with HFP was studied, scheme 4.7. Experiments were set up, one with titanium dioxide present, one without, and irradiated for 2 days (significantly less than the normal dosage). The reactions were agitated to ensure good mixing of the titanium dioxide, which was not soluble in the reaction medium. A comparable amount of HFP was recovered from each reaction (30.6% conversion of HFP with titanium dioxide as opposed to 30.7% without), implying no enhancement of the reaction was achieved.

It can be assumed that the titanium dioxide absorbed the γ-particles, but there was no easy transition for the titanium to excite a substrate molecule. Poor mixing between titanium dioxide and substrate would also be a limiting problem. The extra absorbed γ-particles therefore would not increase the number of free radical chains started.



(39) $R_f = CF_2CFHCF_3$

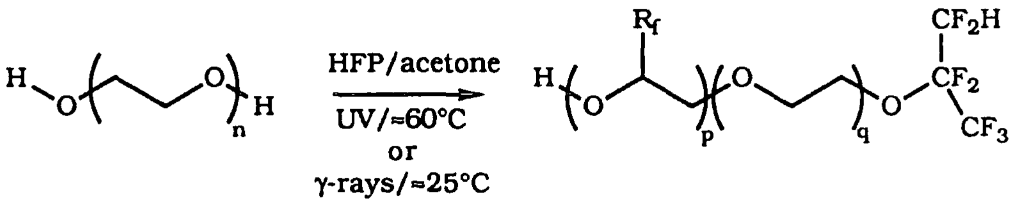
Scheme 4.7

4.4 Addition of Dihydroxy Terminated Polyethers

It has generally seemed preferable to use ethoxy terminated polyethers, because, as has already been mentioned, the ethoxy group tends to direct fluoroalkylation towards the ends. However poly(ethylene glycol) and polytetrahydrofuran are both commercially available as the dihydroxy terminated materials, and reaction with these would allow the overall reaction to be performed in fewer steps.

The free radical reaction of alcohols to fluoroalkenes is well known,[117] and is very similar to the addition of ethers; in both cases an oxygen stabilised radical is formed. Thus it was hoped that reaction would occur at sites adjacent to both the alcohol and ether oxygens.

Two reactions were performed; UV initiated and γ-initiated addition of poly(ethylene glycol) 600 (**60**) to HFP. It was found that the degree of incorporation was severely reduced (between a half and a third of the normal). Furthermore, NMR indicated that a significant amount of addition had proceeded by a nucleophilic process, giving the type of adduct indicated in scheme 4.8. In both cases approximately half the hydroxy groups had reacted in this manner (the structure represents an 'average' for the product mixture).



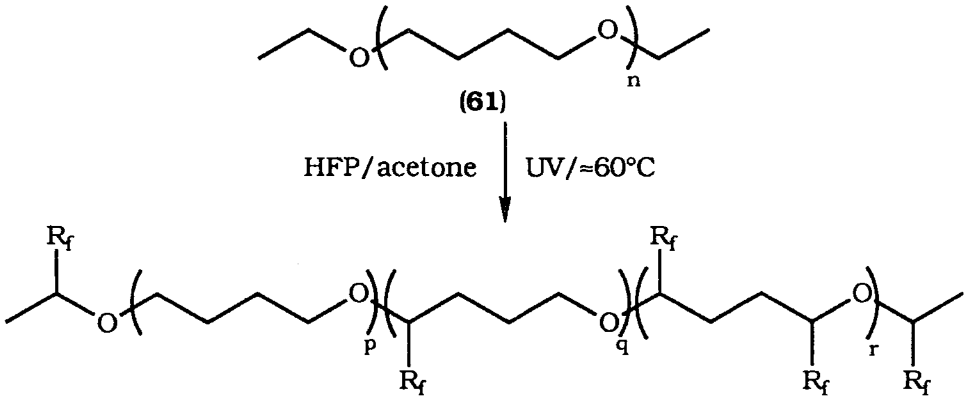
(60) $R_f = CF_2CFHCF_3$, $n \approx 13$, $p + q = n$, $p \approx 3$

Scheme 4.8

Reaction at the polymer ends is not a problem in the synthesis of PFPEs, the presence of a fluoroalkyl group at the polymer ends would aid fluorination. Indeed it would be necessary to react the hydroxy groups in some way later on to avoid the formation of fluoroxy groups during fluorination. The only problem in using hydroxy terminated starting materials is the low conversions achieved, and it is believed that with further purification of the starting materials high levels of incorporation, both at the ends and on the polymer backbone, could be achieved.

4.4 Additions with Diethyl Poly(tetrahydrofuran)

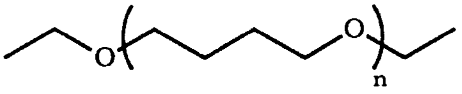
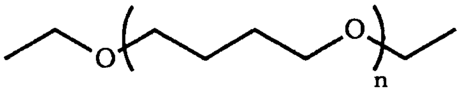
An alternative readily available polyether to DEPEG is PTHF (**61**). It may seem likely that a PFPE derived from this material might not have as good lubricating properties as material derived from DEPEG, on account of the low oxygen to carbon ratio, however, additions to HFP might be expected to proceed more readily, as the site of hydrogen abstraction will be less electrophilic (consider the difference in reactivity of oxane and oxolane compared with 1,4-dioxane).



(62)

$R_f = CF_2CFHCF_3$, n ≈ 13, p + q + r = n

Scheme 4.9

Polyether	Initiation method	Duration/d	Equivalents of HFP incorporated (q + 2r + 2)
 (n≈13, DEPTHF 1000)	UV	3	24
 (n≈13, DEPTHF 1000)	UV	3	26

Addition of DEPTHF to HFP using UV initiation in acetone
(1000W medium pressure mercury lamp, Pyrex reactor)
Table 4.6

Two experiments were performed, table 4.6. As can be seen from scheme 4.9, there are a total of 28 sites readily available for addition to HFP, so values of 24 and 26 represent very near to total reaction (86% and 93% respectively). These materials (**62**) have sufficient fluorine in them to believe that they would readily withstand fluorination. Comparing these results with the seventh reaction of table 4.1, where the dihydroxy material was reacting (with 18 possible sites), only five to six equivalents of HFP were incorporated. A significant improvement has been achieved which has shown to be repeatable.

4.5 Characterisation

Using the data and trends from the NMR spectra of the model compounds, NMR assignments could be made with some confidence. The ^{13}C NMR data were the most useful, the following table sums up some of the important results from the model compounds.

A further point to bear in mind is that proximity to a fluoroalkyl group will lead to broader peaks, due to both the chiral centres present and the fluorine couplings, which are unlikely to be as well resolved in the polymeric materials.

	Chemical shift/ppm			
	$-CH_2O-/-CHR_fO-$		$-CH_2-/CH_3-$	
	From TMS	From starting material	From TMS	From starting material
Diethyl ether and its adducts				
$\underline{C}H_3\underline{C}H_2OCH_2CH_3$	67.4	-	17.1	-
$\underline{C}H_3\underline{C}HR_fOCH_2CH_3$	72.5	+5.1	10.5	-6.6
	75.0	+7.6	12.8	-4.3
$\underline{C}H_3\underline{C}H_2OCHR_fCH_3$	65.5	-1.9	15.3	-1.8
	65.9	-0.5		
$\underline{C}H_3\underline{C}HR_fOCHR_fCH_3$	70.0→76.0	+2.6 → +8.6	9.5 → 15.0	-7.6 → -2.1
1,4-Dioxane and its adducts				
$-CH_2\underline{C}H_2OCH_2-$	66.5	-		
$-CH_2\underline{C}HR_fOCH_2-$	71.5	+5.0		
	74.2	+7.7		
$CHR_f\underline{C}H_2OCH_2$	63.7	-1.8		
	64.4	-2.1		
$CH_2\underline{C}H_2OCHR_f$	66.9	+0.4		
Oxolane and its adducts				
$-\underline{C}H_2\underline{C}H_2OCH_2-$	68.4	-	26.5	
$-\underline{C}H_2\underline{C}HR_fOCH_2-$	75.3	+6.9	24.1	-2.4
	76.9	+8.5		
$-\underline{C}H_2\underline{C}H_2OCHR_f-$	69.9	+1.5	25.7	+0.8
$-\underline{C}H_2\underline{C}HR_fOCHR_f-$	77.8 → 79.2	+9.4 → +10.8	24.0 → 25.6	-2.5 → -0.9

Summary of NMR data for the HFP adducts of diethyl ether, 1,4-dioxane and oxolane

Table 4.7

4.51 The polyadduct of DEPEG 600 to HFP

In depth analysis was performed on a sample of polyadduct from a UV initiated reaction, that contained nine equivalents of HFP (estimated from the mass of HFP reacted, and by integration of the ^1H and ^{19}F spectra using (trifluoromethyl)benzene as a reference as before). Although material with more HFP incorporated was available, the clarity of the NMR spectra decreased significantly with further modification.

The ^{19}F spectrum (appendix one, number 12) showed one broad CF_3 peak at -75.2 ppm, overlapping with a set of small sharp peaks at -75.3 ppm. No difference between RS and RR configurations of the side chains could be discerned (see previous chapter). This may be due to the polymeric nature of the material, leading restricted molecular movement, causing poor averaging and therefore line broadening. The sharper peaks may be due to nucleii at the polymer ends where the molecule can more readily tumble and rotate. Between -128 and -116 ppm was a series of peaks due to CF_2 fluorines. Again unlike the model compounds, no diastereomer pattern was identified. At -208.8 ppm a well defined doublet of multiplets was observed due to CFH fluorines, possibly, again, due to those at the polymer end. Broad peaks were observed at -214.0 (large) and -216.3 ppm (small). The chemical shifts of all these signals corresponded to those found in all the model compounds.

In the ^1H spectrum a triplet due to $C\underline{H}_3CH_2O$- protons was identified at 1.146 ppm (occurring at 1.21 ppm in the starting material) and peaks due to $C\underline{H}_3CHR_fO$- protons at 1.34 (RS or SR configuration in the side group) and 1.38 ppm (RR or SS configuration), compared with 1.32 and 1.34 ppm in both the diethoxy ethane monoadduct and the diethyl ether monoadduct. There is a quartet at 3.47 ppm (CH_3CH_2O- methylene, 3.55 ppm in the starting material) and a large singlet at 3.6 ppm ($-OCH_2CH_2O$- methylene, found at 3.65 ppm in DEPEG). Either side of this, at 3.54 and 3.65 ppm, are two inequivalent $-C\underline{HH}'OCHR_f$- protons (similar to peaks seen in the diethyl ether monoadduct ^1H spectrum at 3.49 and 3.72). Around 3.9 ppm are the $-CH_2OC\underline{H}R_fCH_2$- protons and at 4.1 ppm are the $-CHR_fO\underline{C}HR_fCH_2$- protons. In the model compounds these are seen at 3.85 ppm in the diethyl ether and diethoxy ethane monoadducts, and at 4.2 in the diethoxy ethane triadduct. The CFH proton is seen as a very broad peak at 5.6 ppm, as usual.

Integration of the ^1H spectrum shows the number of methyl protons to be slightly high, but within the limits of error for measurement, indicating little or no incorporation of acetone during reaction (see section 4.31). Looking at the number of CFH protons as a proportion of the total indicated that approximately 10 equivalents of HFP were incorporated into the polyether during reaction.

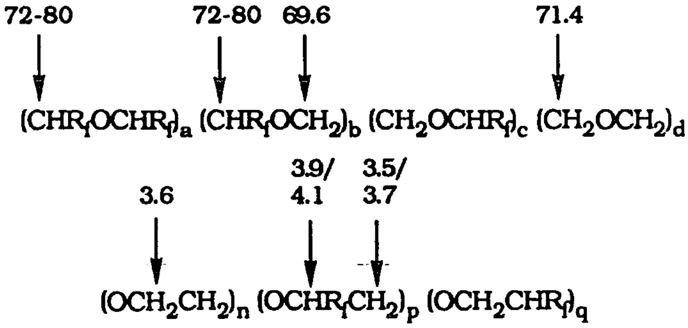
The ^{13}C spectrum has a series of five broad peaks between 115 and 127 ppm attributable to the CF_3 quartet and CF_2 doublet of doublets (with some overlap), as was seen in the model compounds. The CFH carbon was a broad doublet at 84.4 ppm. The diethyl ether diadduct shows a number of peaks in $-CH_2\underline{C}HR_fO$- environments, the carbon nucleii having been shifted downfield by 2.6 to 8.6 ppm from corresponding nucleii in the starting material (at 67 ppm). Similar peaks in the DEPEG polyadduct would be expected in the range 73 to 79 ppm range, matching observed peaks at 78 and 80 ppm (both broad) and at 72.6, 72.8, 73.0 and 73.7 ppm. In the model compound the

$-CH_2\underline{C}HR_fOCH_2-$ and $-CH_2\underline{C}HR_fOCHR_f-$ carbons all overlap, preventing determination of one from the other, though the broader peaks are likely to be those next to a second fluoroalkyl group.

A large singlet at 71.4 ppm was due to $-CH_2O\underline{C}H_2CH_2O-$ carbons (seen at 70.7 in the starting material) and very small ones at 71.2 and 70.8 ppm due to similar carbons in $-CH_2\underline{C}H_2OCH_2CH_3$ environments. Corresponding peaks in the starting material are at 70.7 and 69.9 ppm respectively. Broad peaks around 69.6 ppm arose from $-CH_2O\underline{C}H_2CHR_fO-$ and $-CH_2\underline{C}H_2OCHR_f-$ carbons (*i.e.*, shifted nearly 0.5 to 1.9 ppm upfield from 70.6 ppm as in the diethyl ether case). A minor peak at 67.8 ppm was assigned to $-CHR_f\underline{C}H_2OCHR_f-$, shifted about 2 ppm upfield by both fluoroalkyl groups from 70.6 ppm. A sharp peak at 67.0 ppm was due to $-CH_2O\underline{C}H_2CH_3$ carbons, which lies at 66.6 ppm in the starting material, and at 15.6 ppm due to the $-OCH_2\underline{C}H_3$ carbons (at 15.7 in the starting material). Other methyl carbons were seen at 10 to 14 ppm as a series of multiplets, analogous to peaks at 10.5 and 12.8 ppm in the diethyl ether monoadduct, and between 9.5 and 15.0 ppm in the diadduct.

No peaks attributable to quaternary carbons were observed, but such a peak would be very small and with the degree of resolution it well may have been undetected.

Figure 4.3 summarises the data for the polymer backbone.



Numbers indicate chemical shifts for the nuclei indicated, ^1H and ^{13}C, in ppm

Figure 4.3

Relationships between the variables *a*, *b*, *c* and *d*, and between *n*, *p* and *q* can be estimated from the integrations of the ^1H NMR spectrum (*b* and *c* are, of course, equivalent, as are *p* and *q*). The peak at 3.6 ppm was about twice the magnitude of the total for those at 3.5 and 3.7 ppm. This suggested a relationship, $n = p + q$, which indicated (when the total, $n + p + q \approx 13$, was taken into account) that the mean number of fluoroalkyl groups present in the polymer backbone, $p + q$, was approximately 7.5 (more or less agreeing with the figure of 9 earlier). Comparing peaks at 4.1 and 3.9 ppm, found to be in the ratio of approximately 1:2, gave a second relationship, $2a = b + c$. The number of fluoroalkyl side groups must be equal so, $p + q = 2a + b + c = 7.5$, and from this it follows that the number of oxygens with a fluoroalkyl group on one side,$b + c$, will be approximately 3.8, those that have two fluoroalkyl groups, a, will be about 1.9 and those with none will number 8.3.

Two important conclusions can be made from these figures. Firstly, the tendency for fluoroalkyl groups to lie either side of an ether bridge is highly suggestive of the same sort of intramolecular hydrogen abstraction mechanism that was indicated in the formation of the diethyl ether monoadduct (see previous chapter), if not to nearly the same extent. It may well be that the bulk of the polymer ends reduces the likelihood of a suitable conformation that would lead to an intramolecular hydrogen abstraction. Secondly, there are significant sections of the polyether which have not been modified at all. This will clearly be a problem when the material is fluorinated, and shows that even with seven to eight equivalents of HFP incorporated into DEPEG 600, it is still unlikely to withstand fluorination, emphasising the importance of a high degree of incorporation.

4.52 The polyadduct of PTHF 1000 to HFP

In the PTHF 1000 adduct the CF_3 quartet and CF_2 doublet of doublets are again identifiable at 122.3 and 119.5 ppm respectively. The quartet is again further split as a doublet, the triplet is not so well defined. The CFH peak at 84.5 ppm is a broad doublet, no finer splitting is determinable.

In the region between 82 and 65 ppm the most notable feature is the absence of any $-CH_2O\underline{C}H_2CH_2-$ peak (which appears at 70.6 ppm in the starting material). Even if these carbons were shifted by more distant substituents, a reasonably sharp peak would be expected in approximately the same region of the spectrum as neither fluorine nucleii nor chiral centres are in the vicinity. This is not observed. Also, no peak is seen around 65 ppm, the expected position of $-CH_2\underline{C}H_2OCHR_f-$ carbons, by analogy with the diethyl ether monoadduct.

However, a peak at 72.8 ppm is indicative of a $-CH_2O\underline{C}HR_fCH_2-$ environment, suggesting that $-CHR_fCH_2OCHR_fCH_2-$ sections are present. A well defined triplet at 33.7 ppm was attributed to $-CH_2\underline{C}HR_fCH2-$, shifted some 7 ppm downfield from 26.6 ppm in the starting material, which supports this hypothesis. A peak at 71.2 ppm was tentatively assigned to $-CHR_fCH_2O\underline{C}H_2CH_2-$ and $CHR_f\underline{C}H_2OCHR_fCH_2$ carbons though no model compound data was available to support this.

Peaks at 75.4, 77.5, 79.3 and 80.9 ppm are due to $-CHR_fO\underline{C}HR_fCH_2-$ carbons (expected at 73 to 79 ppm by comparison with the diethyl ether diadduct). These are all broadened due to the proximity of two fluoroalkyl groups. A peak at 66.8 ppm is assigned to $-CH_2O\underline{C}H_2CH_2-$ carbon environments. Several very broad overlapping peaks lie between 28 and 23 ppm, assigned to carbons in $-CH_2\underline{C}H_2CH_2CHR_f-$

environments (the down field peaks) and $-CHR_fCH_2\underline{C}H_2CHR_f-$ environments (the upfield peaks). No noticeable $-OCH_2\underline{C}H_2CH_2CH_2-$ peak is seen (expected at 26.6 ppm in the starting material) indicating that (approximately) all tetramethylene units have been modified.

Three sharp resonances stand out, also in this region, at 23.9, 23.1 and 21.4 ppm, a triplet, a doublet and a triplet respectively. The magnitude of the splitting is consistent with $^3J_{CF}$ coupling, and the sharpness of the peak and degree of coupling suggests only one fluoroalkyl group in the vicinity; $-CH_2CH_2\underline{C}H_2CHR_fOCH_2-$ environments.

There is a peak at 18.6 ppm. Too far downfield for a methyl, this must be a methylene adjacent to two fluoroalkyl side groups (*i.e.*, $-CHR_f\underline{C}H_2CHR_f-$), shifted significantly upfield. Being between two fluoroalkyl groups, this peak is fairly broad.

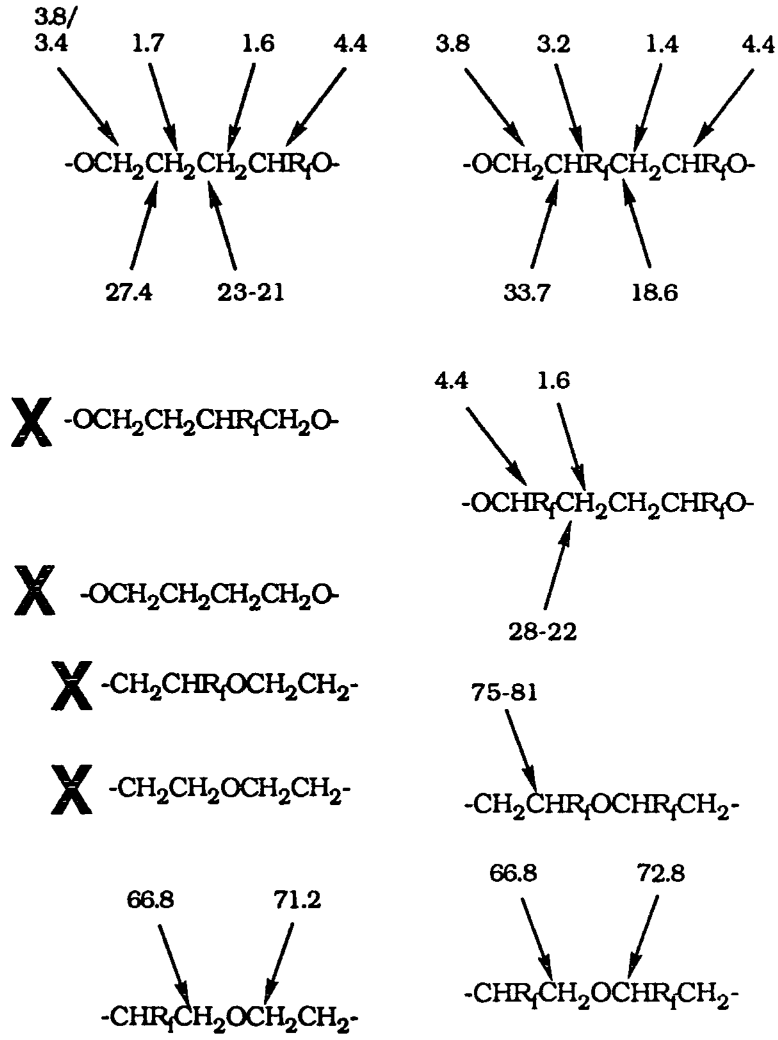
A peak at 15.6 ppm is assigned to $\underline{C}H_3CH_2O-$ carbons. Comparison with the 1,2-diethoxy ethane monoadduct suggests $\underline{C}H_3CHR_fOCH_2-$ carbons would lie at 13.0 and 11.0 ppm, and with the diethyl ether diadduct suggests that $\underline{C}H_3CHR_fOCHR_f-$ carbons would lie between 15 and 9 ppm as eight peaks (at least). None of these peaks were identified, though they would necessarily be small and may be lost in the base line.

In the ^{19}F spectrum peaks due to CF_3, CF_2 and CFH fluorine environments are attributable as before. The only unusual peaks make up an AB system at about -112 ppm, and it is suggested that this is due to $-CH_2CHR_fCH_2-$ units in the material. Integration of this, in comparison with the other CF_2 fluorines gives a ratio of 10:1 for the number of additions of HFP adjacent to oxygen as opposed to additions to the middle of the tetramethylene units.

The ^1H spectrum shows a peak at 1.14 ppm ($-OCH_2C\underline{H}_3$ protons) and two, at 1.35 and 1.38 ppm, due to $-OCHR_fC\underline{H}_3$ protons, RS and RR respectively. A broad peak at 1.4 ppm is assigned to $-CHR_fC\underline{H}_2CHR_f-$ protons, at 1.6 ppm due to $-OCHR_fC\underline{H}_2CH_2-$ protons and at 1.7 ppm due to $-OCH_2C\underline{H}_2CH_2$ protons.

Looking upfield, a peak at 3.42 ppm is assigned to $CH_2OC\underline{H}_2CH_2-$. At 3.76 and 3.88 ppm the $-CHR_fOCH_2CH_2-$ and $-CH_2OCH_2CHR_f-$ protons are observed, though which is which cannot be determined. A peak at 3.17 ppm may be due to $CH_2C\underline{H}R_fCH_2-$ protons, and the strong, broad peak at 4.36 ppm will be due to $-OC\underline{H}R_fCH_2-$ protons. The CHF protons occur as usual at 5.7 ppm.

Figure 4.4 sums up these findings, and indicates the polymer sections present and also those that were not found (possibilities with fluoroalkyl groups on adjacent carbons are not considered as no evidence for these types of structures has ever been found in the model compounds).



Numbers indicate NMR shifts for the nuclei indicated , ^1H and ^{13}C, in ppm

Figure 4.4

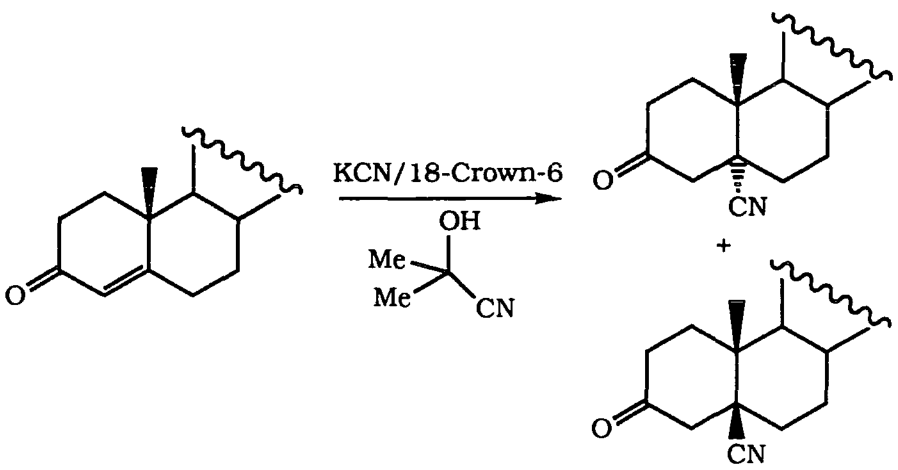
4.6 Crown Ethers

4.61 Introduction

Crown ethers are an unusual class of polyethers which have received much attention in the past on account of their complexing ability with metal cations. Considerable effort has been expended on their synthesis, and many crown ether catalysed reactions have been reported, such as those in scheme 4.10.[137,138]

$$H_2NNH_2 \xrightarrow[\text{18-Crown-6}]{CHCl_3/KOH} CH_2N_2$$

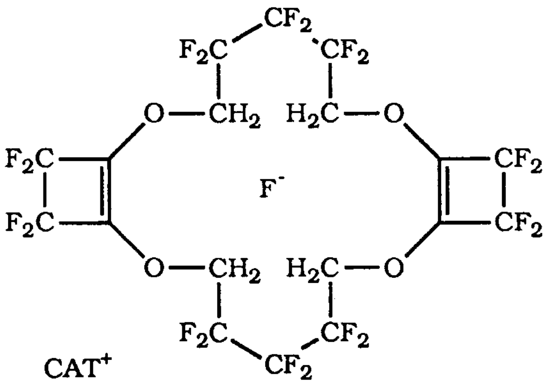
(48%)



(86%, 1:10 ratio of isomers)

Scheme 4.10

The different crown ethers synthesised exhibit different complexing ability with various metal cations. The major factor that determines how well a crown compound complexes with a cation is the size of the ring, compared with the size of the cation, but electronic factors play an important, if more subtle, rôle. This is, perhaps, most dramatically illustrated by the fluorinated macrocycle (**63**),[139] figure 4.1, which will act as a stable host for fluoride ion, electron withdrawal being so great as to allow complexation with the anion through the methylene units.



(63)

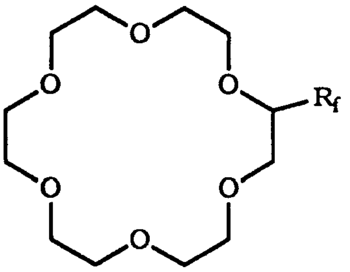
CAT = $S(NMe_2)_3$

Figure 4.1

The complex (**63**) was prepared by the addition of tris(dimethylamino)sulphonium trimethyldifluorosilicate to the macrocycle in oxolane, after evaporation of the oxolane, white crystals were obtained, melting at 108-110°C. X-ray crystallography data was presented, which showed the fluoride ion "nested" in the macrocycle, which adopted a twisted conformation. The nearest cation was positioned above the fluoride ion. Lagow and coworkers[140] have also observed fluoride ion complexes, formed in the gas phase between perfluoro-18-crown-6 and vinylidene fluoride (VDF), inside a mass spectrometer. No further evidence was presented.

4.62 Crown ethers fluorinated in the side group

How would a pendant fluoroalkyl group effect the complexing ability of a crown ether such as 18-crown-6 (**64**) (figure 4.2)? With an electron withdrawing group such as this, it might be expected that, with less electron density on oxygen, complexation with a cation will be less favourable. However, it maybe that the fluorines have a beneficial effect, the 2*H*-hexafluoropropyl group reaching over the plane of the complex to bond in some way, through fluorine, with the cation. Similar complexes, with bonding to oxygen in the side arm are known, and have been termed 'lariat' ethers.[141,142]

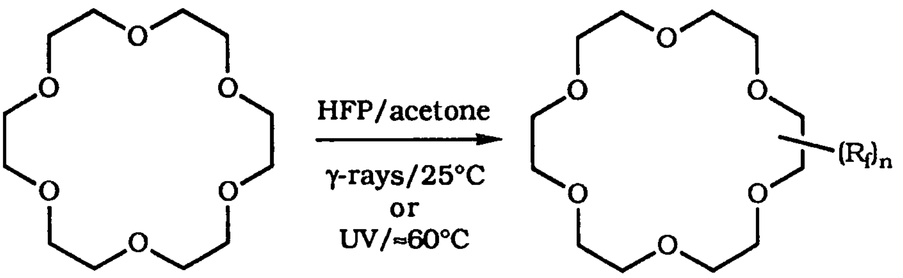


$R_f = CF_2CFHCF_3$

Figure 4.2

4.63 Addition of 18-crown-6 to HFP

Nevertheless, reaction between 18-crown-6 (**64**) and HFP was performed, to provide material of this type for evaluation, scheme 4.11. GLC analysis of the product (**65**) showed mono-, di-, tri- and tetraadducts all to be present (NMR analysis indicated approximately two equivalents of HFP had been incorporated).



(64) **(65)**

$R_f = CF_2CFHCF_3$

n = 0 to 5

Scheme 4.11

By altering the reaction conditions a range of materials could be synthesised in which the *average* incorporation of HFP in a sample could be varied from zero up to over five. However, each sample was a mixture of adducts, and isomers of those adducts.

Attempts were made to purify the resultant materials. Separation was attempted by column chromatography (alumina column), distillation (the adducts distilled at 100 to 200°C at 0.05mmHg), preparative GLC and recrystallisation (chloroform and also ethyl acetate), with little success. Each technique afforded fractions in which the starting material and specific adducts could be concentrated, but other adducts could not be eliminated completely from a fraction. Attempts to remove the starting material by extraction in to water were also unsuccessful, the adducts tending to form an emulsion in water.

Attempts were also made to separate the complexed materials after work by Stoddart and coworkers.[143] Using potassium nitrate, complexes were formed of a sample having an average of one equivalent of HFP incorporated, and recrystallisation from chloroform and ethyl acetate attempted. Various fractions were obtained, and although some monoadduct was crystallising, the starting material was the least soluble component in either medium (even so, it could not be removed completely from the adduct mixture). A good quantity of the potassium complex of 18-crown-6 was obtained, mixed with some monoadduct complex in varying proportions. The residue after evaporation of solvent was analysed and found to be primarily the uncomplexed diadduct.

A second attempt was made, using material with substantially more HFP incorporated (just over 2 equivalents). It was hoped that the lower adducts could be crystalised out selectively, however no crystals were observed at any stage, possibly because the complexed adducts are still liquids. It would seem that the starting material and various adducts are too similar to be readily separated.

4.64 Characterisation by ^{252}Cf plasma desorption mass spectrometry

^{252}Cf plasma desorption mass spectrometry* has been shown to be a useful tool, looking at the complexing abilities of crown ethers and similar compounds,[144] and it was believed that such analysis would also be fruitful in this case, where a mixture of compounds is present. Spectra were run on samples absorbed on a nitrocellulose matrix. Alkali metal salts (lithium chloride, sodium acetate or potassium acetate) could be washed over the samples prior to analysis. Peaks due to the tetraadduct were generally too small to be useful.

The first sample was left unwashed, and most notably shows two peaks at m/e 436.9 and 587.0. These correspond to the mono- and diadducts complexed with sodium from the matrix. A peak at 737 corresponds to the sodium complex of the triadduct. No free ligand is observed, and this gives some idea of the good complexing ability of all

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* ^{252}Cf plasma desorption mass spectrometry was kindly performed by Dr. J. Becher of Odense University, Denmark.

these compounds (in a similar experiment, 15-crown-5 showed significant amounts of uncomplexed ligand,[144] despite its high affinity for sodium ions over other alkali metal cations).

A sample was washed with lithium chloride. Again no uncomplexed mono- and diadduct is seen. Instead three sets of peaks are observed where the ligands complex with lithium (peaks 421.0 and 571.0), water (peaks 432.0 and 582.1) and sodium (again from the matrix, peaks 436.9 and 587.0). The last two peaks suggest better complexation with sodium over lithium, especially for the monoadduct to judge from the size of the peak. Four peaks are attributable to the triadduct; 714.8 (uncomplexed), 721.1 (lithium complex), 731.5 (complex with water) and 737.1 (sodium complex). The general lack of affinity for lithium will be a result of the size of the aperture in 18-crown-6 derivatives.

The next sample was washed with sodium acetate. Three very strong peaks are seen principally corresponding to sodium complexes with the monoadduct (m/e 437.3), the diadduct (587.3) and the triadduct (737.4) indicating a high affinity between all the adducts and sodium cations. The largest peak is that due to the diadduct, suggesting that this may form a stronger complex with sodium than the other adducts.

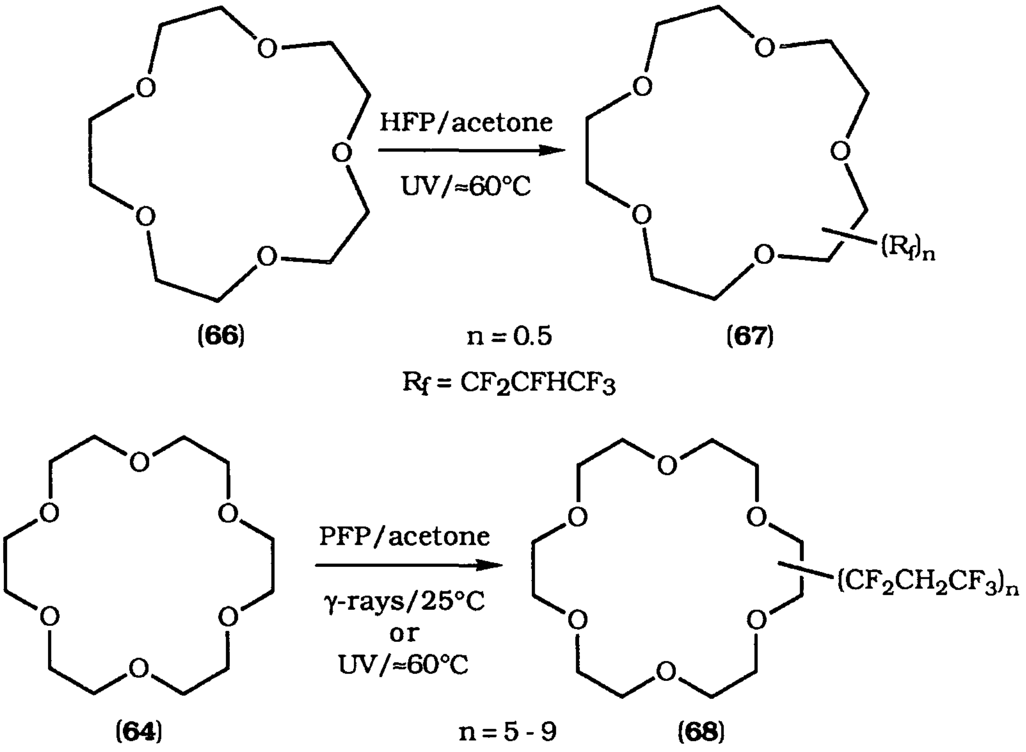
In the spectrum of the potassium acetate washed sample strong potassium complexed peaks are observed at m/e 453.5, 603.7 and 754.1. From the monoadduct two other smaller peaks; complexes with water and sodium, though both are small, suggesting that this adduct may complex better with potassium. Two other peaks arise from the diadduct; the sodium complex and the uncomplexed ligand (very small). Uncomplexed triadduct is also seen.

The final sample was washed with a 1:1:1 mixture of the three cations. The resultant spectrum is fairly complicated, but a strong peak is seen at 454.3, the potassium complex with the monoadduct, suggesting that this adduct has a greater affinity towards potassium.

4.65 Other additions of crown compounds to fluoroalkenes

Two other reactions were attempted, scheme 4.12, in which 15-crown-5 (**66**) was added to HFP and 18-crown-6 (**64**) was added to 2*H*-pentafluoropropene (PFP).

The former experiment would provide compounds (**67**) that readily distil, it was hoped. A deficiency of HFP was used to reduce the number of products. As only one chiral centre can form in additions to PFP, a simpler product mixture (**68**) would ensue, and, in the latter reaction, it was hoped that purification would be markedly easier as the boiling point would be lower.



Scheme 4.12

This was not to be the case. The 15-crown-5 adducts (**67**) were just as irresolvable as the 18-crown-6 derivatives (**65**), and attempts to distil single components were still unsuccessful. Due to unknown side reactions, the product mixture (**68**) obtained from the reaction with PFP was considerably *more* complicated than that with HFP (numerous inexplicable peaks now appearing in the GLC trace). Experiments with excess amounts of PFP showed that materials with up to *nine* equivalents of PFP incorporated could be obtained (despite the findings of other workers that PFP is a good deal less reactive than HFP[145]). This suggests either that two additions are occurring between oxygens (never observed with HFP), or that the PFP is telomerising, though this has also not previously been observed. In either case the number of isomers possible would be large. No significant effort was made to separate any of the components.

It would seem that the number of isomeric possibilities and the similarities between these isomers combine to make these materials, and indeed all the higher molecular weight adducts, inseparable. It is believed that a more viable method of obtaining adducts may well be to react HFP with a precursor to 18-crown-6 (**64**), and then to form the macrocycle with the fluoropropyl group already attached.

CHAPTER FIVE

SOME FREE RADICAL ADDITIONS OF POLYETHERS TO HFP

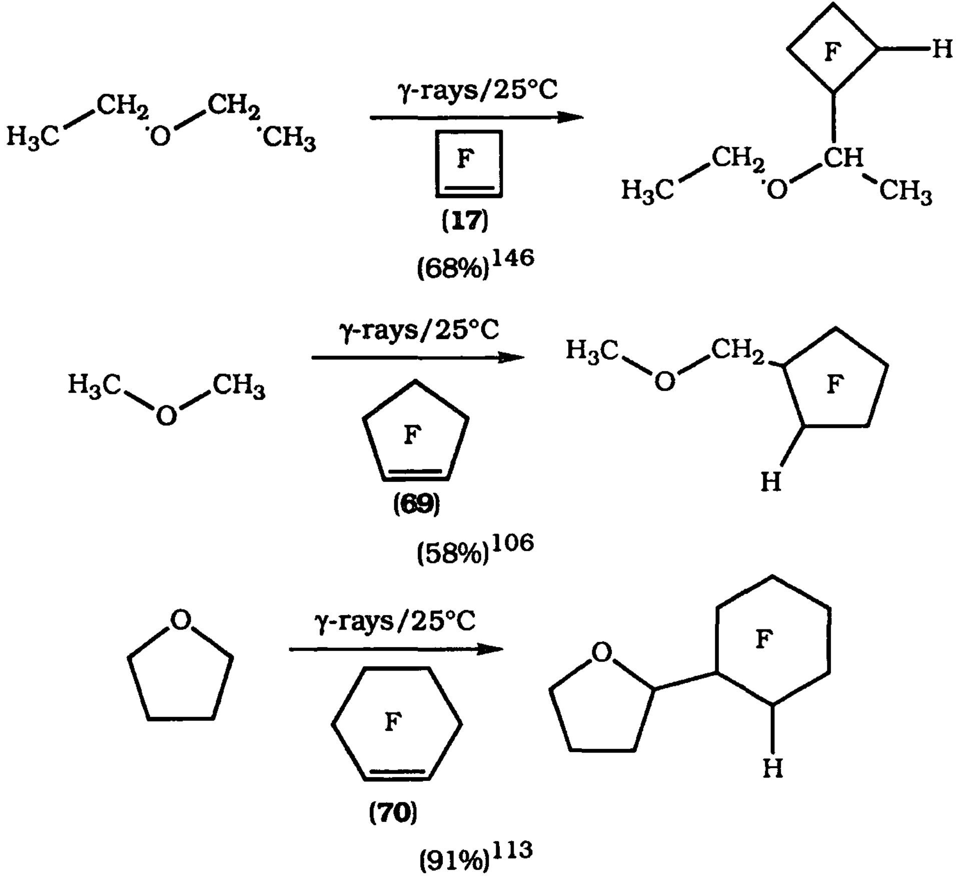
5.1 Alternative Fluoroalkenes

HFP is a particularly good fluoroalkene to use in free radical additions, as it is reactive and does not homopolymerise. The use of other fluoroalkenes would, however, greatly enhance the range of PFPEs eventually synthesised. Some experiments were performed to evaluate the suitability of other fluoroalkenes.

5.2 Non-terminal Fluoroalkenes

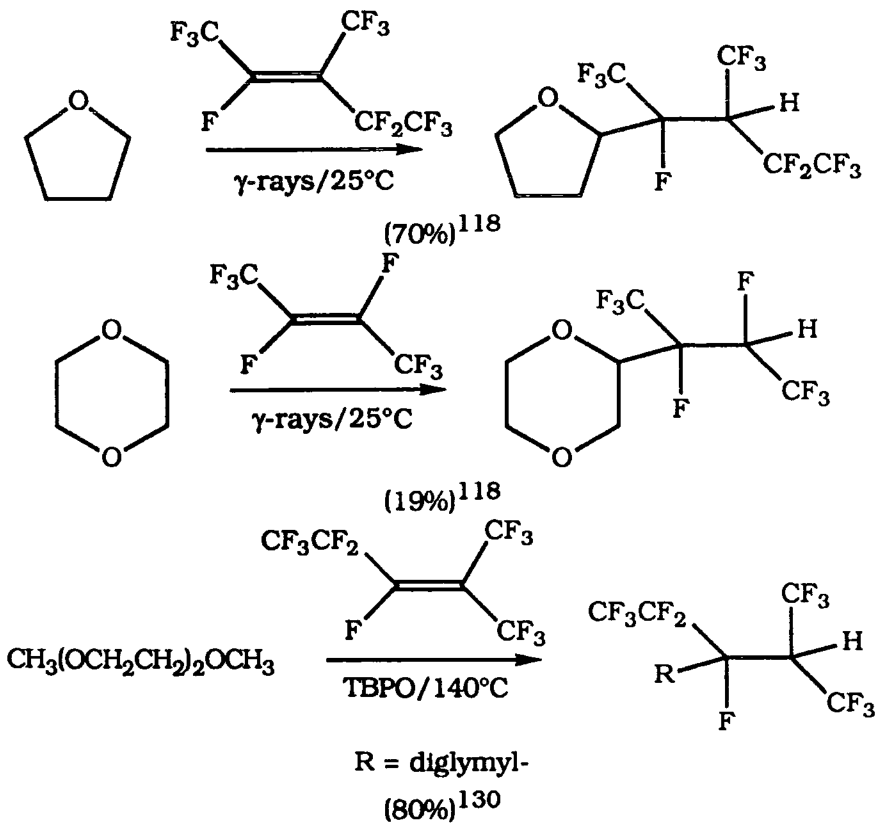
Addition of a non-terminal fluoroalkenes would potentially provide PFPEs with very bulky side groups. Such materials would be expected to have especially large liquid ranges. Cyclic fluoroalkenes would give a particularly unusual structure to a PFPE.

Free radical additions of ethers to cyclic fluoroalkenes, such as hexafluorocyclobutene (HFCB) (**17**), octafluorocyclopentene (OFCP) (**69**) and decafluorocyclohexene (**70**), are known, and some examples are given in scheme 5.1.



Scheme 5.1

In general these reactions proceed less readily than the corresponding reaction with HFP. This will be a problem with any non-terminal fluoroalkene, and reactions with acyclic non-terminal fluoroalkenes are notably fewer, though some examples are shown in scheme 5.2.

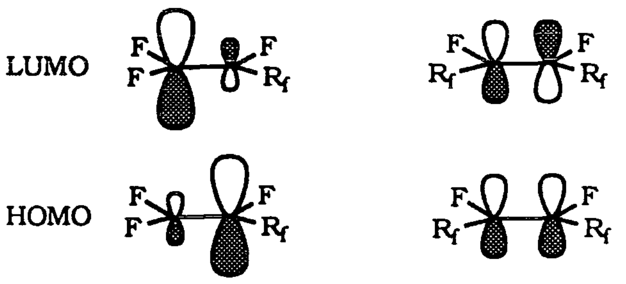


Scheme 5.2

Two reasons account for the reduced reactivity of non-terminal fluoroalkenes. Steric factors will clearly have an effect and this may be the entire explanation. However, Frontier Orbital Theory suggests that the reduction in the orbital coefficients in the lowest unoccupied molecular orbital (LUMO) at the site of attack may also be important.

The important interactions in free radical additions of this type, a nucleophilic radical attacking an electron deficient double bond, is between the singly occupied molecular orbital (SOMO) of the radical and the LUMO of the alkene. The effect of an electron withdrawing group, such as a fluoroalkyl group, on an alkene is to reduce the energy of the LUMO [and the highest occupied molecule orbital (HOMO) too]. In the case of a non-terminal alkene, therefore, the LUMO will be lower than in HFP, for instance, and therefore more accessible to the SOMO of the radical. The lower reactivity in these systems must therefore be attributed to some other effect.

The second effect of substituents on the LUMO and HOMO is to modify the orbital coefficients.[147] Frontier Orbital Theory says that an electron withdrawing group will increase the size of the orbital coefficient adjacent to it in the HOMO, and reduce it in the LUMO, figure 5.1. In HFP, for instance, the orbital β to the trifluoromethyl is significantly enlarged, facilitating attack at this position. Conversely, an electron donor, such as fluorine (through the lone pair), decreases the adjacent orbital coefficient in the HOMO, raises it in the LUMO. In a cyclic fluoroalkene, however, the coefficients are equal and reactivity is reduced.

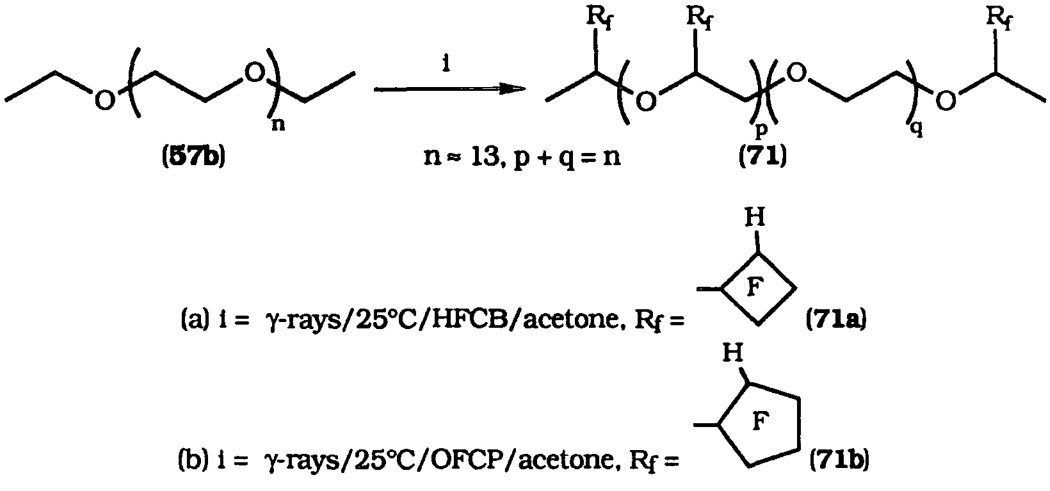


Terminal alkene Non-terminal alkene

Figure 5.1

5.21 Additions to HFCB and OFCP

Attempts were made to react HFCB (**17**) and OFCP (**69**) with a polyether, DEPEG 600 (**57b**), scheme 5.3.



(**57b**) n ≈ 13, p + q = n (**71**)

(a) i = γ-rays/25°C/HFCB/acetone, R_f = (**71a**)

(b) i = γ-rays/25°C/OFCP/acetone, R_f = (**71b**)

Scheme 5.3

Fluoroalkene	p + 2†
HFCB	10
OFCP	5

Addition of fluoroalkenes to DEPEG 600 in acetone
(UV initiation, 1000W medium pressure mercury lamp, in Pyrex reactors)

Table 5.1

Originally, γ-irradiation was employed as the initiation technique, with little success. Further reactions were performed with UV initiation, and they proceeded well under these conditions, table 5.1.

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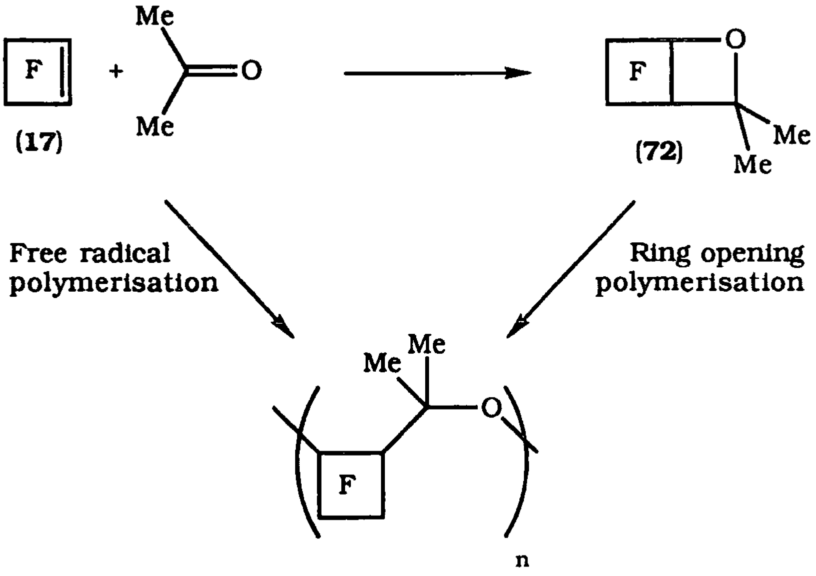
† Values of *p* were derived from ^1H and ^{19}F NMR using (trifluoromethyl)benzene as a reference.

These figures confirm the findings of other workers, that HFCB is less reactive than HFP towards free radical addition, and OFCP is less reactive still. This is rationalised on the basis of far greater release of steric strain in HFCB.

Inspection of the NMR spectra of these materials showed a significant amount of acetone had been incorporated into them (see also chapter 4, section 4.31). Attempts were made to obviate this problem, and two options presented themselves: As it had previously been observed that acetone incorporation was greater at higher temperature, performing reactions at low temperature would, it was hoped, significantly reduce acetone incorporation; More simply, acetone could be left out of the reaction, and another solvent and photosensitiser system employed.

Three reactions were performed, reacting HFCB with DEPEG 600 in acetone at low temperature.* In the first and second reactions a gel-like material became deposited on the reactor wall, apparently the product of a side reaction between acetone and the fluoroalkene, as was confirmed by the UV reaction of acetone with HFCB (in the absence of polyether). The involatile material obtained was believed to be polymeric, possibly forming by one of two routes suggested in scheme 5.4; either by forming the 1:1 adduct (72),[148] and then ring opening, or by a free radical polymerisation mechanism.



Scheme 5.4

The reaction between acetone and the fluoroalkene could be obviated by the use of a Pyrex reactor, rather than quartz, as in the third reaction. Table 5.2 sets out the results.

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* The low temperature UV reactor was of a different geometry to that used in other reactions using a 500W lamp for 5 days, and so an exact comparison of the extent of reactions is not applicable.

Temp/°C	Reactor	p + 2†
-30	quartz	6
0	quartz	4
-15	Pyrex	3

Addition of HFCB to DEPEG 600 in acetone at various temperatures
(UV initiation, 1000W medium pressure mercury lamp)
Table 5.2

However, NMR analysis showed acetone incorporation into the polyether was just as prevalent as in the previous reactions.

Benzophenone was used as a photosensitiser, and 2,2,2-trifluoroethanol as a solvent in two reactions, with HFCB and with OFCP. After UV irradiation, incorporation of the benzophenone was observed. Two further reactions were attempted without photosensitiser. Clearly this would stop these side reactions, but would the desired reaction proceed? NMR analysis of the products showed that reaction had still occurred, table 5.3.

Fluoroalkene	p + 2†
HFCB	4
OFCP	5

Addition of fluoroalkenes to DEPEG 600 in 2,2,2-trifluoroethanol
(UV initiation, 1000W medium pressure mercury lamp, in quartz reactors)
Table 5.3

It is assumed that the fluoroalkene is absorbing UV light. These results tend to suggest that OFCP acts to a comparable extent to acetone as a photosensitiser, HFCB to a lesser extent (it has already been established that generally HFCB is the more reactive of the two). It is apparent that these reactions can be performed without any other photosensitiser, and the problem of acetone incorporation avoided. The levels of incorporation may well be increased by further subsequent reactions. Alternatively, if these materials are too deactivated towards incorporation of further cyclic fluoroalkene, reaction with HFP would give materials with mixed side groups, with sufficient fluorine

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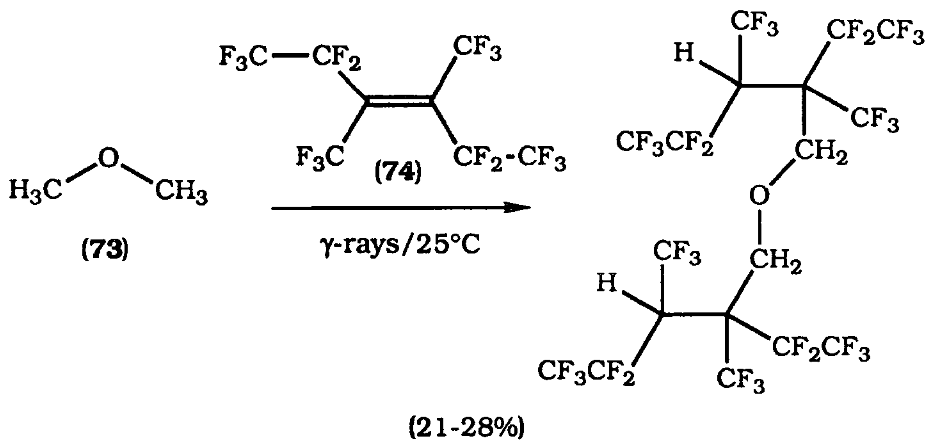
† Values of *p* were derived from ^{1}H and ^{19}F NMR using (trifluoromethyl)benzene as a reference.

incorporated to withstand fluorination, but properties unlike those of the simple HFP/polyether derived materials.

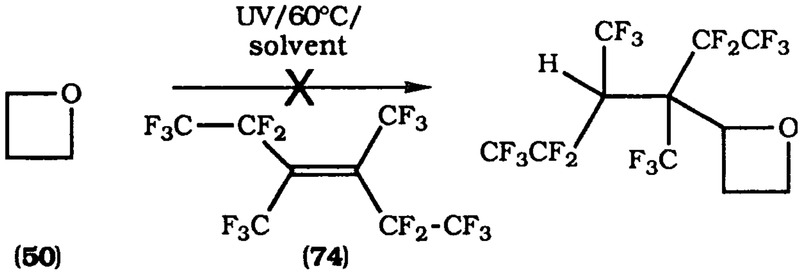
5.22 Attempted additions to decafluoro-3,4-bis(trifluoromethyl)hex-3-ene

Decafluoro-3,4-bis(trifluoromethyl)hex-3-ene (**74**) is the tetramer of TFE, and as such is reasonable readily available. In the past it has been reacted successfully with dimethyl ether (**73**), scheme 5.5,[149] but no reaction was observed with diethyl ether.[132] Both these reactions were performed at room temperature, using γ-initiation. The steric bulk of decafluoro-3,4-bis(trifluoromethyl)hex-3-ene was cited as the reason that diethyl ether did not react.



Scheme 5.5

It was hoped that the use of UV irradiation would allow the steric hindrance to be overcome, as not only would the reaction be performed at a higher temperature, but also molecules in high energy states would be present in the system. The first two reactions were performed, in acetone, with oxetane (**50**), scheme 5.6, and 1,4-dioxane (**38**). Oxetane was chosen for its stereochemistry, allowing decafluoro-3,4-bis(trifluoromethyl)hex-3-ene (**74**) the best opportunity for approach, whilst 1,4-dioxane was chosen as the best model for DEPEG.

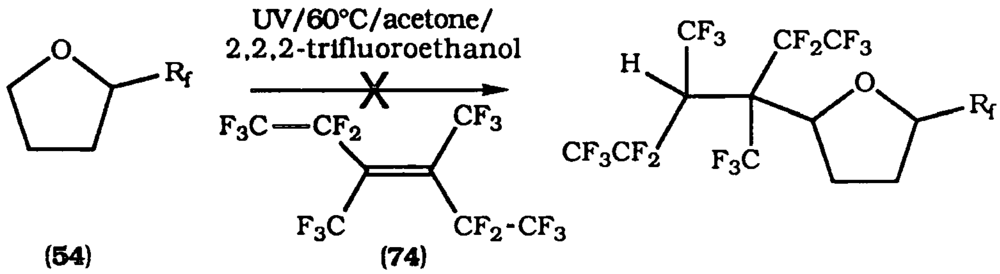


Scheme 5.6

No reaction was observed in either case, and this was, at least partly, attributed to poor mixing, decafluoro-3,4-bis(trifluoromethyl)hex-3-ene (**74**) being insoluble in acetone. Further reactions were performed between decafluoro-3,4-bis(trifluoromethyl)-

hex-3-ene and oxetane. 2,2,2-Trifluoroethanol was used as a solvent after it was established that decafluoro-3,4-bis(trifluoromethyl)hex-3-ene was soluble in it. In one reaction a small amount of acetone was also added as a photosensitiser. In both cases, however, the addition of oxetane caused the decafluoro-3,4-bis(trifluoromethyl)hex-3-ene to separate out of solution, and two layers formed. Again no reaction was observed.

In two subsequent reactions starting materials were used that would be more soluble in fluorinated systems, the HFP adducts of oxolane (**54**), scheme 5.7, and 1,4-dioxane. Reactions were again performed in 2,2,2-trifluoroethanol, with a small amount of acetone added.



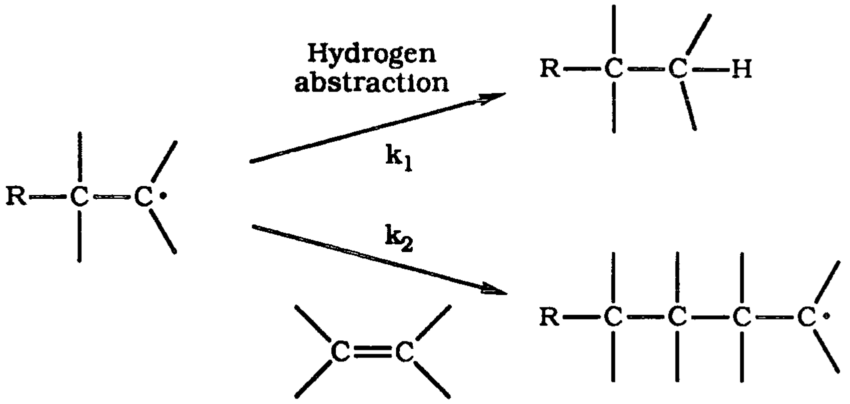
Rf = CF_2CFHCF_3

Scheme 5.7

In both cases the reaction mixture remained homogeneous, however NMR showed that no reaction had occurred. An ether with a 2*H*-hexafluoropropyl group attached is deactivated towards further reaction, and so it may be that in this last case reaction did not occur for this reason, though the oxolane adduct (**54**) was chosen as it is known to be fairly reactive (see chapter 3, section 3.83). It may be that only a fluoroalkylated ether will be sufficiently miscible with decafluoro-3,4-bis(trifluoromethyl)hex-3-ene (**74**) to allow adequate mixing, but such a material will be too deactivated to undergo reaction. Possibly a fluorinated ether with the fluorines well away from the ether linkage would be both reactive and miscible and in such a case the reaction would occur. No attempts to react decafluoro-3,4-bis(trifluoromethyl)-hex-3-ene with a polyether were made.

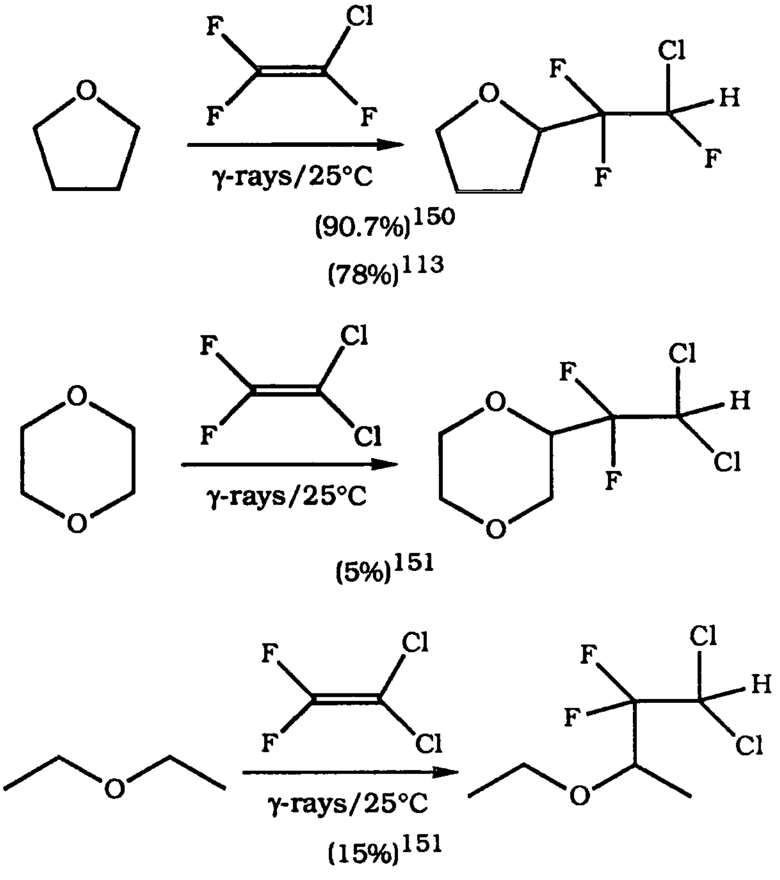
5.3 Additions to Telomerisable Fluoroalkenes

All the fluoroalkenes mentioned so far, including HFP, have given radicals that undergo hydrogen abstraction more or less exclusively over propagation, *i.e.*, process k_1 over k_2, scheme 5.8. Other fluoroalkenes, such as TFE, 1,1-difluoroethene (VDF) and chlorotrifluoroethene (CTFE), readily homopolymerise indicating that k_2 is the predominant process. The differences are clearly due to steric effects.



Scheme 5.8

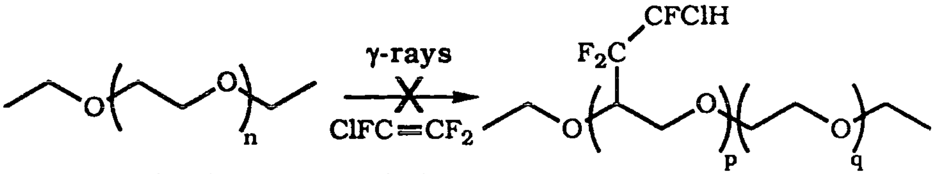
Nevertheless, some compounds have been isolated in which a single molecule of telomerisable fluoroalkene is incorporated into an ether, scheme 5.9.



Scheme 5.9

5.31 Attempted additions to chlorotrifluoroethene

Two reactions were attempted between DEPEG 600 (**57b**) and CTFE (**75**), in acetone and in 2,2,2-trifluoroethanol, using γ-irradiation, scheme 5.10.



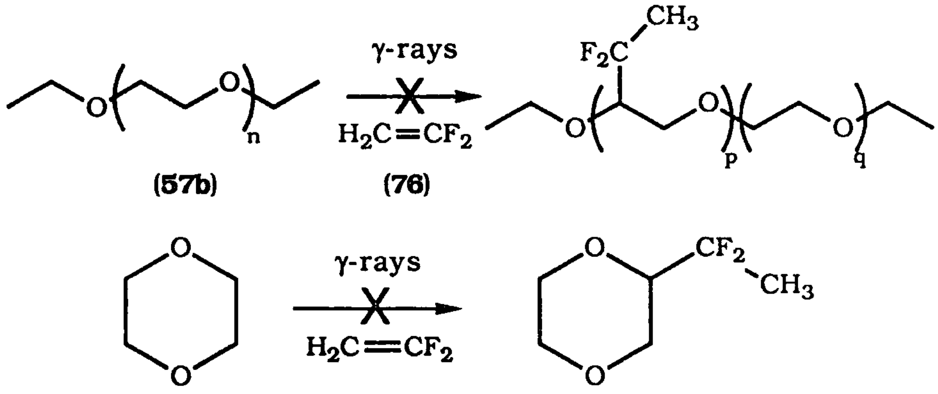
(57b) (75)

Scheme 5.10

In both cases a white solid was recovered after removal of the solvent. NMR analysis showed the product principally to be a mixture of poly(CTFE) and DEPEG. Whether the polymer chains were linked, *i.e.*, the polyether had acted as a telogen and the poly(CTFE) was grafted on, was unclear, as nucleii in the relevant environments would be so few in number. However, the two polymers could not be separated, for example by attempting to dissolve the polyether in acetone, which does suggest the that they were bonded together. The length of the poly(CTFE) chains could not be estimated.

5.32 Attempted additions to 1,1-difluoroethene

Attempts were made to add DEPEG 600 (**57b**) and also 1,4-dioxane (**38**) to VDF (**76**), using γ-initiation, scheme 5.11. As in the case with CTFE, the fluoroalkene was seen to polymerise, a white solid being obtained from the reaction vessel after removal of solvent.



(57b) (76)

(38) (76)

Scheme 5.11

The product of the reaction with 1,4-dioxane (or components of it) was sparingly soluble in acetone. IR analysis indicated the presence of carbon-hydrogen and carbon-fluorine bonds, as well as ether groups. This, together with elemental analysis, suggested the product was a telomer with an average of 250 VDF monomer units grafted on to a dioxane molecule.

In both this reaction and that with CTFE isolation of a simple 1:1 adduct would be possible, as has already been shown,[113,150,151] if the fluoroalkene is in a deficiency; the greater concentration of the ether favouring hydrogen abstraction over propagation. Any unreacted ether can be removed by distillation. With a polyether, however, several fluoroalkene units must be incorporated into the polymer backbone and this will not be possible with a deficiency of fluoroalkene. Performing the reaction in several stages, with a deficiency of fluoroalkene may be a way around the problem, but it seems likely that at very most one more fluoroalkene can be incorporated at each stage.

It should also be noted that oxolane was found to give far better yields than diethyl ether or 1,4-dioxane. The ease of formation the oxolanyl radical means that the k_1 process (scheme 5.8) becomes more favourable compared with the k_2 process. Like 1,4-dioxane, DEPEG will be significantly less likely to form a radical, and so k_2 will become more predominant.

5.4 Conclusions

It seems apparent that the addition of polyethers to cyclic fluoroalkenes can be accomplished with only a little more effort than additions to HFP, and PFPEs based on these types of structures could readily be synthesised, and it is likely that acyclic, disubstituted, non-terminal fluoroalkenes would react similarly. However, additions to more sterically crowded fluoroalkenes (such as decafluoro-3,4-bis(trifluoromethyl)-hex-3-ene) are less fruitful, and PFPEs containing the structural elements that would result from such additions are likely to be beyond this methodology.

Similarly, it is unlikely that PFPEs could be produced by the simple adducts of polyethers to VDF or CTFE, and by analogy to TFE. However, synthesis of intermediates with short chain telomers of these fluoroalkenes grafted on may be accomplished by the use of a chain transfer agent.[152] The fine control of the molecular weight ranges of the products which is a major advantage of this route to PFPEs would inevitably be lost.

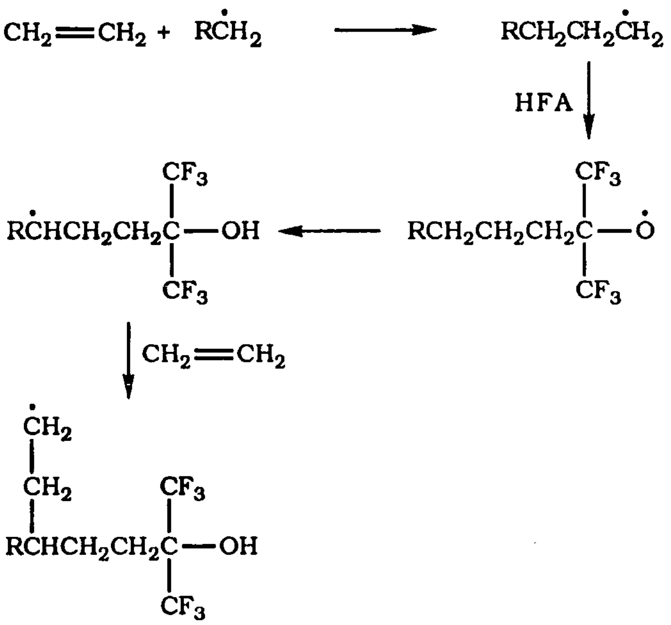
CHAPTER SIX

ADDITIONS TO HEXAFLUOROACETONE

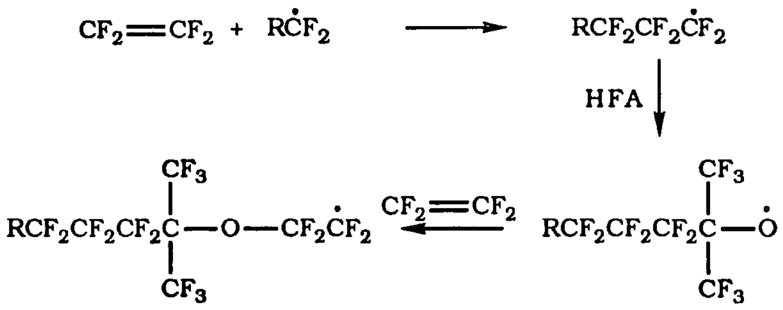
6.1 Fluoroketones

Carbonyl compounds rarely undergo free radical additions, and those few examples are generally not chain reactions.[153] Fluoroketones, by contrast, readily undergo free radical chain reactions by virtue of particularly good electron withdrawing groups on carbon, and the electronic arrangement has been described as more closely resembling a slightly polar alkene than a normal carbonyl.[154] The fluoroalkyl groups also greatly reduce the donating potential of the oxygen severely reducing its reactivity towards electrophiles (little or no protonation is observed in strong acids such as SbF_5-FSO_3H in SO_3[155]). Reactivity towards nucleophiles such as alcohols is increased; the several hydrates of hexafluoroacetone (HFA), for instance, form very readily in the presence of water, and are sufficiently acidic to form salts.[156]

HFA does not homopolymerise,[157] but has been copolymerised *via* free radical routes with a number of alkenes.[158] Reaction proceeds through two pathways, depending on the number of hydrogens on the alkene, and hence the ease with which the oxygen centred radical can abstract hydrogen, schemes 6.1 and 6.2.[159]



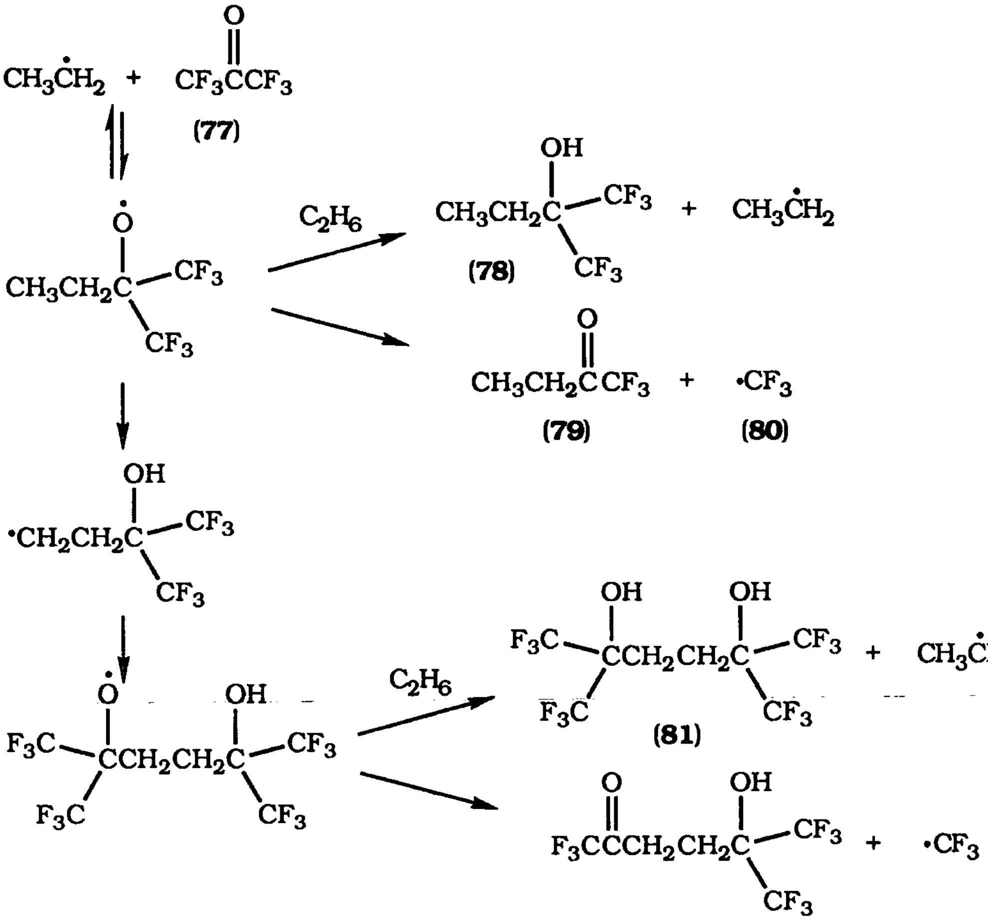
Scheme 6.1



Scheme 6.2

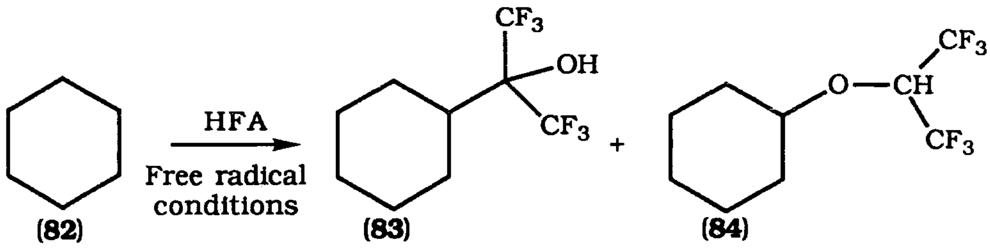
6.11 Free radical additions to hexafluoroacetone

Despite the ease with which HFA (**77**) undergoes free radical chain reactions few additions have been reported, compared with the number involving HFP. Several additions with hydrocarbons have been reported and are the most extensively studied. Gordon and coworkers have looked at the gas phase, photochemically induced reaction with ethane,[160] obtaining an alcohol (**78**) and a diol (**81**) as the primary products. The important steps that they proposed are summarised in scheme 6.3. The 1,1,1-trifluorobutan-2-one (**79**) (identified by GLC) was only significant when the concentration of ethane was low. The trifluoromethyl radicals (**80**) were believed to combine in a termination step, forming hexafluoroethane.



Scheme 6.3

Howard *et al.* have studied the addition of cyclohexane (**82**) to HFA, scheme 6.4,[154] looking at the distribution of the products at various temperatures (-10 to 200°C).

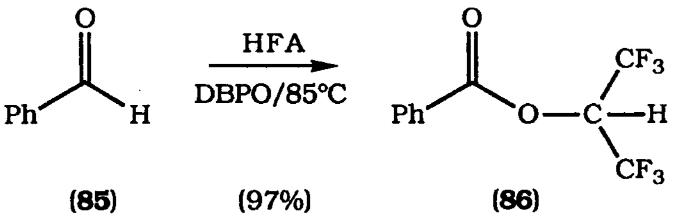


(*e.g.*, 15%, 83:17 isomer ratio)

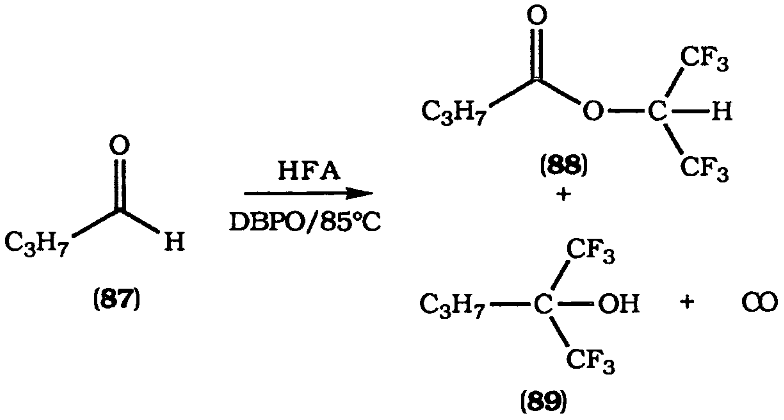
Scheme 6.4

A mechanism was proposed in which attack of an alkyl radical, *etc.*, on HFA is a reversible process, occurring mostly at the less sterically hindered oxygen to give the most stable radical. Hydrogen abstraction, however, is more favoured from the reverse addition product and so the alcohol (**83**) predominates at lower temperatures. At higher temperature the carbon centred radical can more readily abstract a hydrogen, so the proportion of the respective product (**84**) increases. However, another, somewhat simpler explanation is that the nucleophilic cyclohexanyl radical attacks preferentially at carbon, to give the alcohol (**83**), but at higher temperature the process is less selective, and the proportion of ether becomes greater.

Urry *et al.* have reacted some aldehydes with HFA;[161] benzaldehyde (**85**), butanal (**87**) and heptanal, scheme 6.5. Benzaldehyde afforded a 97% yield of the ester product (**86**), but a three fold excess of initiator was used! Butanal and heptanal reacted with only a few percent of initiator to give the ester (**88**), and also the alcohol (**89**) after loss of carbon monoxide from the propyl carbonyl radical. The carbonyl radical is presumably particularly electrophilic and so either attacks more or less exclusively at oxygen, or cleaves a carbon-carbon bond to eliminate carbon monoxide. The radical resultant from the latter process reacts in the same manner as the cyclohexanyl radical to give the alcohol predominantly, and presumably some of the respective ether, the latter in too small a quantity to be detected.



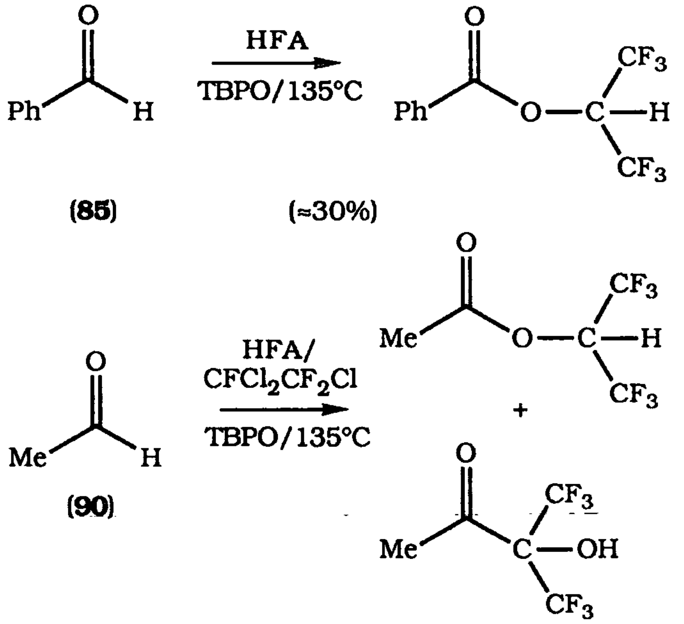
Scheme 6.5



(83% and 10% respectively)

Scheme 6.5 (continued)

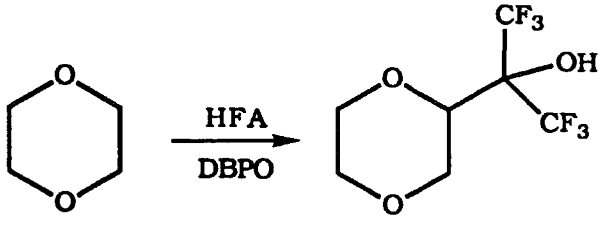
Other workers have found that the first of these reactions proceeds adequately with only minimal peroxide present (using TBPO).[154] Reaction was also performed with ethanal (**90**), without loss of carbon monoxide, scheme 6.6.



(60% and 27% respectively, in different experiments)

Scheme 6.6

Only one reaction with an ether has been reported, involving 1,4-dioxane, scheme 6.7.[154] The alcohol product (**91**) only was identified; it is likely, however, that the other product formed too and was lost during the work up procedure which involved extracting the product mixture into aqueous base.

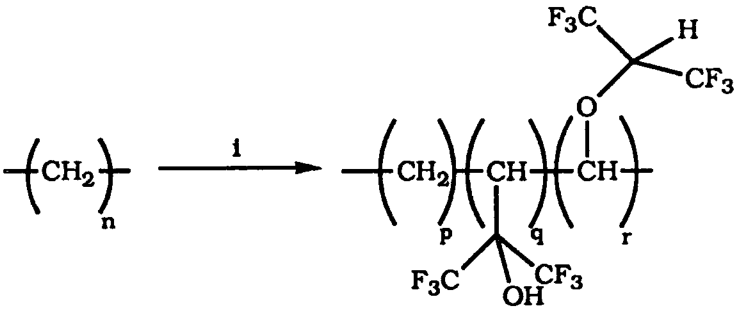


(38) (25%) **(91)**

Scheme 6.7

Reaction with methyl ethanoate and methyl methanoate gave alcoholic products, with addition occurring at either end of the ester, the former also affording the diol.[154] The ethyl esters were also reacted, but gave a complex mixture of products, including some cyclic compounds.

Addition of polyethylene (**24**) to HFA, scheme 6.8, has been investigated by several groups due to the possible applications of modifying a very simple polymer. Both peroxide and γ-ray initiation have been used, to produce materials containing up to 30.7% fluorine.[104,154,162,163]



(24) $n = p + q + r,\ p \gg q + r$

i = HFA/benzene/TBPO/135°C

or HFA/γ-rays/21°C

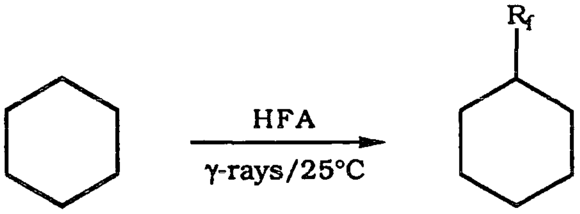
Scheme 6.8

It appeared that the addition of polyethers to HFA could be achieved readily, despite the general lack of reactions with ethers. The products of such additions would be interesting materials in their own right, having pendant fluoroalkylhydroxy groups present, and would also provide especially unusual materials upon fluorination.

6.2 Additions to Model Compounds

6.21 Addition to cyclohexane

Reaction was attempted between cyclohexane and HFA, scheme 6.9, to confirm the results of work already discussed.



(82)

R_f = $-C(CF_3)_2OH$ and $-OC(CF_3)_2H$

Scheme 6.9

Reaction with cyclohexane provided material with an average of up to 1.7 equivalents of HFA incorporated, which ^{19}F NMR showed was a mixture of both the alcohol and the ether products, agreeing with the work discussed earlier.

6.22 Addition to oxolane

Initially oxolane was selected as an ether that particularly readily undergoes free radical additions, scheme 6.10.

(37) **(92)**

R_f = $-C(CF_3)_2OH$ **(92a)** and $-OC(CF_3)_2H$ **(92b)**

i = DBPO/80°C

or γ-rays/25°C

or γ-rays/25°C/acetone

Scheme 6.10

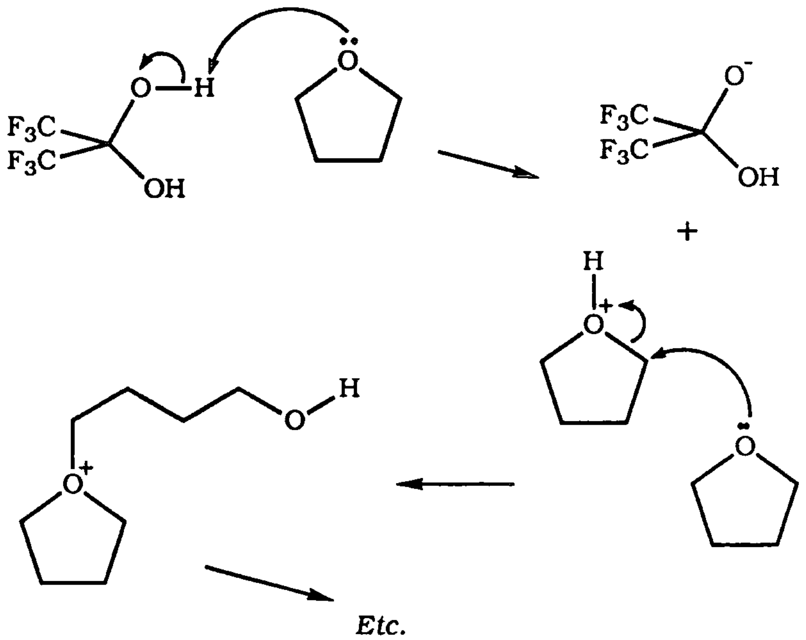
At first, by contrast with the cyclohexane reaction, only a 10 to 20% conversion of oxolane was achieved. GLC analysis of the reaction mixture showed that at room temperature only one product formed, assumed to be the alcohol (**92a**) after the work of Howard and coworkers.[154] At higher temperature two products were found. The product distribution is set out in table 6.1 and was determined from GLC/MS data. Reasons for the low conversions were not established.

Purification of the reaction mixture was attempted by distillation, but led only to severe decomposition, indicated by the rapid darkening of the material (though this had not been observed during reaction at 80°C) and subsequent absence of products in the distillate. It was believed that moisture was present, which formed hydrates with HFA. These hydrates are acidic (the monohydrate has a pK_a of 6.58,[156] for instance) and so may easily have caused oxolane or its adducts to decompose or polymerise. A possible mechanism by which polymerisation may occur is proposed in scheme 6.11.

Temperature	Solvent	Initiator	Oxolane (37)	Alcohol product (92a)	Ether product (92b)
80°C	-	DBPO	87.9%	8.7%	3.4%
25°C	-	γ-rays	82.2%	17.8%	-
25°C	Acetone	γ-rays	93.3%	6.7%	-

Distribution of products and starting material for the reaction of oxolane (37) with HFA

Table 6.1



Etc.

Scheme 6.11

The reaction was repeated, using rigorously dry conditions. UV initiation was used to force the reaction to completion. Although a good conversion of HFA was achieved, the NMR and GLC showed the presence of several components (around 12). It is believed that the less stable, and therefore more reactive, radicals of figure 6.1 are behaving in a far less selective manner than the corresponding radicals in fluoroalkene reactions. Addition occurred at the β– as well as the α-positions, and diadduct formation is common, with a resultant plethora of products.

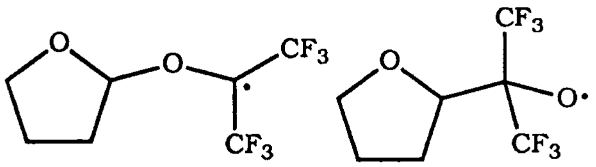
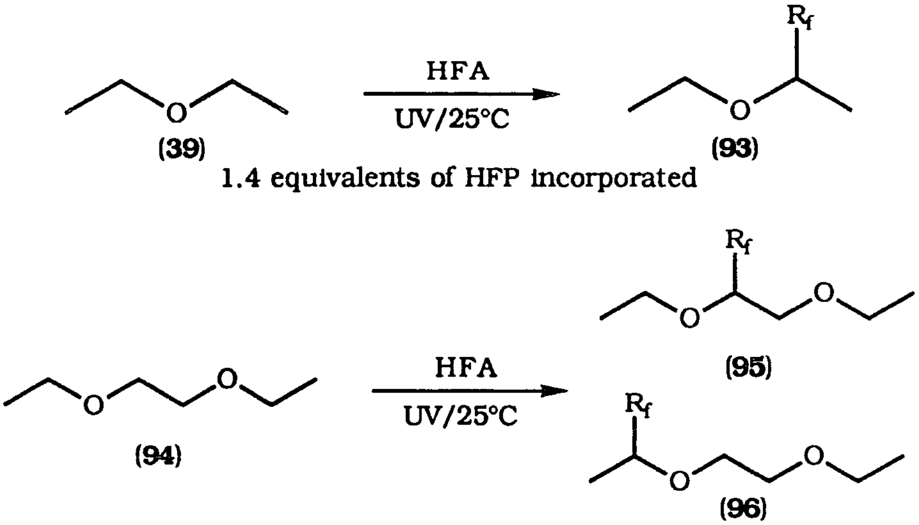


Figure 6.1

6.23 Additions to acyclic ethers

Reaction was attempted with diethyl ether (39) and diethoxy ethane (94), scheme 6.12, using UV initiation, as neither of these ethers can polymerise *via* the sort of process outlined in scheme 6.11.



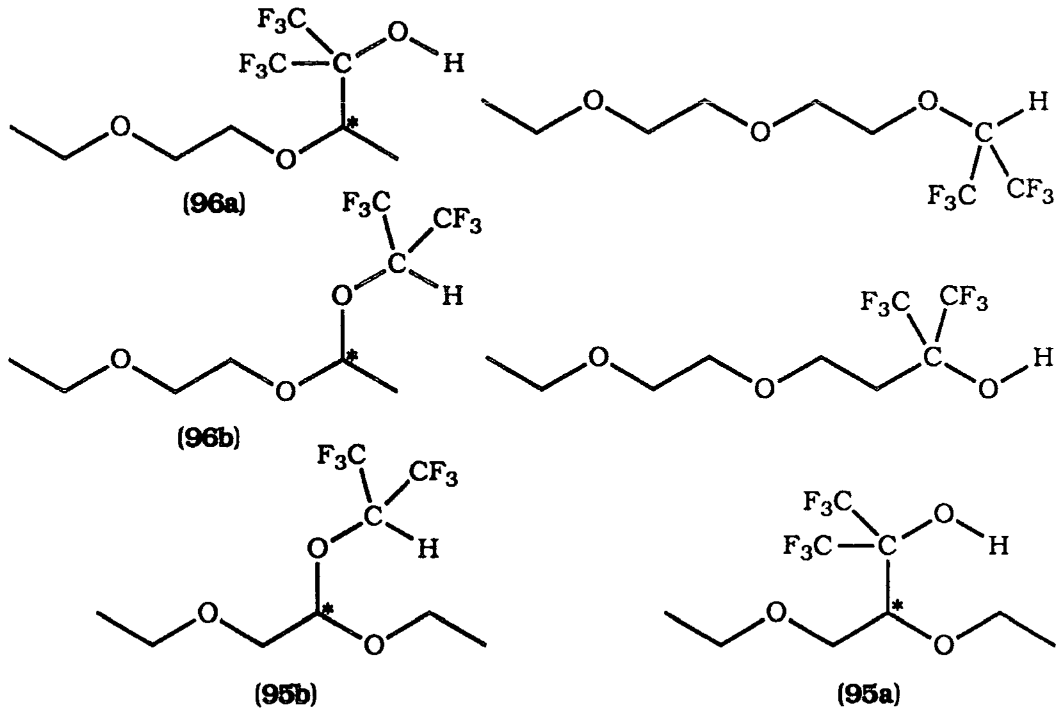
0.4 equivalents of HFP incorporated

R_f = -$C(CF_3)_2OH$ **(93a, 95a, 96a)** and -$OC(CF_3)_2H$ **(93b, 95b, 96b)**

Scheme 6.12

As with oxolane, inspection of the NMR spectra showed the presence of more peaks than could readily be accounted for from the simple α-addition products, and GLC showed the presence of several components.

The ^{19}F NMR spectra of the two product mixtures showed an array of peaks, in the range of -74 to -82 ppm. A 2D COSY spectrum of the diethoxy ethane reaction mixture showed that several of these peaks were coupled to each other. There were two pairs (at -74.5 and -80.5 ppm, and at -75.0 and -80.9 ppm) in which one peak was separated from the other by about 6 ppm. These are likely to be alcohol products (95a, 96a), in which the trifluoromethyl groups are close to the chiral centre (see figure 6.2), and so the diastereotopism is particularly great. Two more pairs were separated by only 1 ppm (-76.9 and -77.9 ppm, and also -76.9 and -78.1 ppm), these are likely to be from the ether products (**95b**, **96b**), the trifluoromethyl groups being further removed from the chiral centre. Other peaks were apparently not coupled, presumably due to addition at the methyl carbons of diethoxy ethane, which would not lead to the formation of a chiral centre, and so both trifluoromethyl groups would be identical. The presence of further peaks was attributed to higher adducts.

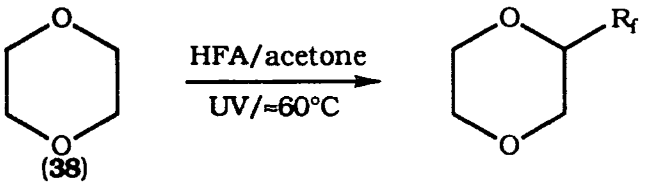


Structural possibilities for the monoadduct of HFA to diethoxy ethane

Figure 6.2

6.24 Addition to 1,4-dioxane

1,4-Dioxane (**38**) has four equivalent sites and so the number of isomers of the monoadduct is therefore restricted. It also has very little ring strain, and it was believed that polymerisation would be unlikely to occur. It was also successfully added to HFA, scheme 6.13.



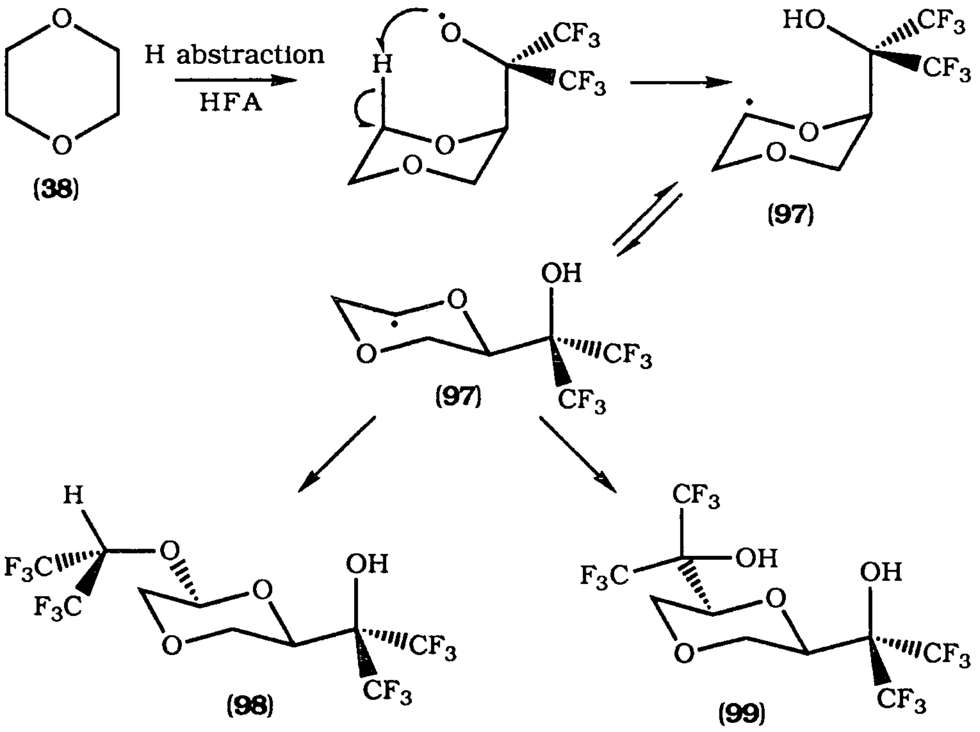
R_f = -C(CF$_3$)$_2$OH and -OC(CF$_3$)$_2$H

(10.1% diadduct)

Scheme 6.13

The product crystallised out of solution during reaction, and was sufficiently stable to undergo sublimation. GLC/MS analysis showed some starting material still present [repeated attempts at purification could not completely remove 1,4-dioxane (**38**) from the product], and two other peaks assigned to diadducts - no monoadduct was identified. Thus, either the monoadduct is very reactive and any that forms promptly reacts further to give the diadduct, or an intramolecular hydrogen abstraction process is occurring in this reaction, exactly as in the addition of diethyl ether to HFP. The former seems unlikely as fluoroalkyl groups tend to reduce the reactivity of ethers towards free radical addition, as was seen in chapter three. The latter theory is, however, supported by the relatively low number of isomers found; an intramolecular mechanism will force a particular substitution pattern for the diadduct. ^{19}F NMR clearly showed the presence of three sets of peaks, each set comprising two coupled quartets, in approximately equal amounts. In one set the quartets were close (-80.4 and -80.7 ppm), and this was assigned to CF_3 fluorines next to an ether linkage. The other two (at -76.8 and -79.8 ppm, and at -77.1 and-80.1 ppm) were attributed to CF_3 fluorines next to an alcohol group.

It is suggested that two diadducts form, both with the bulky fluorinated side group equatorial (*i.e.*, with a *cis* configuration), one with two carbon alkylated HFA units attached (**99**), one (forming twice as much) with one carbon alkylated HFA unit, and one oxygen alkylated (**98**). An explanation is tentatively proposed, scheme 6.14. As has already been said, carbon alkylation of HFA proceeds more readily, this, then, is the first step. Intramolecular hydrogen abstraction then occurs across the oxygen. This radical (**97**) is very affected by the bulky hexafluoro-2-hydroxyprop-2-yl substituent, and this has two effects, first to cause an equatorial-equatorial conformation in the product (forcing *cis* substitution), and second to favour attack at the more accessible oxygen of the HFA [note that 1,4-dioxane (**38**) is known to favour the chair formation[164]].

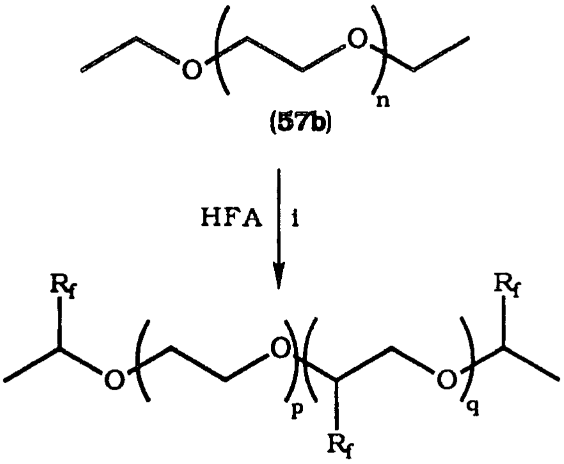


1:2 ratio of (98) to (99)

Scheme 6.14

6.3 Additions to Polyethers

Using UV initiation, DEPEG 600 (**57b**) was reacted with HFA to provide material with several equivalents of HFA incorporated into the polyether, scheme 6.15. γ-Ray initiation was also attempted with negligible success.



$R_f = -C(CF_3)_2OH$ and $-OC(CF_3)_2H$
i = γ-rays/25°C/acetone
or UV/60°C/acetone
For example; $p \approx 10$, $q \approx 3$
Scheme 6.15

Due to the polymeric nature of the product, the material could not be purified as previously (*i.e.*, by vacuum distillation, sublimation or recrystallisation) and so it was especially important that water was rigorously removed from these experiments. In the absence of HFA hydrate, the products could be heated to 200°C under vacuum (0.4 mmHg) without significant darkening, to remove all solvent and remaining HFA, which had a very high solubility in the product (about 8 molar equivalents of HFA that had been dissolved in the material were thus removed). The resultant material had 5 molar equivalents of HFA incorporated, as established by NMR, with an average of 6 carbon alkylated HFA units to every one oxygen alkylated unit.

Although this is not a particularly high conversion of HFA it clearly demonstrates the feasibility of adding polyethers to HFA, at least as easily as the addition of polyethers to fluoroalkenes other than HFP.

CHAPTER SEVEN
SURFACE MODIFICATION

7.1 Fluorine at Surfaces

7.11 Fluoropolymer coatings

The surfaces of fluorine containing materials are notable for their low coefficients of friction, their non-stick properties and their chemical inertness, as was mentioned in chapter one. Some other important properties include hydrophobicity (for reducing water absorption), and resistance to UV light and microorganisms. These effects are clearly the effects of the strong carbon fluorine bond and the density of electrons surrounding the molecules. Such properties will also be present in materials in which only the surface is fluorinated.

The two obvious methods of obtaining a fluorine containing surface are; to react a surface with fluorine or some other fluorinating agent, or to apply a fluorine containing coating to the surface. The former technique is applicable to polymers such as polyethylene.[165] Fluorinated high density poly(ethylene)is, for example, used increasingly in the car industry for fuel tanks.

For applications with metals, a fluoropolymer coating is used, and PTFE is probably the best example of this. PTFE has found numerous uses such as lining for tanks, drums and vessels designated for corrosive chemicals, coatings for machine parts that are difficult to lubricate (such as artificial hearts and satellites) and, most well known, as a coating for cookware.

However, there are several drawbacks to using PTFE that have restricted its use to some extent, to certain special cases. These disadvantages are: low adhesion to a surface (clearly an inherent problem with any material with such exceptional non-stick properties); and its processability problems.[166] PTFE softens at 342°C, but does not properly melt, and films must instead be formed by hot sintering (applying powdered PTFE to a heated mold under pressure) at about 340-400°C, and, due to the lack of flow, pin holes can arise. Several coatings are therefore generally required.

Though less inert, poly(CTFE) is less crystalline than PTFE and can be melt processed.[166] It is, however, soluble in hot halogenated solvents and swells in some hydrocarbons. It is slightly less inert than PTFE (it reacts with molten alkali metals and fluorine) and has found applications similar to those of PTFE, if in less harsh conditions.

7.12 Fluoropolymers as additives to pre-treated metal coatings

Poly(VDF) [and poly(vinyl fluoride) to some extent] has found quite a market as an additive for metal coatings. Despite its lower fluorine content it still imparts a major improvement in chemical resistance, stain resistance and self-cleaning properties to metal coatings. So long lasting is the surface that manufacturers of poly(VDF) coatings have offered warranties of up to twenty years.[166,167] The lower fluorine content means that poly(VDF) is a good deal easier to apply and adhere to a surface. All this has worked to create a large market for poly(VDF) on metal sidings for industrial and commercial buildings.

Poly(VDF) is applied as a resin blended with heat stable pigments and other additives, and mixed with a solvent.[168] It can be applied to a metal surface by coil coating (applied to metal sheet as it unwinds from a coil) or spray techniques, normally on aluminium or galvanised steel. This is then cut and shaped for the application.

More recent innovations that have yet to reach the market place have been proposed such as the use of fluorine containing epoxides; for example, those of figure 7.1.[169] PTFE can readily be suspended in these compounds (giving mixtures containing up 40% PTFE), which can then be cured, to provide a tough, cross linked, highly fluorinated surface. Due to the incompatibility of conventional curing agents, fluorinated anhydrides and silicone amines, figure 7.2, have been developed in this rôle.[170] Such coating would combine a very high fluorine content with ease of processability, as curing can be performed after coating.

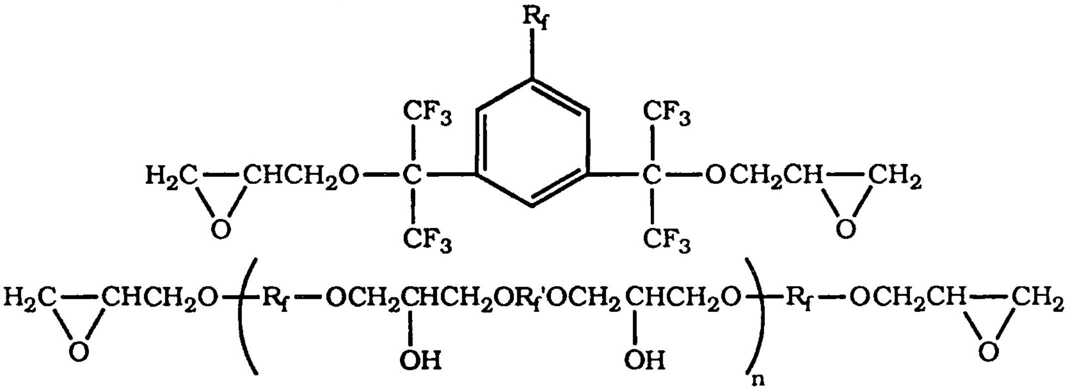


Figure 7.1

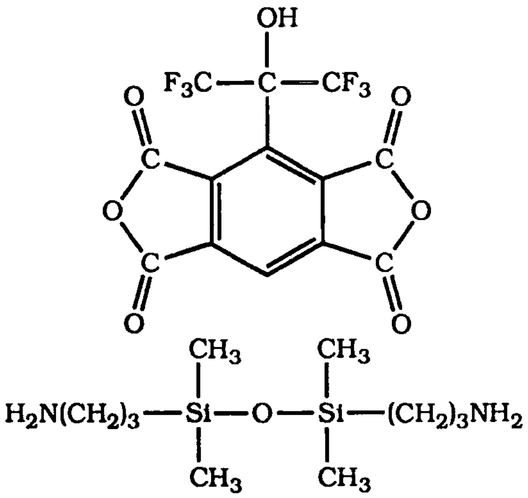


Figure 7.2

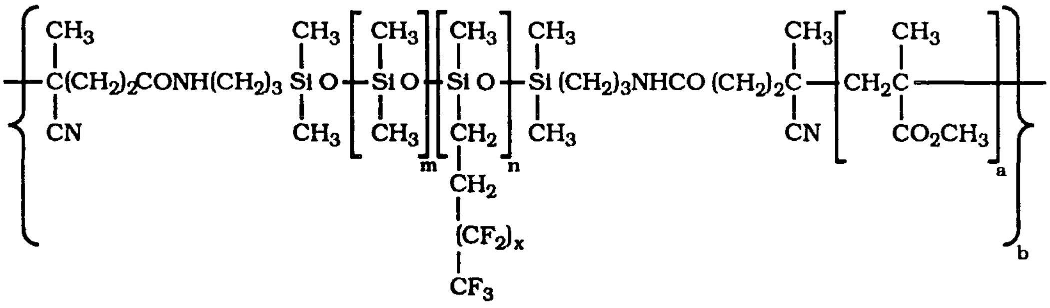
7.13 Fluoropolymers in paint

All these materials suffer from one drawback for the domestic market in that they are all factory applied. A truly universal fluorinated coating could be applied with a paint brush in the home. The sort of material required would necessarily have to be a polymer (for low volatility), with a high fluorine content, and still readily form a suspension, or even better a solution, in common solvent, such as are found in paints. Clearly the cost of such additives would also be a consideration.

The materials discussed in chapter four presented themselves as candidates for these applications, fulfilling the first three criteria, being polymeric, containing 50-55% fluorine and being soluble in, for instance, acetone and chloroform, and even forming suspensions in water.

Furthermore, papers have recently been published in which fluorine containing polymers have been added to polymer solutions, and during evaporation of the solvent, the fluoropolymer has migrated to the interface, giving a highly fluorinated surface, with relatively little fluorine in the bulk. This would have major financial savings as clearly the quantity of fluoropolymer required would be kept to a minimum.

Inoue and coworkers have added fluoroalkylsilicone-polymethylmethacrylate (PMMA) block copolymers (**100**), figure 7.3, to PMMA in chloroform.[171]



$$\left\{ -C(CH_3)(CN)(CH_2)_2CONH(CH_2)_3Si(CH_3)_2O - \left[Si(CH_3)_2O \right]_m \left[Si(CH_3)(CH_2CH_2(CF_2)_xCF_3)O \right]_n - Si(CH_3)_2(CH_2)_3NHCO(CH_2)_2C(CH_3)(CN) - \left[CH_2C(CH_3)(CO_2CH_3) \right]_a - \right\}_b$$

(100)

$x = 5, m = 59, n = 9$

and

$x = 7, m = 49, n = 9$

Figure 7.3

Films were prepared on glass, the solvent evaporated over three days. They found that contact angles at the air interface were greater than at either the glass interface, or the air interface in a sample containing non-fluorine-containing silicone-PMMA copolymer, and furthermore, there was an abrupt rise in the contact angle as the proportion of copolymer to PMMA was raised from 0.0 to 0.2%. ESCA analysis also showed a sudden rise in fluorine and silicon content, compared with carbon, in the surface over the same range. It appeared that the fluoropolymer was tending to aggregate at the surface. Polarisation IR also indicated that the surface had a high proportion of fluoroalkyl groups in it, aligned parallel to each other, perpendicular to the surface.

A further set of experiments was done using a copolymer with only three fluorine atoms in the side chain (*i.e.*, with $x = 0$, and with $m = 0$, $n = 14$) blended with PMMA. In this case, ESCA and contact angle measurements indicated that the fluoroalkyl groups were oriented towards the bulk of the composite, and in fact were solubilising the polysilicone units in the PMMA structure. This effect of a trifluormethyl group is well known, especially in the plant protection industry,[172] but these two sets of results contrast well the difference between a small number of fluorines in a molecule increasing lipophilicity, and a large number dramatically lowering lipophilicity and hydrophilicity.

Other workers have looked at a urethane acrylate derived from a polyol having hexafluoropropyl side groups. Again ESCA was used to show migration to the surface, this time by looking at the proportion of fluorine at the surface relative to the bulk .[173-175]

A more significant development within the year is the marketing by Imperial Chemical Industries of a Teflon containing varnish. However, no details as to how the PTFE is dispersed in the varnish has appeared in the literature.

7.2 DEPEG/HFP Adducts in PMMA

To evaluate the feasibility of using DEPEG adducts (**58b**) of HFP in paint, some samples were prepared by dissolving the adducts in acetone and mixing this with PMMA (**101**), also dissolved in acetone. The solution was applied to a glass slide and the solvent allowed to evaporate.

ESCA analysis of the surface of the slides was performed, the results for the sample with 50% adduct added are presented in depth. The fluorine ESCA spectrum showed one peak at 689.0 eV, with an adjusted intensity of 7754,* due to fluorine bonded to carbon. The oxygen spectrum showed two peaks due to oxygen next to silicon (531.3 eV; from the glass slide; an indication of accuracy) and next to carbon (533.7 eV), with intensities 349 and 2346 respectively.

Deconvolution of the carbon spectrum showed 8 peaks, detailed in table 7.1.

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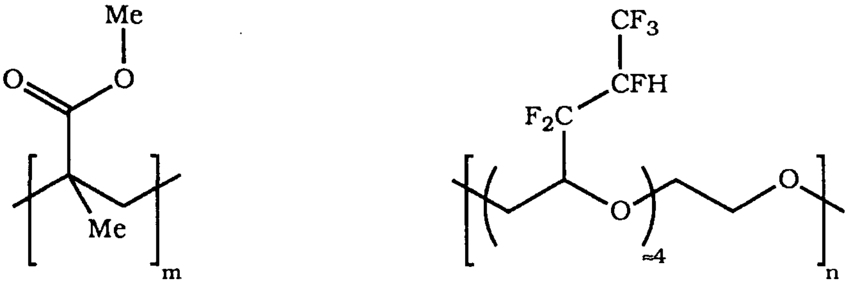
* Areas are adjusted, relative to carbon, allowing for different photoionisation cross-sections of an atom.

Binding energy/eV	Intensity	Assignment
283.1	788	[HC *(glass)*]
285.5	1407	HC *(PMMA)*
287.3	2179	C-O *(adduct & PMMA)*
288.0	1058	O-C-R_f *(adduct)*
289.0	585	-CO_2- *(PMMA)*
289.7	1002	CFR_f *(adduct)*
291.5	1065	CF_2 *(adduct)*
294.0	1119	CF_3 *(adduct)*

Peaks and assignments for the ^{1}s carbon ESCA spectrum
50% DEPEG/HFP (**58b**) adduct in PMMA (**101**)
Table 7.1

A calculation of the elemental ratio gave a formula of $CF_{0.84}O_{0.29}Si_{0.06}$,[†] which corresponds to $CF_{0.92}O_{0.28}$ when signals from the glass slide are subtracted. Figure 7.4 gives the elemental ratios for the components.



(101)
$CO_{0.4}$

(58b)
$CF_{1.09}O_{0.22}$

Figure 7.4

Calculations based on the oxygen ratios indicates that the surface is 71% adduct (**58b**), 39% PMMA (**101**). Interestingly, a calculation based on fluorine content suggests the surface to be 86% adduct, indicating that the fluoroalkyl groups are orientated towards the surface, agreeing with the findings of Inoue mentioned earlier.

Further samples were prepared, in which the amount of adduct in the composite was reduced, from 50 to 1%.

As can be seen from the table the CF_3 carbon has a very distinctive binding energy, quite different to other carbon environments, which tend to overlap in the ESCA

[†] Hydrogen atoms are not detected by ESCA.

spectrum to a large extent. The most elegant procedure, it was felt, would be to compare the intensity of the CF$_3$ peak as a proportion of the whole in the ^{1}s carbon spectrum. The graph below shows this expressed as a percentage with both the theoretical values (assuming perfectly homogeneous mixing) and actual values, plotted against the percentage of adduct in PMMA in the bulk.

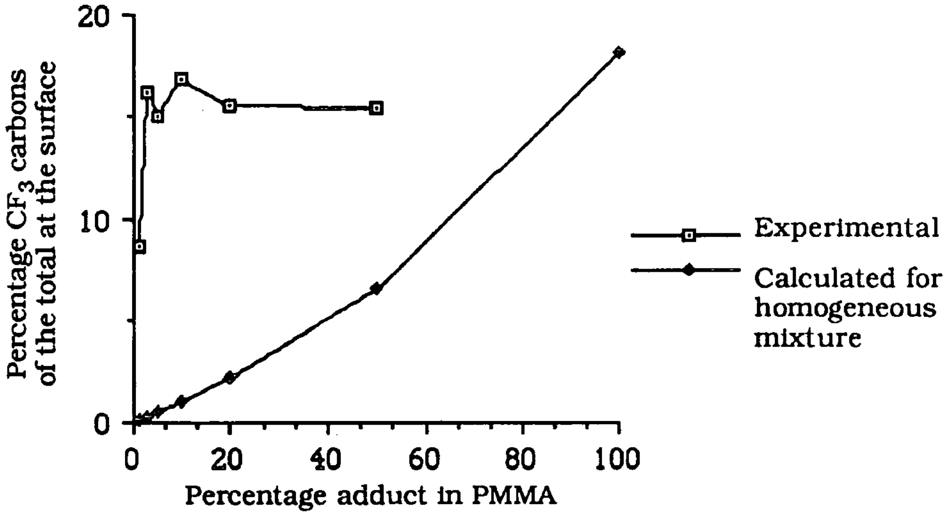


Figure 7.5

There is a pronounced deviation between the two sets of data. The amount of adduct at the surface is independent of the concentration in the bulk in the range of 2.5 to 50%. Clearly, migration does occur.

The value of 15% CF$_3$ carbons is equivalent to the surface being about 95% adduct. This is higher than either the figure derived from the oxygen to carbon ratio (71%) or the fluorine to carbon ratio (86%) in the 50% sample discussed earlier, and this presumably reflects the orientation of the adduct. The fluoroalkyl groups tend to lie nearer the surface than the rest of the adduct, but the CF$_3$ groups are particularly predominant at the surface.

Finally, as these experiments are only models for a paint system, some samples were prepared mixing the same adduct with white paint to varying amounts. Due to its nature, it was not possible to measure the amount of paint used, and so quantitative results were unobtainable, however, ESCA analysis of these samples showed a highly fluorinated surface, comparable to that observed with the PMMA samples.

CHAPTER EIGHT
DIRECT FLUORINATIONS

8.1 Liquid Phase Fluorinations

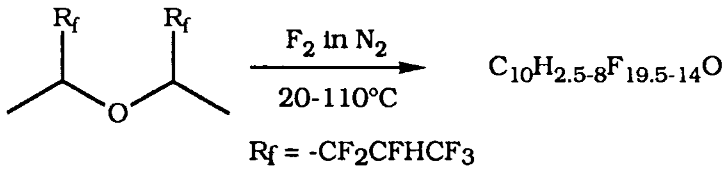
Several techniques for the perfluorination of organic substrates have already been discussed in chapter two, though it is worth while reiterating the main practices used for moderating the action of fluorine on a substrate:

(i) Reduce the population of atomic fluorine present - lower the temperature or reduce the concentration of fluorine.

(ii) Allow efficient and rapid dissipation of heat to avoid localised energy 'hotspots', which may lead to bond cleavage - achieved by using substrates with a high degree of vibrational freedom or by using metal packing.

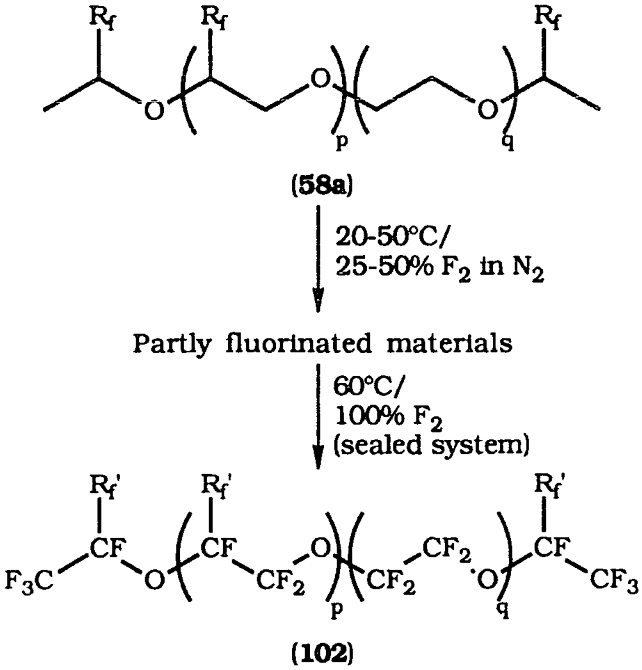
(iii) Reduce the number of collisions between fluorine atoms and the substrate that lead to reaction. This can be done by using a deactivated substrate, such as one already containing fluorine atoms.

Workers in these laboratories have developed their own methodology involving liquid phase fluorination for fluorine containing compounds, specifically various adducts of hydrocarbon derivatives with HFP.[104,121] In the early stages of reaction dilute fluorine is used to reduce the concentration of fluorine atoms present. The pendant fluoroalkyl groups provide an efficient energy dissipation mechanism, and also protect the molecule. The technique originally involved passing fluorine diluted in nitrogen down a stainless steel capillary, into a tall, narrow, glass vessel containing the substrate.[121] The large surface area of the vessel helped with temperature control. As reaction proceeded, and fluorine concentration was increased, it was found that the substrate became more and more deactivated and it proved exceedingly difficult to obtain a perfluorinated product by this technique, scheme 8.1.



Scheme 8.1

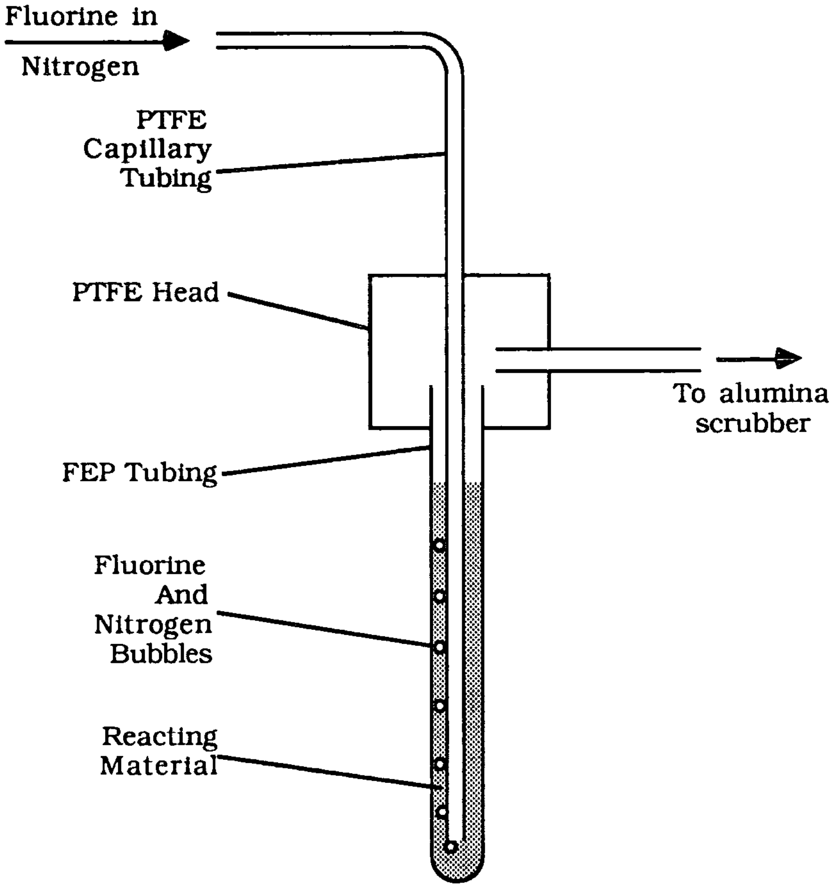
The adduct between HFP and DEPEG 400 (**58a**) was similarly reacted with fluorine in nitrogen. Again the perfluorinated material (**102**) could not be made. This was, however, subsequently obtained by further reacting the material in a sealed vessel under an atmosphere of pure fluorine at 60°C, scheme 8.2.



$p = 4\text{-}5,\ q = 3\text{-}4$

$R_f = \text{-}CF_2CFHCF_3,\ R_f' = \text{-}CF_2CF_2CF_3$

Scheme 8.2

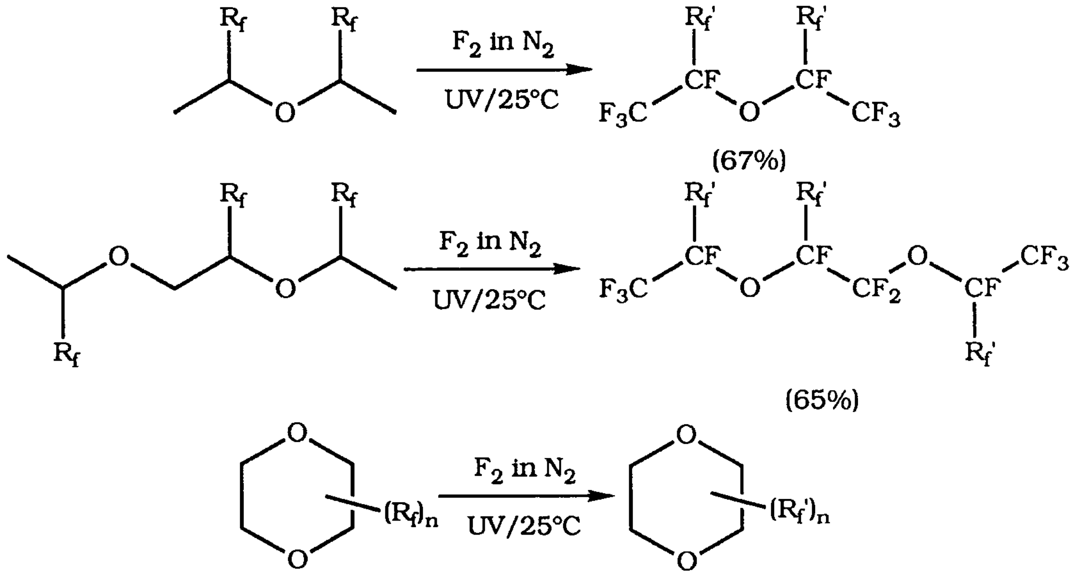


Fluorination apparatus

Figure 8.1

The apparatus was subsequently developed into that of figure 8.1, the stainless steel capillary being replaced by PTFE, and the glass vessel by a fluorinated ethylene-propylene (FEP) reactor (*i.e.*, a copolmer of TFE and HFP).[104]

This had some advantage over the previous technique in that the apparatus was virtually inert to fluorine, and so could stand up to the reaction conditions more readily. More importantly, FEP is transparent to UV light so, in the later stages of reaction, this could be used to promote the formation of fluorine atoms in the substrate, enhancing reaction. It was thus possible to completely fluorinate a number of compounds, scheme 8.3.



n = 1 (43%), n = 2 (64%), n= 3 (60%), n = 4 (58%)

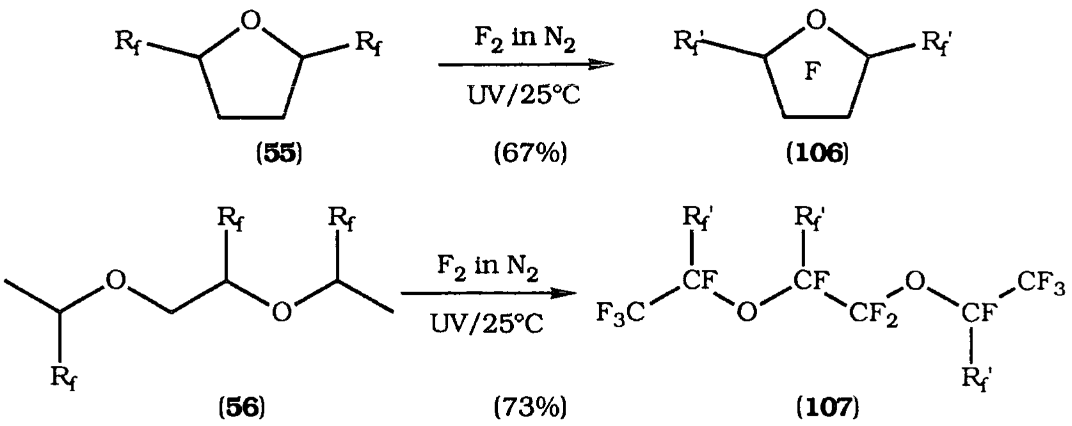
$R_f = -CF_2CFHCF_3$, $R_f' = -CF_2CF_2CF_3$

Scheme 8.3

This demonstrated the feasibility of this exceptionally simple experimental technique. Attempts were also made to perfluorinate the 1:1 adduct of oxolane with HFP without success. Fluorination of *tert*-amines and ketones were likewise unsuccessful, but the 1:2 adduct of cyclohexane with HFP was fluorinated in 57% yield.

8.2 Fluorination of Model Compounds

In the present work, as a preliminary to more complicated fluorinations, two reactions were attempted on model compounds; 2,5-di(2*H*-hexafluoropropyl)oxolane (**55**) and 1,2-di(2,2,3,4,4,4-hexafluoro-1-methylbutoxy)-3,3,4,5,5,5-hexafluoropentane (**56**), scheme 8.4. The concentration of fluorine was raised from 5% to 50%, UV irradiation only being used in the last stage.

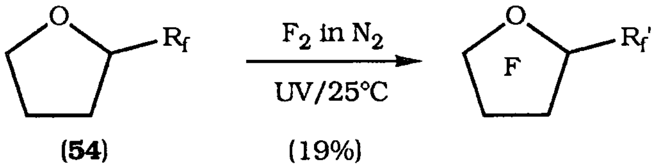


Rf = $-CF_2CFHCF_3$, Rf '= $-CF_2CF_2CF_3$

Scheme 8.4

These high yields confirm the viability of the technique, and suggested that it could be readily applied to the fluorination of higher molecular weight materials.

The reaction was also attempted with 2-(2*H*-hexafluoropropyl)oxolane (**54**), scheme 8.5, but with a very low yield. This was attributed to the volatility of the starting material, product and intermediates, resulting in them being entrapped in the gas flow and so escaping from the reaction vessel. This could clearly be overcome by the incorporation of a low temperature condenser into the apparatus, but this presented problems with hydrogen fluoride (HF) also being condensed (it has a boiling point of 19°C) and allowed to accumulate in the reaction vessel, leading to possible decomposition. In general, the HF is removed by the constant flow of gases through the reaction vessel. As this project is more concerned with high molecular weight materials, this was pursued no further.

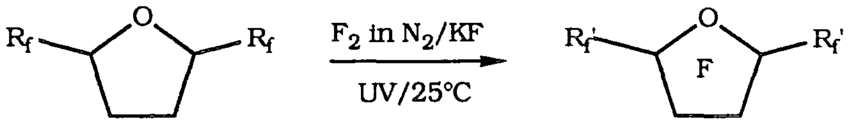


Rf = $-CF_2CFHCF_3$, Rf '= $-CF_2CF_2CF_3$

Scheme 8.5

8.21 Use of a hydrogen fluoride scavenger

As has already ben alluded to, the inevitable by-product of direct fluorination of hydrocarbon derivatives is HF, which is, of course, very corrosive. It was felt that the presence of HF, even in small quantities, may be having a detrimental effect on the yield of these reactions and some investigation of this effect was felt to be in order. Much of the more recent work on direct fluorination has used sodium fluoride as an HF scavenger (as it readily forms sodium hydrogen difluoride),[68,72,74,76] and so reaction was performed with potassium fluoride present in the reactor. For comparison with previous work, 2,5-di(2*H*-hexafluoropropyl)oxolane (55) was chosen as the substrate, scheme 8.6, the same conditions otherwise being used.



(55) **(106)**

$R_f = -CF_2CFHCF_3$, $R_f' = -CF_2CF_2CF_3$

Scheme 8.6

The product obtained contained no hydrogen, but did contain a large proportion of involatile material, and mass spectrometry indicated the presence of components with masses in excess of 800. It was obvious that the potassium fluoride was having an adverse effect, possibly promoting crosslinking or polymerisation reactions. As no definite evidence of the deleterious effects of HF was available, it seemed unproductive to investigate any further.

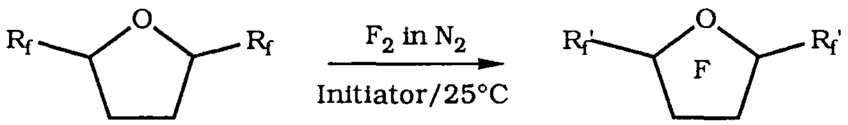
8.22 Attempted perfluorination by addition of starting material

Although the use of UV irradiation is highly convenient on a laboratory scale, it is unsuitable for an industrial sized reaction. The effect of UV light is to homolytically break the fluorine-fluorine bond, increasing the number of fluorine atoms present. The free radical chain is thereby initiated, and reaction proceeds. This is only necessary towards the end of the reaction. In the early stages, fluorine molecules will react directly with the substrate to produce fluorine atoms and carbon centred radicals, both of which will initiate the reaction chain, scheme 8.7 (see also chapter two, section 2.4).

$$R_3C—H \;+\; F—F \longrightarrow R_3C^\bullet \;+\; H—F \;+\; F^\bullet$$

Scheme 8.7

It therefore seemed possible that the addition of small amounts of starting material during the final stages of reaction would lead to perfluorination, and this was supported by work by Lagow^{96}. It was hoped that the fluorine would readily react with the starting material, and once fluorine atoms were produced the free radical chain would proceed readily with the highly fluorinated intermediates.



(55) **(106)**

Scheme 8.8

Again reaction conditions were chosen to allow a comparison between this and previous reactions; 2,5-di(2*H*-hexafluoropropyl)oxolane (**55**) was used as the substrate. Instead of using UV irradiation, a few drops of the starting material were admitted to the reaction vessel on five occasions during the last period of fluorination, scheme 8.8. The course of the reaction was followed by ^{1}H and ^{19}F NMR, comparing the integrations using (trifluoromethyl)benzene as a standard. There was no discernible increase in the degree of fluorination. It was believed that this was due to the already low reactivity of the starting material towards elemental fluorine.

8.23 Perfluorination by addition of hydrocarbon

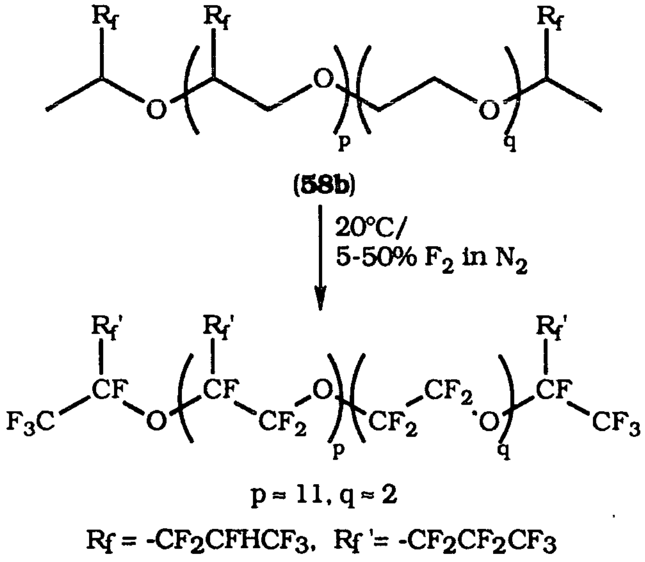
Given that 2,5-di(2*H*-hexafluoropropyl)oxolane (**55**) was insufficiently reactive to promote perfluorination, reaction was attempted with a hydrocarbon, benzene, known to be extremely reactive towards fluorine. The previous experiment, with 2,5-di(2*H*-hexafluoropropyl)oxolane, was repeated.

Reaction proceeded to give a perfluorinated product. There was some amount of involatile residue present in the product mixture, which, it it believed, was the cross-linked products of fluorinating benzene.

It is believed that such residues could be kept to a minimum by using a very slow, but constant, introduction of benzene (or similar) into the reaction vessel. With only a very small concentration of benzene present, the chances of oligomerisation and similar reactions would be greatly reduced. However, the overall amount of benzene added would be comparable, and so a corresponding number of free radical chains would be initiated. Furthermore, the initiation would take place evenly as time passed rather than occurring mainly as a measure of benzene was added, avoiding sudden exotherms. Although somewhat complicated for laboratory use, such a technique should readily be possible on an industrial scale.

8.3 Fluorination of the Adduct of HFP with DEPEG 600

Given the ease of fluorinating low molecular weight materials using this technique, it was believed that the HFP adducts of polyethers (**58**) would behave just as well, and was achieved, to some extent, by previous workers.[103] Fluorination was attempted with the DEPEG 600 adduct (**58b**), with 13 equivalents of HFP incorporated, scheme 8.9.



Scheme 8.9

Although the reaction proceeded without problem at first, the liquid became steadily more viscous, presumably due to increased hydrogen bonding as the number of fluorines increased. Eventually the stage arrived where the gas mixture could no longer form bubbles and the flow stopped.

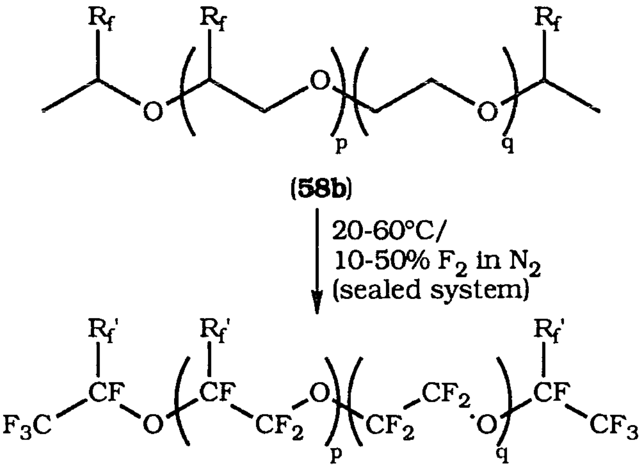
8.31 At elevated temperature

The previous reaction was repeated, this time the reaction vessel was heated to reduce the viscosity of the substrate. Initially fluorine was introduced diluted 5% in nitrogen at room temperature. Later the reaction was heated up to 50°C, whilst fluorine diluted 5% in nitrogen was admitted. In the next stage the temperature remained at 50°C as the fluorine concentration was increased.

At this point the experiment was abandoned as formidable darkening of the reaction mixture had occurred, indicative of decomposition. It was clear that the reaction conditions were too severe.

8.32 In a sealed system

After the work of Telford,[121] it was believed that perfluorination could more readily be achieved using a sealed system, scheme 8.10. In such an experiment the rate of fluorination is limited by the diffusion of fluorine into the substrate, and this will speed up as the substrate becomes more and more fluorinated, and so a better solvent for fluorine. The vessel can be heated, and fluorine (diluted in nitrogen) could be used under pressure. One drawback of this technique, however, is that the reaction mixture is not visible during reaction, preventing ideal assessment of reaction state and conditions.



$p \approx 11, q \approx 2$

$R_f = -CF_2CFHCF_3$, $R_f' = -CF_2CF_2CF_3$

Scheme 8.10

The material was examined after being treated with 10% fluorine in nitrogen. Although the surface had darkened, the bulk of the material appeared to have survived the conditions. Indeed, NMR analysis suggested that it had not been altered at all. It appeared that only the surface was being fluorinated, and this was occurring under conditions too harsh for it to endure. The experiment was taken no further.

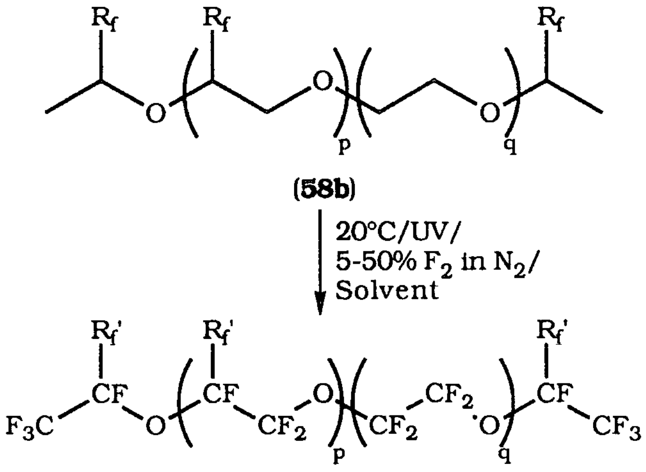
8.33 In a solvent

It was clear that the viscosity problem would not be solved by heating, as this inevitably led to too harsh reaction conditions. Thus it was decided that a solvent would be necessary. The solvent required had to dissolve the partly fluorinated starting material, the highly fluorinated intermediates and the perfluorinated product. Furthermore it had to be able to withstand the effects of elemental fluorine.

The model compounds (**55** and **56**) discussed at the beginning of this chapter were selected for this rôle. As has already been seen, they do react with elemental fluorine under the conditions prescribed. However, they will readily dissolve the polyether adducts, and as they themselves become fluorinated they will become progressively better solvents for the highly fluorinated intermediates. Towards the end of the reaction the solvent will be more or less perfluorinated, and so will dissolve the more or less perfluorinated substrate.

For consideration on an industrial scale, this technique is attractive in that the perfluorinated solvent can be marketed for application such as vapour phase soldering, *etc.* discussed in chapter one. After fluorination the two components can be readily separated.

The HFP adduct with DEPEG 600 (**58b**) was fluorinated, scheme 8.11, using the triadduct of diethoxy ethane with HFP (**56**) as a solvent.



(58b)

(103)

(48-54%)

$p \approx 11, q \approx 1$

Rf = $-CF_2CFHCF_3$, Rf '= $-CF_2CF_2CF_3$

Scheme 8.11

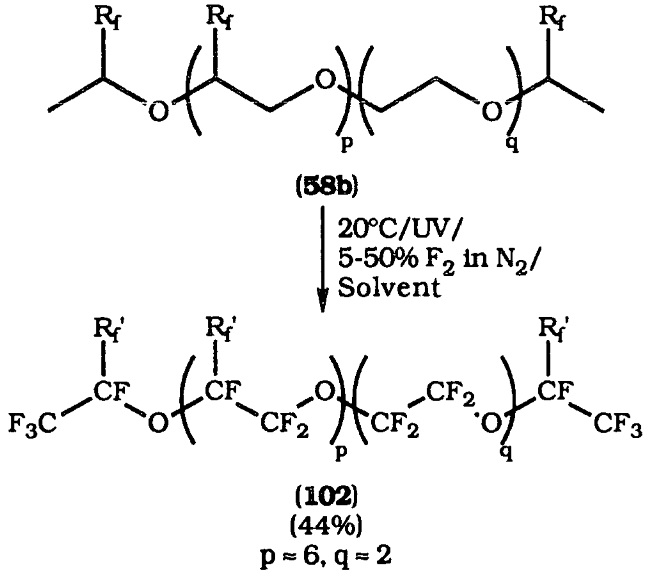
Reaction proceeded with ease. In the early stages the substrate mixture decolourised and remained clear and colourless for the rest of the reaction. After the reaction mixture was perfluorinated (followed by ^1H NMR), the solvent was removed by distillation under vacuum to leave the PFPE product (**103**), yield 48%. The major cause of a reduced yield was the viscosity of the product, leading to losses during sample handling. It is believed that such losses would be minimised if these reactions were performed on a large scale.

A second reaction was also performed, this time using 2,5-di(2*H*-hexafluoropropyl)oxolane (**55**) as a solvent. This medium is preferable as it is more readily synthesized and the perfluorinated analogue more volatile (and therefore easier to remove after reaction). Again fluorination proceeded with ease, yield 54%.

8.4 Fluorination of Other Polyfluoropolyethers

8.41 Fluorination of the adduct of HFP with DEPEG 400

DEPEG 400 with approximately 8 molar equivalents of HFP incorporated (**58b**) was fluorinated in 2,5-di(2*H*-hexafluoropropyl)oxolane (**55**), scheme 8.12. Reaction proceeded smoothly to afford the perfluorinated product (**102**).

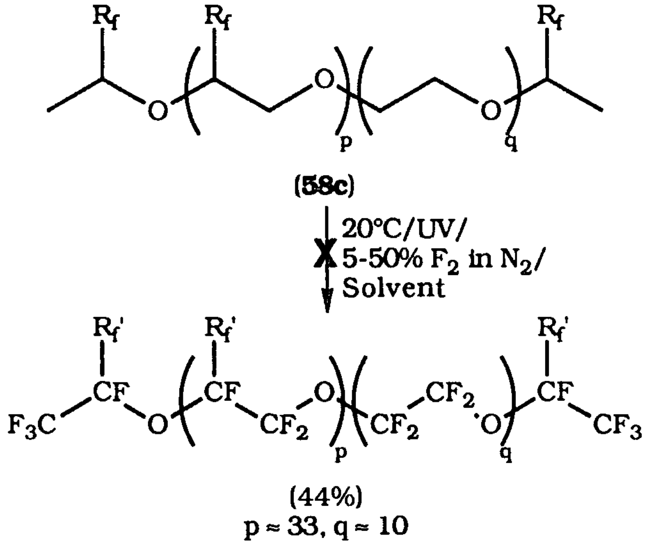


$R_f = -CF_2CFHCF_3$, $R_f' = -CF_2CF_2CF_3$

Scheme 8.12

8.42 Fluorination of the adduct of HFP with DEPEG 2000

The HFP polyadduct of DEPEG 2000 (approximately 35 molar equivalents of HFP incorporated) (**58c**) was fluorinated in 2,5-di(2*H*-hexafluoropropyl)oxolane, scheme 8.13. Due to the very high molecular weight of the polyether, a larger amount of solvent was required - about twice the mass of the polyether.



$R_f = -CF_2CFHCF_3$, $R_f' = -CF_2CF_2CF_3$

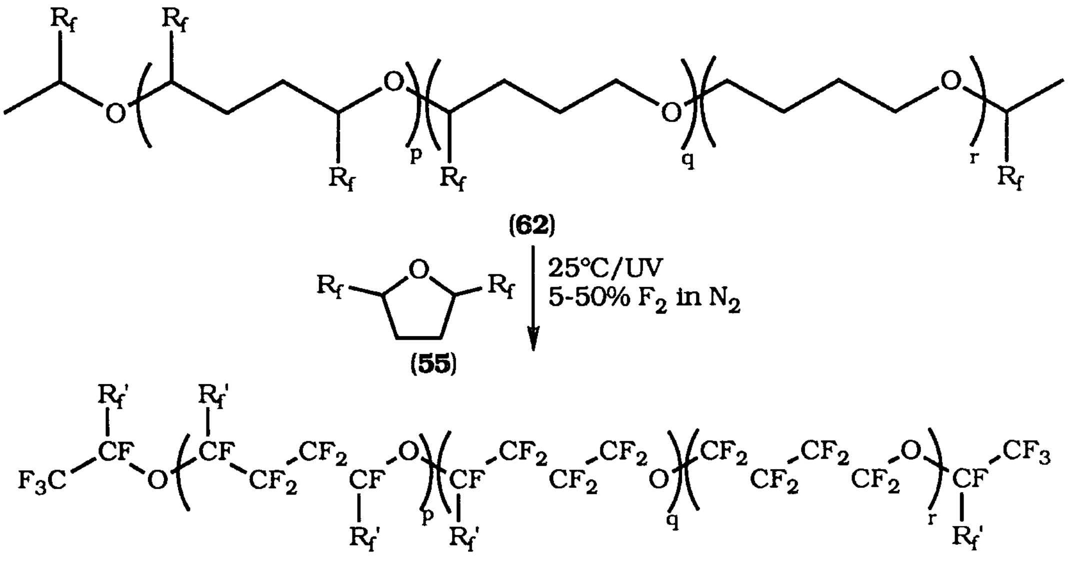
Scheme 8.13

Despite the presence of solvent the reaction mixture was still fairly viscous, and some difficulty was experienced in forcing the gas mixture through. After a short time it became apparent that there was some decomposition occurring (as was indicated by the darkening of the reaction mixture) and further fluorination was abandoned.

It is believed that two factors contributed towards the failure of the experiment. The problems with viscosity have already been discussed, and this got steadily worse as the reaction proceeded. The molecular formula suggests that on average ten dimethylene units per molecule are not fluoroalkylated and clearly if these are together then there will be significant sections of polyether that have not been modified at all, and thus could not withstand the fluorination conditions.

8.43 Fluorination of the adduct of HFP with PTHF

PTHF with approximately 25 molar equivalents of HFP incorporated (**62**) was fluorinated by the method already outlined, using 2,5-di(2*H*-hexafluoropropyl)oxolane (**55**) as the solvent, scheme 8.14.



(104)

(64%)

$2p + q = 22, \; p + q + r = 13$

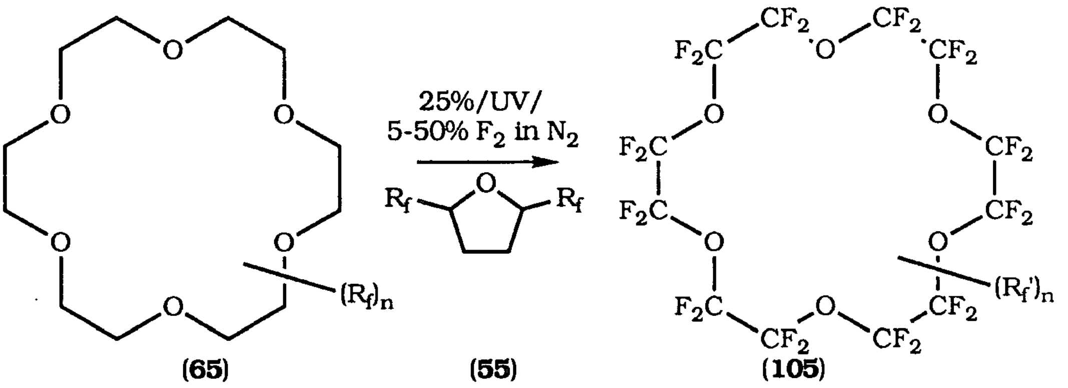
$R_f = -CF_2CFHCF_3, \; R_f' = -CF_2CF_2CF_3$

Scheme 8.14

A clear, colourless liquid (**104**) was obtained, upon vigorous removal of the solvent. The product could be distilled (≈200°C at 0.02 mmHg), despite a molecular weight of around 6500-7000. However, the solvent, perfluoro(2,5-dipropyloxolane), was free of any possible low molecular weight decomposition products indicating that the polyether remained intact throughout fluorination. The volatility perhaps reflects the general tendency of perfluorocarbons and their derivatives towards particularly low boiling points, compared with the analogous hydrocarbon or derivative.

8.44 Fluorination of the adduct of HFP with 18-crown-6

18-Crown-6 adduct with HFP (with about 5 molar equivalents of HFP incorporated) (**65**) was fluorinated in 2,5-di(2*H*-hexafluoropropyl)oxolane (**55**), scheme 8.15. A slightly turbid, colourless liquid (**105**) was obtained after removal of the solvent which distilled at 150-175°C at 0.03 mmHg.



(53%)

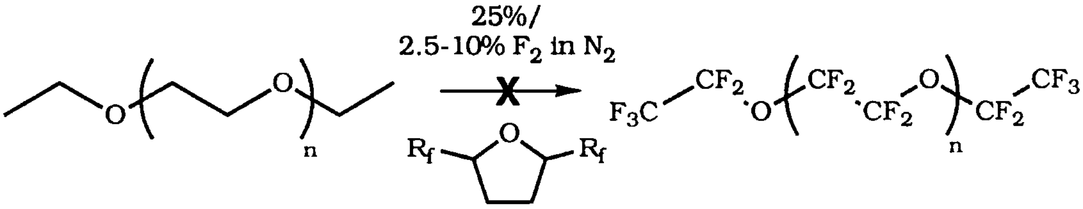
n ≈ 5

R_f = $-CF_2CFHCF_3$, R_f' = $-CF_2CF_2CF_3$

Scheme 8.15

8.5 Attempted Fluorination of DEPEG

Given the success of fluorinating the HFP adducts of the polyethers in these solvents, the possibility of fluorinating the polyether precursor was considered, scheme 8.16. It was hoped that the fluorinated solvent would sufficiently slow the reaction, as well as acting as a heat sink, dissipating the energy of fluorination.



R_f = $-CF_2CFHCF_3$

Scheme 8.16

Although very dilute fluorine was used (2.5% in nitrogen) the reaction mixture rapidly darkened, and it was obvious that decomposition had occurred. The experiment was abandoned. This clearly shows the reduction in reactivity caused by the presence of fluoroalkyl groups within a molecule (in the other fluorinations), illustrating the importance of achieving high levels of HFP incorporation in polyethers (see also sections 8.22 and 8.23), and also the difference in efficiency between intramolecular energy dissipation, as opposed to an intermolecular process.

8.7 Characterisation

Three problems combine to make the NMR analysis of these materials formidable, beside the complications already discussed in chapters three and four:

(i) They are insoluble in common NMR solvents. NMR experiments can not be run using a deuterium lock, and must either be done neat, with loss of resolution, or in a fluorinated solvent (such as hexafluorobenzene), with the complication of extra (and large) peaks in the spectrum. 2H COSY experiments are not readily applicable.

(ii) The peaks all tend to occur in the same areas of the spectra. All the carbon nucleii appear in the region 107 to 117 ppm, and most of the fluorine nucleii in the region -117 to -131 ppm.

(iii) Fluorine couplings are large, even over long ranges (as was seen chapter three, section 3.8). This leads to very complicated spectra, with numerous resonances overlapping. The lack of fluorine decoupling facilities prevents the acquisition of 2H HETCOR spectra.

Despite these difficulties some interpretation was possible, and most peaks could be assigned. As before, the simpler compounds were looked at first.

Lagow and coworkers have published a number of ^{19}F chemical shifts and some ^{13}C shifts of perfluoro-carbons, -ethers and -polyethers, upon which some assignments could be based, table 8.1.

A few points are worth noting. The CF_3 environments fall into a very small range, 116 to 118 ppm in the ^{13}C spectra, -84 to -91 ppm in the ^{19}F, except for the anomalous ^{19}F datum of number 4. Similar assignments were made for related compounds in the same paper, though it clearly contradicts the figure in number 5.

The CF_2 resonances are seen over a slightly greater range in the carbon spectra, from 114 to 117.5 ppm, except for the last two examples at 106.7 ppm, the difference possibly due to the large number of adjacent fluorines. ^{19}F resonances vary over a much greater range, apparently related to the number of nearby fluorines; from -77.1 ppm (an example with only one adjacent fluorine) to -132.2 (the environment with five adjacent fluorines).

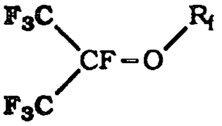
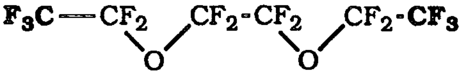
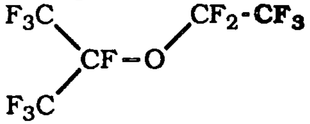
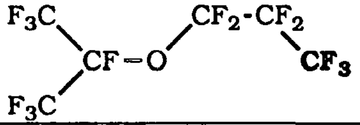
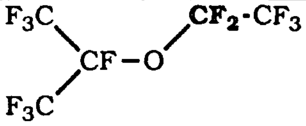
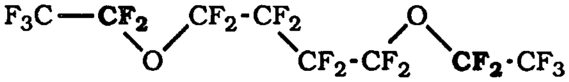
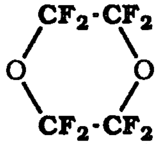
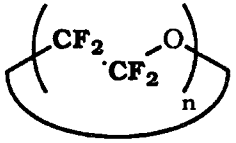
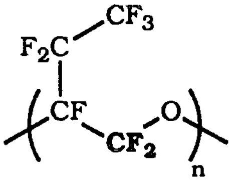
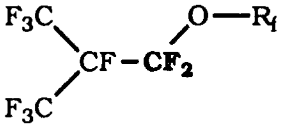
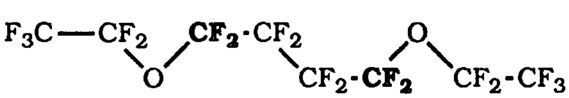
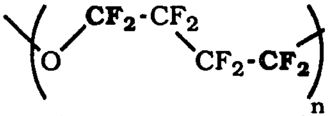
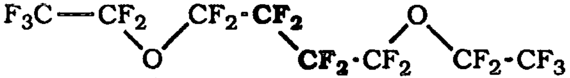
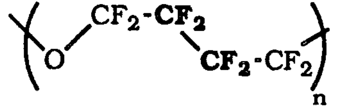
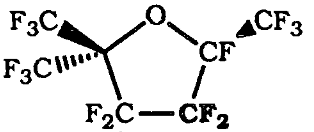
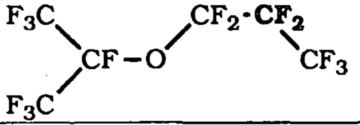
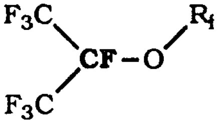
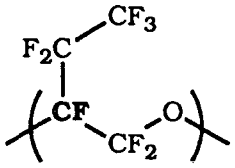
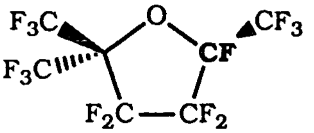
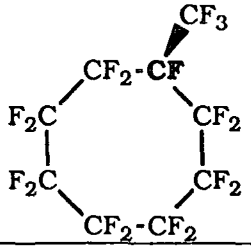
	Perfluoro-carbon, -ether or -polyether	Chemical shift/ppm	
	CF_3 environments	^{13}C	^{19}F
1		117.6 to 118.0	-83.1 to -84.2[70,75]
2			-91.0[69]
3		116.0	-90.7[75]
4	$C\left(CF_2OCF_2CF_2\mathbf{CF_3}\right)_4$	116.1	-66.5[67]
5		117.2	-84.1[75]
	OCF_2 environments		
6		114.3	-89.2[75]
7			-91.3[176]
8			-90.8[69]
9		114.9	-90 to -92[73]
10			-89.0[177]
11		116.7 115.9 117.3	-77.1[70] -79.0 -78.4[75]
12			-86.0[176]
13			-83.3[177]
14	$C\left(CF_2O\mathbf{CF_2}CF_2CF_3\right)_4$	117.4	-83.3[67]

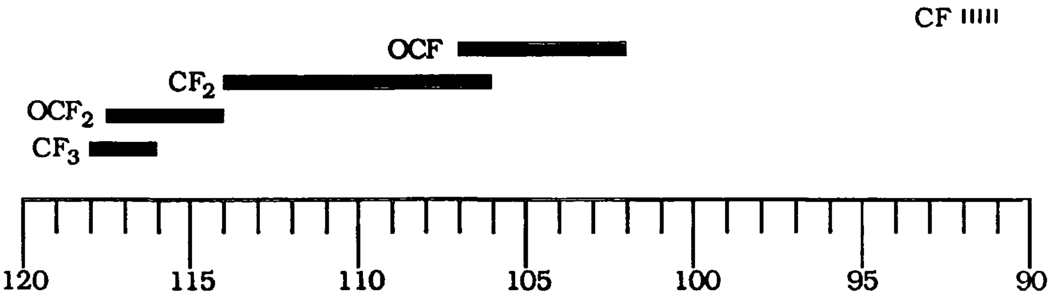
Table 8.1

	Perfluoro-carbon, -ether or -polyether	Chemical shift/ppm	
	CF$_2$ environments	^{13}C	^{19}F
15			-126.7[176]
16			-125.7[177]
17		114.1	-127.2 -116.0[75]
18		112.8	-110.7 -115.4[68]
19		112.6	-116.0[68]
20		106.8	-131.6[67]
21		106.7	-132.2[75]
	CF environments		
22		103.0 102.1 102.3	-143.2[70] -147.5 -147.3[75]
23			-141.2[177]
24		105.7	-124.8[75]
25		91.7	-181.2[68]

Example chemical shifts of perfluoro-carbons, -ethers and -polyethers (all spectra run as neat liquids)

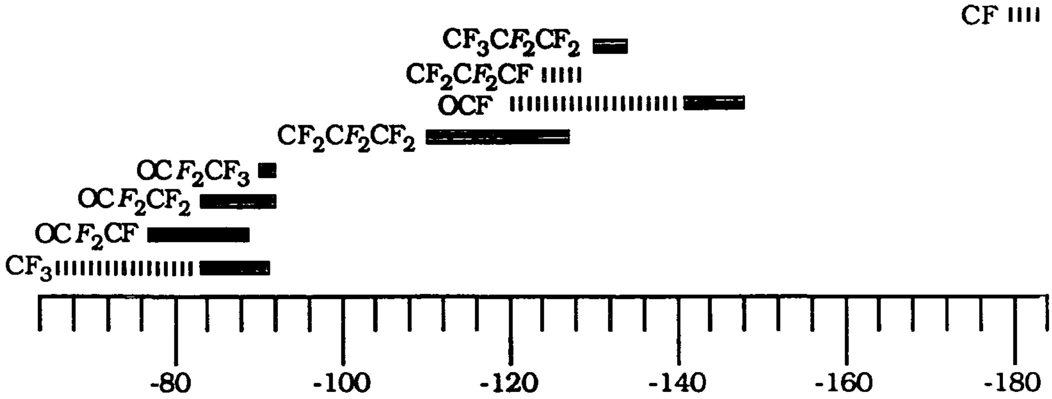
Table 8.1

The methine carbons again occur in a fairly narrow part of the spectrum, from 102 to 106 ppm, with one exception at 91.7 where there is no adjacent oxygen. The related fluorines, however, range from -124 to -181 ppm. With three substituents on the methine, the variations in the ^{19}F spectrum are perhaps to be expected, and it is the very narrow range of the ^{13}C resonances that is surprising. These tends are summarised in figures 8.2 and 8.3.



Correlation of ^{13}C shifts in perfluoro-carbons, -ethers and -polyethers

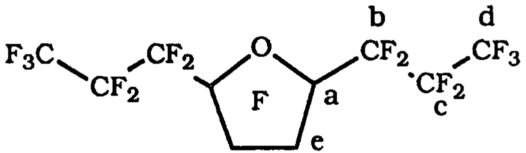
Figure 8.2



Correlation of ^{19}F shifts in perfluoro-carbons, -ethers and -polyethers

Figure 8.3

8.61 Perfluoro-2,5-dipropyloxolane



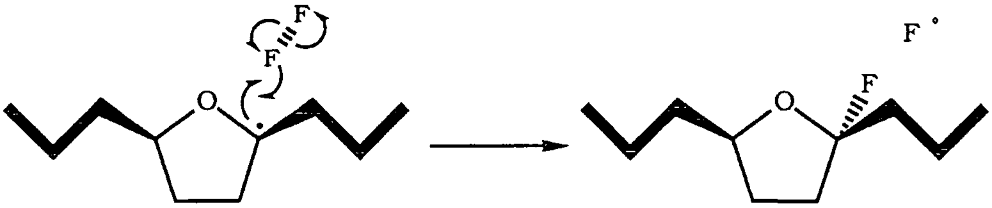
(106)

Figure 8.4

Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Assignment
^{13}C			
108.01	t	$^1J_{CF}$ = 268.1	c
	q	$^2J_{CF}$ = 37.2	
	t	$^2J_{CF}$ = 32.6	
108.33	t	$^1J_{CF}$ = 266.7	b
	t	$^2J_{CF}$ = 33.7	
	d	$^2J_{CF}$ = 33.7	
109.73	t	$^1J_{CF}$ = 267.0	e
	t	$^2J_{CF}$ = 33.7	
	d	$^2J_{CF}$ = 33.7	
112.44	d	$^1J_{CF}$ = 285.0	a
	t	$^2J_{CF}$ = 23.9	
	t	$^2J_{CF}$ = 23.9	
116.66	q	$^1J_{CF}$ = 285.2	d
	t	$^2J_{CF}$ = 32.2	
^{19}F			
-79.12	t		d
-79.14	t		d
-117.69	d of m	$^2J_{FF}$ = 307.1	e
-118.22	d of m	$^2J_{FF}$ = 306.3	e
-118.92	s		a
-120.26	s		a
-121.51	d of m	$^2J_{FF}$ = 307.1	e
-121.63	d of m	$^2J_{FF}$ = 306.3	e
123.23	d	$^2J_{FF}$ = 268.3	b
124.93	d of m	$^2J_{FF}$ = 259.6	c
128.71	d of m	$^2J_{FF}$ = 259.6	c
130.39	d	$^2J_{FF}$ = 268.3	b

Table 8.2

Perfluoro-2,5-dipropyloxolane (**106**) has two chiral centres, and so exists as two diastereomers, with the propyl side groups *cis* or *trans* to each other. It appeared that in general the chemical shifts of the two isomers (run as the neat liquid) were identical in the ^{13}C spectrum, but not in the ^{19}F. As was observed in chapter three, the ratio of one isomer to the other is not unity, suggesting some stereocontrol during fluorination (as this is a radical process, the stereochemical information from the adduct forming reaction will obviously be lost). The important step will be a radical at the α-carbon on the ring attacking a fluorine molecule, scheme 8.17. Which configuration is favoured cannot be said with any certainty; however, the imbalance is slight, so the difference maybe minimal (although the far less selective nature of fluorination must also be a factor).



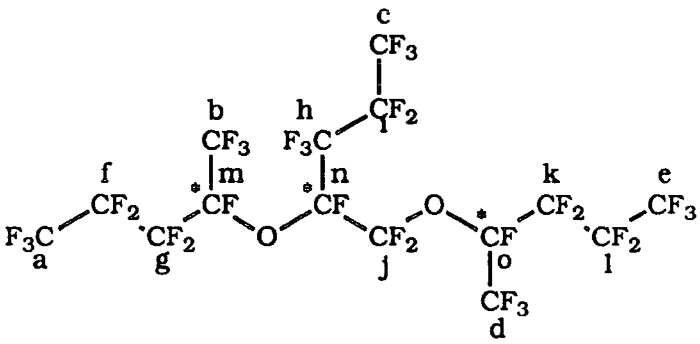
All unmarked bonds may be to fluorine or hydrogen

Scheme 8.17

In the ^{13}C spectrum, table 8.2, the CF_3 carbon was easily identifiable as a quartet of triplets. Some other resonances could also be assigned with some confidence on the basis of the splitting patterns: A large doublet, further split as a pentet, at 112.4 ppm was assigned to the CF carbon. A resonance at 108.01 ppm was split first as a triplet with a large coupling constant, then further split as a quartet and then as a triplet, and so was assigned to the CF_2 carbon next to the CF_3. Further assignments were made on the basis of chemical shift trends, based on the data of table 8.1; comparing examples six and fourteen suggested that a nearby CF_3, rather than a CF_2, would give a somewhat higher field resonance (though the fact that there is an extra CF_2 separating these structural features makes the assignment less than certain).

In the ^{19}F spectrum, table 8.2, the CF_3 fluorines were again readily distinguished at -79.1 ppm. The remaining peaks were tentatively assigned: Two AB systems at -117.69 and -121.51 ppm and at -118.22 and -121.63 ppm due to the CF_2 fluorines on the ring, one pair from each isomer (compare with number 17 in table 8.1). Two peaks, at -118.92 and -120.26 ppm, were due to the CF fluorine on the ring, again one from each isomer (see number 24 in the table of examples). An AB system at -123.23 and -130.39 ppm arising from the CF_2 fluorines next to the ring (the two resonances being comparatively far apart as they are next to a chiral centre). An AB system at -124.93 and -128.71 ppm from the remaining CF_2 away from the ring (the resonances closer to each other as the atoms are farther from the chiral centre).

8.62 Perfluoro[1,2-di(1-methylbutoxy)pentane] (4 isomers)



(107)

Figure 8.5

Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Assignment
^{13}C			
117.27	q of m	$^1J_{CF}$ = 317.5	a, b, c, d, e
110.41	t of m	$^1J_{CF}$ = 275.3	f, i, l
105.9	t of m (broad)	$^1J_{CF}$ ≈ 315	g, h, k
	(j, m, n, o not identified)		
^{19}F			
-78.43	s		a, c, e
-85.65	s		b, d
-117	m		f, g, h,
-122	m		i, k, l,
-130	m		m, n, o
-137	m		j

Table 8.3

As with the starting materials, the degree of complexity between the triadduct of 1,2-diethoxy ethane with HFP compared with the diadduct of oxolane is much greater. Figure 8.3 shows each environment and the three chiral centres, the latter giving rise to eight enantiomers, and therefore four magnetically inequivalent isomers. Each isomer has five CF_3 environments (*a* to *e*), seven CF_2 environments (*f* to *l*) and three CF environments (*m* to *o*).

In the ^{13}C spectrum, performed on the neat sample, the CF_3 carbons were all seen as a quartet of multiplets at 117.2 ppm. A triplet of multiplets was seen at 110.6 ppm, and also at 105.9 ppm and it is suggested that these correspond to CF-$\underline{C}F_2$-CF_2- and CF_3-$\underline{C}F_2$-CF_2- environments respectively, from the Lagow data (predicted at about 114 and 106 ppm from example 17 and examples 20 and 21 in table 8.1 respectively). The CF-$\underline{C}F_2$-O and CF carbons were not identified, it is fairly certain that they are obscured by the other peaks, both will be small.

A peak at -78.43 ppm in the ^{19}F spectrum was attributed to the CF_3 fluorines at *a*, *c* and *e* by analogy with the similar peaks in perfluoro-2,5-dipropyloxolane. A peak at -85.65 was assigned to the CF_3 fluorines,*b* and *d*. All the CF_3 resonances were about 6 ppm downfield of those given by Lagow. A small group of peaks at -72 to -78 ppm was due to the two inequivalent fluorines at *j*, several peaks because of the variety of stereochemical possibilities. There were two broad groups at -117 ppm (*f*, *i*, and *l* fluorines, expected at -106 ppm) and at -122 ppm (*g*, *h* and *k* fluorines, expected at -116 to -128 ppm).

Two smaller peaks, at -130 and -137 ppm, were assigned to the tertiary fluorines. The *n* fluorine was assigned to the peak at -130 ppm, this being half the size of the other. The -137 ppm peak was thus assigned to *m* and *o*, which would be virtually identical. These values are perhaps downfield of the expected, -140 to -150 ppm, but as was mentioned earlier, these resonances are subject to large deviations.

8.63 Commercial PFPEs

Hexafluorobenzene was used as the NMR solvent for these materials (which is occurs at -163 in the ^{19}F spectrum and as a doublet at 137.6 in the ^{13}C spectrum). It should be noted that solvent can have a fairly dramatic effect on fluorine chemical shifts. The spectra of all the PFPEs synthesized were very similar to that of perfluoro[1,2-di(1-methylbutoxy)pentane].

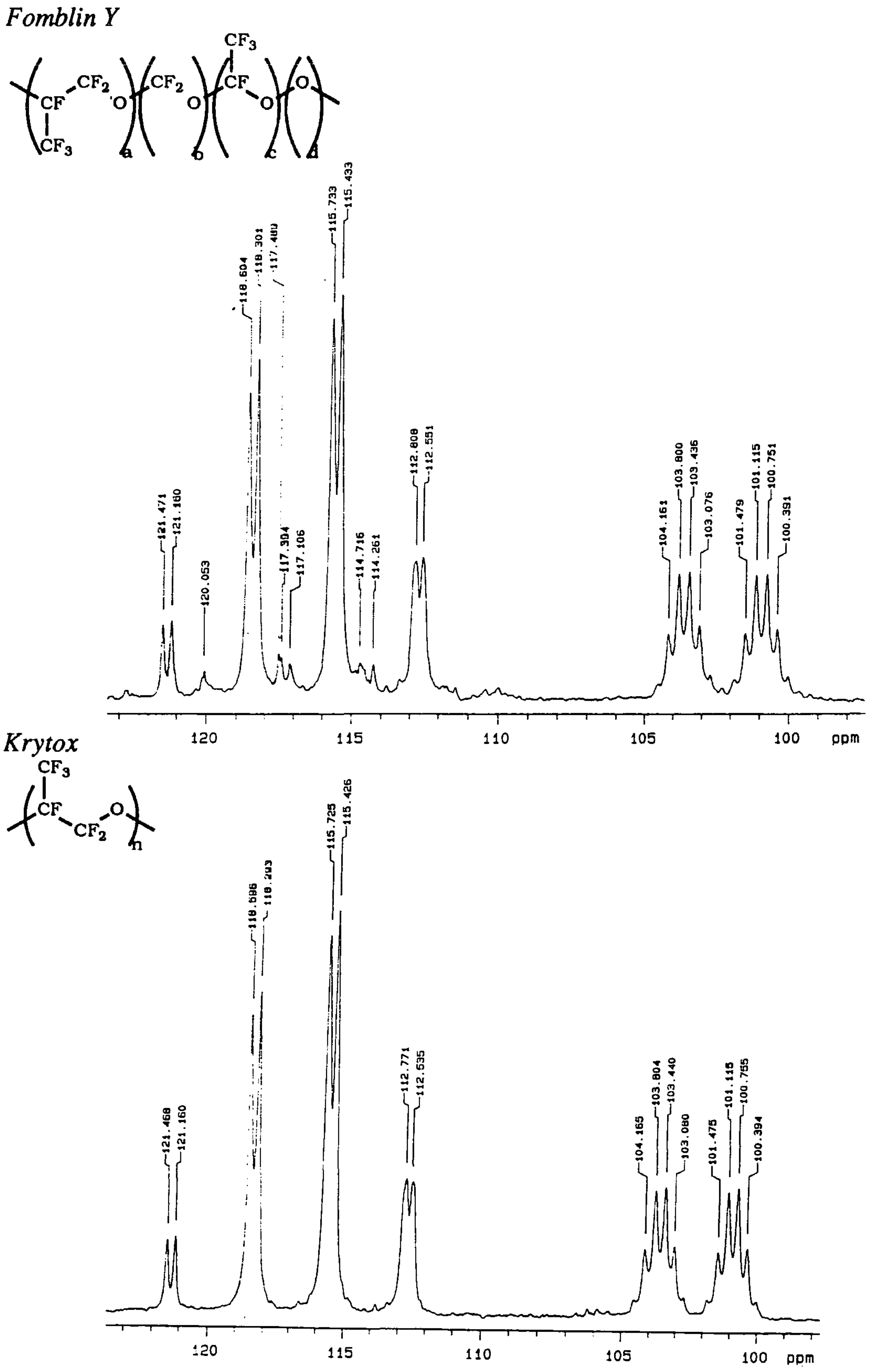
For reference, ^{13}C and ^{19}F spectra of Fomblin Y and Krytox are presented. In both the ^{13}C spectra, figure 8.6, the CF_3 carbons appear as a quartet of doublets at 117 ppm, the CF_2 carbons, by a very curious coincidence, overlap with these peaks, occurring as a triplet of doublets at 115 ppm. The CF carbons appear as a well defined doublets of apparent sextets at 102 ppm. The CF_3 and CF_2 fluorines appear at -79 ppm, discernible as two peaks, though close together, in the ^{19}F spectra, figure 8.7. The CF occurs at -142 ppm. In general the Krytox spectra are simpler due to the more regular structure of that material, but the generally high resolution of all four spectra is exceptional for any polymeric material.

8.64 Synthesised PFPEs

Based on the data from 8.1 and figures 8.2 and 8.3, and also from the model compounds, assignments of groups of peaks could be made. In the ^{13}C spectra quartets could be identified, and thus assigned to the CF_3 carbons. Groups of triplets (overlapping) were also discernible, and these could be assigned to CF_2 next to oxygen or CF_2 away from oxygen. The CF carbons were assigned to the peaks at highest field.

The CF_3 fluorines were also readily identified in the ^{19}F spectra, being well defined. Other peaks in the same area, -66 to -84 ppm, were assigned to CF_2 next to oxygen. All the other peaks were grouped at -116 to -127 ppm, and assigned to both CF_2 fluorines away from oxygen, and to CF fluorines. The latter is significantly shifted from the corresponding peaks in Fomblin Y and Krytox, but is by no means in disagreement with other similar compounds, as was seen from table 8.1 and the model compounds.

The structure given for perfluoro[polypropyl-α-ethyl-ω-ethoxy poly(tetramethylene oxide)] (**104**) is derived from that proposed for poly(2*H*-hexafluoropropyl)-α-ethyl-ω-ethoxy poly(tetramethylene oxide) (**62**) in chapter four.

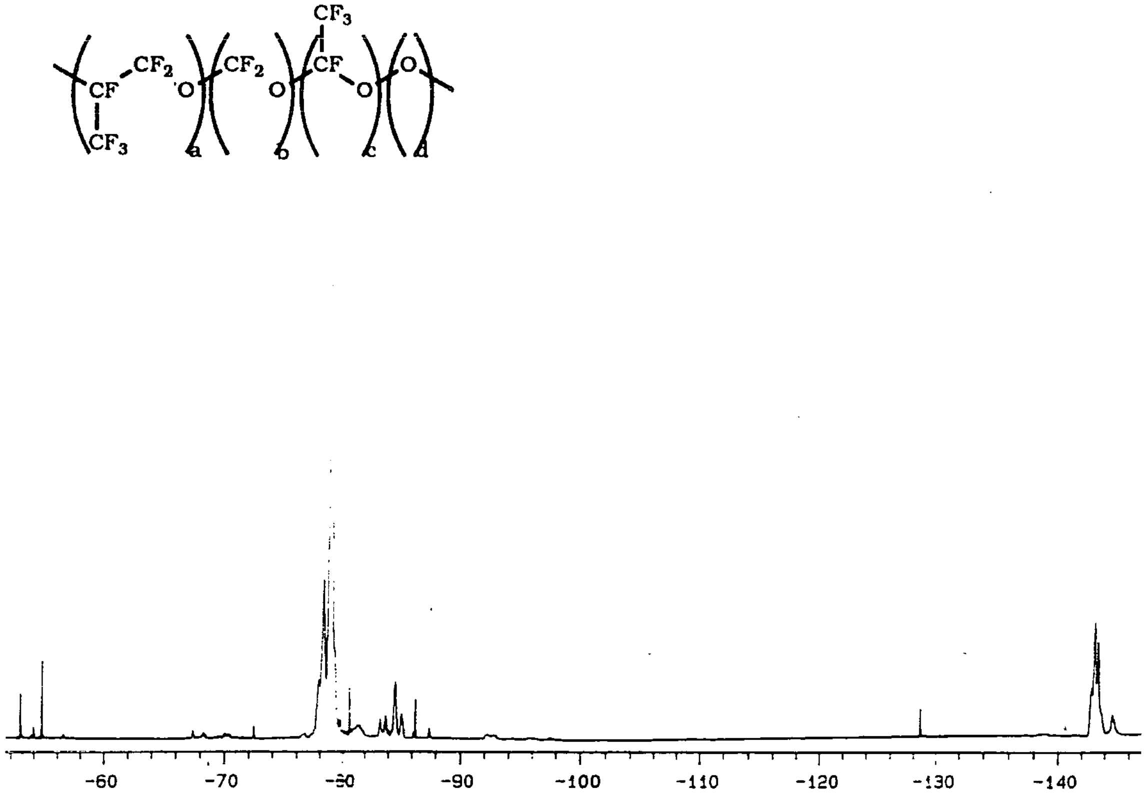

Fomblin Y

Krytox

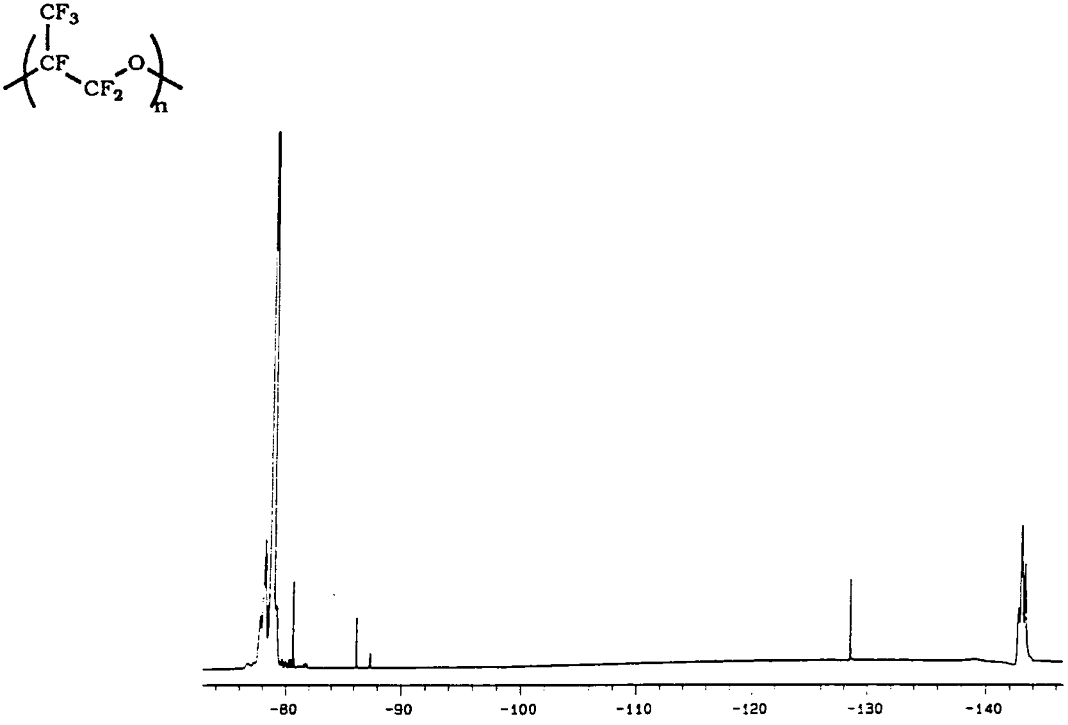
^{13}C NMR spectra for Fomblin Y and Krytox

Figure 8.6

Fomblin Y



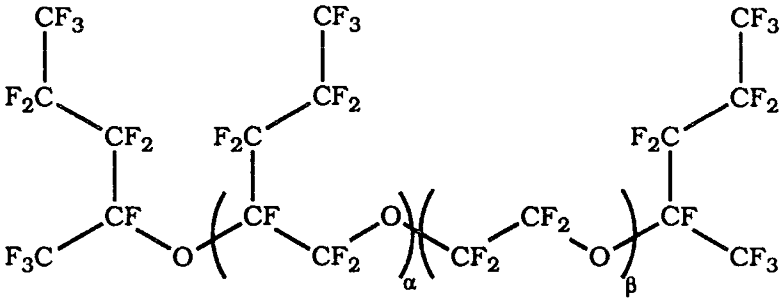
Krytox



^{19}F NMR spectra for Fomblin Y and Krytox

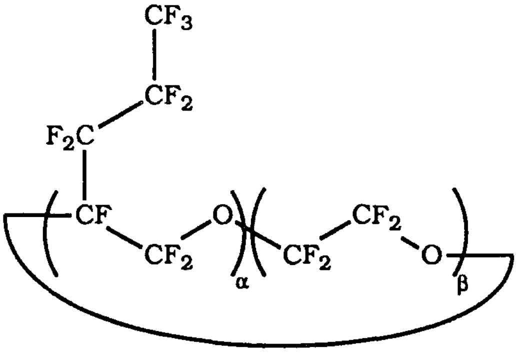
Figure 8.7

*Perfluoro[polypropyl-α-ethyl-ω-ethoxy poly(ethylene oxide) 600] (**103**)*



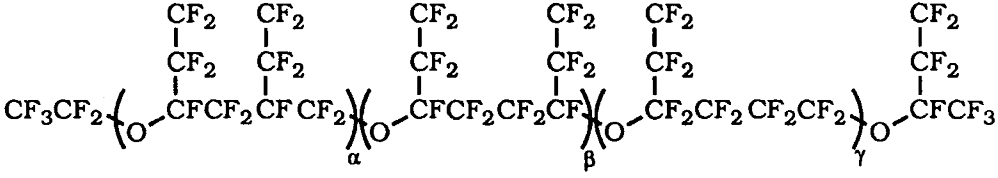
α ≈ 11 (mean), β ≈ 2 (mean)

*Perfluoropolypropyl-18-crown-6 (**105**)*



α + β = 6, α ≈ 5 (mean)

*Perfluoro[polypropyl-α-ethyl-ω-ethoxy poly(tetramethylene oxide)] (**104**)*

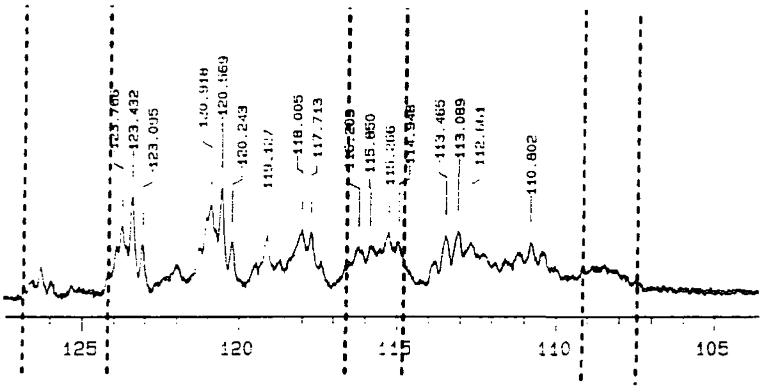


2α + 2β + γ ≈ 22 (mean), α + β + γ ≈ 13 (mean)

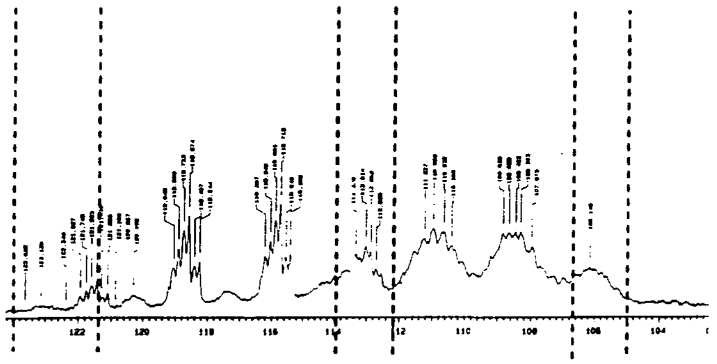
Structures of synthesised PFPEs

Figure 8.8

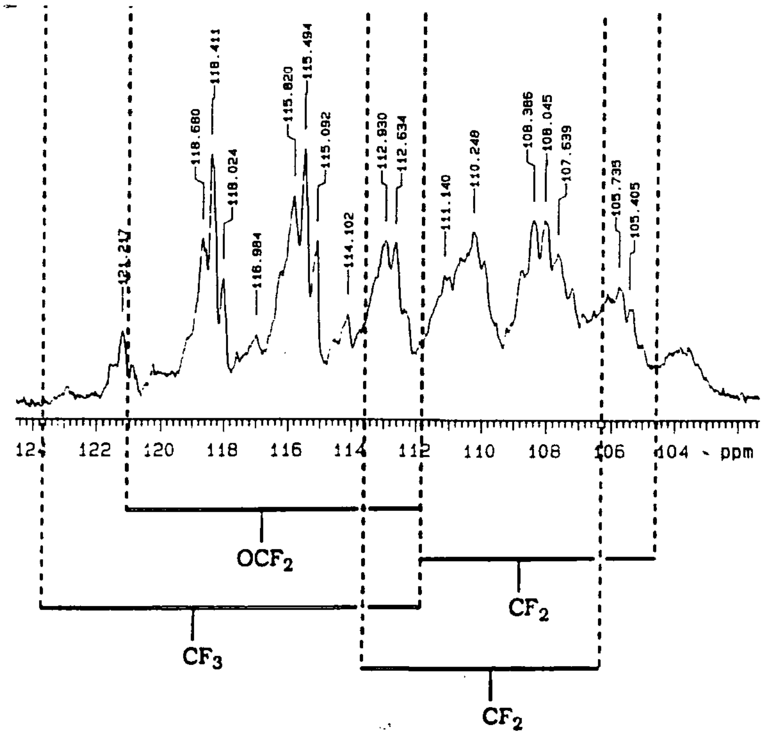
Perfluoro[polypropyl-α-ethyl-ω-ethoxy poly(ethylene oxide) 600] ***(103)***



Perfluoro[polypropyl-α-ethyl-ω-ethoxy poly(tetramethylene oxide)] ***(104)***



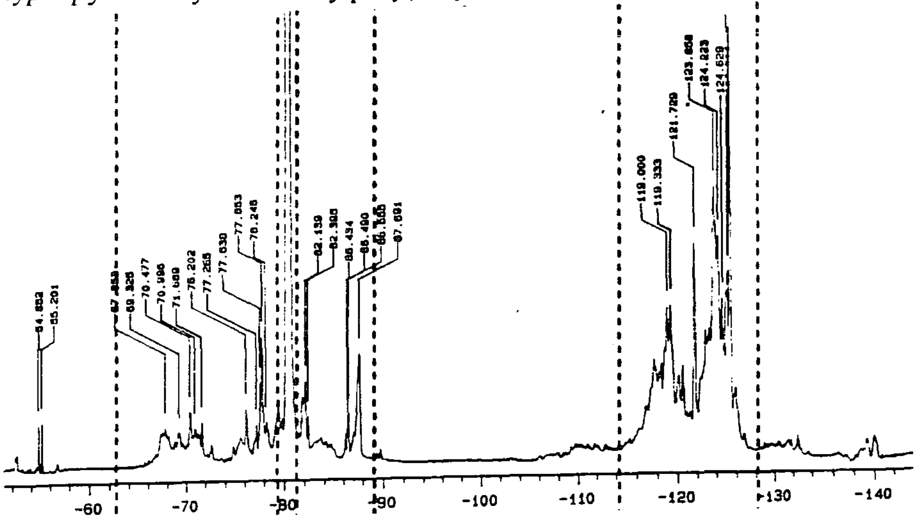
Perfluoropolypropyl-18-crown-6 ***(105)***



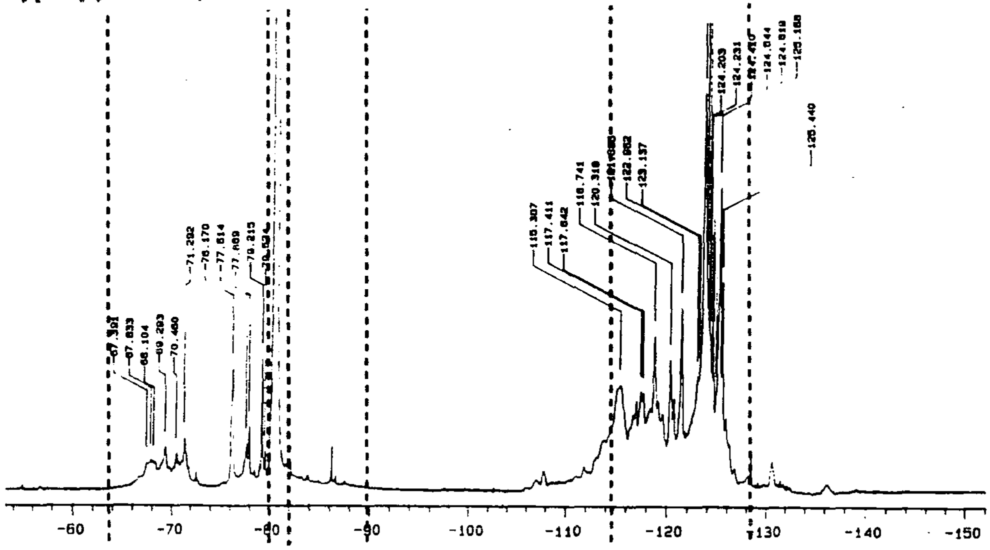
^{13}C NMR spectra of synthesised PFPEs

Figure 8.9

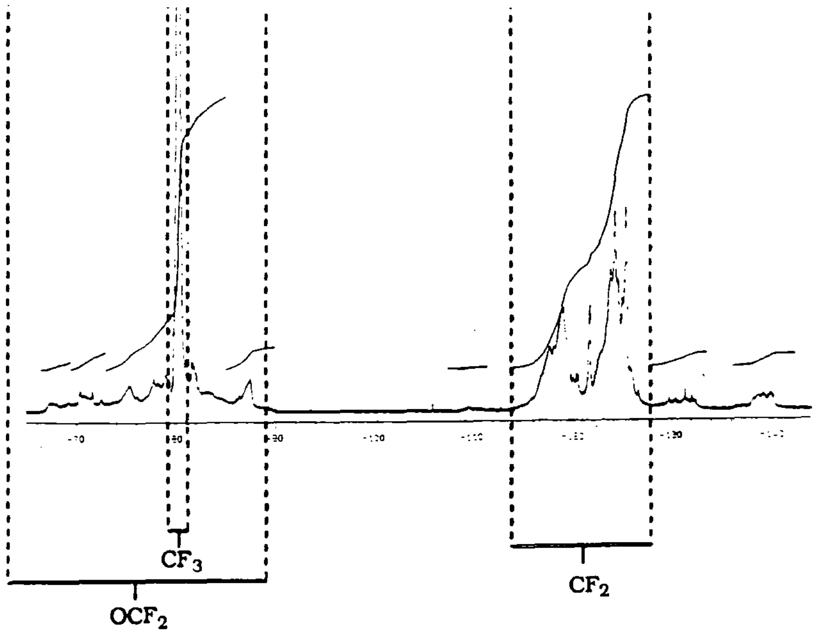
Perfluoro[polypropyl-α-ethyl-ω-ethoxy poly(ethylene oxide) 600] ***(103)***



Perfluoro[polypropyl-α-ethyl-ω-ethoxy poly(tetramethylene oxide)] ***(104)***



Perfluoropolypropyl-18-crown-6 ***(105)***



^{19}F NMR spectra of synthesised PFPEs

Figure 8.10

8.65 Further analysis

Fourier transform IR analysis[*] of the PFPE derived from DEPEG 600 and HFP (**103**) showed the material to be highly fluorinated, with only 10 ppm hydrogen present. The same figure was recorded for a sample of Krytox.

Viscosity measurements of the DEPEG derived sample were also taken,[*] and found to be somewhat greater than that of Krytox and Fomblin Y, even when compared with samples of significantly higher molecular weight, as indicated in table 8.2. This is attributable to the relatively low ratio of oxygens in the material.

	Viscosity/cSt	
Temperature	Krytox AC	Perfluoro-(DEPEG/HFP) (**103**)
40°C	270	1541[†]
100°C	25	122
150°C	8.8[†]	29.2
300°C	1.59	3.21[†]
Mol. Wt.	≈6000	≈3500

[†] Data extrapolated

Temperature-viscosity relationship of Krytox and perfluoro(DEPEG/HFP) (**103**)

Table 8.2

Supercritical fluid chromatography was also performed[*] and, as with the viscosity measurements, compared with a trace obtained from Krytox 143 AC. These traces are presented in the appendix. The Krytox trace shows numerous evenly spaced peaks in a fairly wide molecular weight range. This reflects the regular structure obtained from the polymerisation of hexafluoropropene oxide, each peak having progressively one more monomer unit in it.

The material derived from DEPEG and HFP (**103**) gave a much less regular trace, as there are now two variables determining molecular weight - the number of monomer units in the DEPEG and the number of HFP units - as well as a greater variation in structural possibilities. However, it is important to note that this material has a much smaller *range* of molecular weights, as can be seen from the narrower band of peaks (though the shorter retention time will also have had an effect on the distribution).

---

[*] Analysis performed by Ms L. Gschwender, Wright Laboratories, Ohio.

Although the Krytox material is more regularly defined, the PFPEs synthesized by the techniques described here have a much narrower molecular weight distribution *despite never having been distilled or otherwise fractionated.*

8.7 Conclusions

It can be seen that fluorination of polyethers can be achieved through the use of solvent systems such as the two described here. These have advantages over other systems used (chlorofluorocarbons[96,100,101] or perfluorocarbon derivatives[96-98,102]) in that they are particularly good solvents for both starting material and product. It is believed that the technique could be extended to other fluorine containing, high molecular weight materials, and could also be used industrially.

INSTRUMENTATION

Distillation

Fractional distillation of lower boiling product mixtures (up to 200°C/1mmHg) was carried out using a Fischer Spahltrohr MMS 255 small concentric tube apparatus. Higher boiling materials were distilled using a Büchi kugelrohr GKR-51 apparatus. Boiling points were recorded during distillation.

Elemental Analysis

Carbon, hydrogen and nitrogen elemental analyses were obtained using a Perkin-Elmer 240 Elemental Analyser or a Carlo Erba Stumentazione 1106 Elemental Analyser. Analysis for halogens were performed as described in the literature.[178]

ESCA

ESCA was performed on a Kratos ES300 spectrometer.

GLC Analysis

Gas liquid Chromatography (GLC) analysis was carried out on a Hewlett Packard 5890A gas chromatograph fitted with a 25m cross-linked methyl silicone capillary column. Preparative GLC was performed on a Varian Aerograph Model 920 (catharometer detector) gas chromatograph.

GPC analysis

GPC was performed on a 5μm PL gel three column system (100Å, 10^3Å and 10^5Å columns) using a Waters R401 Differential Refractometer, connected to an SIC Chromatacorder 12. Samples (100μl) were run in oxolane.

IR Spectra

IR spectra were recorded on either a Perkin-Elmer 457 or 577 Grating Spectrophotometer using conventional techniques.

Mass Spectra

Mass spectra were recorded on a VG 7070E spectrometer. GLC/MS were recorded on the VG 7070E spectrometer linked to a Hewlett Packard 5790A gas chromatograph fitted with a 25m cross-linked methyl silicone capillary column. FAB spectra were run on the VG 7070E spectrometer using a xenon.

NMR Spectra

^{1}H NMR spectra were recorded on a Hitachi Perkin-Elmer R-24B (60MHz), a Bruker AC250 (250.13MHz), a Varian VXR400S (399.952MHz) and a Bruker AMX500 (500.135MHz) NMR spectrometer.

^{13}C NMR were recorded on a Varian VXR400S (100.577MHz) and a Bruker AMX500 (125.773MHz) NMR spectrometer.

^{19}F NMR spectra were recorded on a Varian EM3601 (56.45MHz), a Bruker AC250 (235.34MHz) and a Varian VXR400S (376.289MHz) NMR spectrometer.

Coupling constants are given in Hz.

Reagents and Solvents

Unless otherwise stated, reagents were used as supplied by the manufacturers.

CHAPTER NINE

EXPERIMENTAL TO CHAPTER THREE

9.1 General Procedure

9.11 γ-Ray initiated reactions

Solid and liquid reagents were introduced into a Pyrex Carius tube (*ca.* 60 ml) together with solvent if used, and degassed twice by freeze-thawing. HFP was then introduced into the cooled (liquid air) Carius tube using standard vacuum line techniques, the tube then being sealed, and placed in a metal sleeve. After regaining room temperature, the Carius tube was irradiated with γ-rays from a ^{60}Co source (85 krad hr^{-1}). Subsequently, the tube was cooled (liquid air) and opened. Any remaining HFP was recovered as the tube returned to room temperature. Products were poured out.

9.12 UV initiated reactions

For a UV reaction a Carius tube was charged, degassed and sealed exactly as before. It was then irradiated with UV light (1000 W, medium pressure, mercury lamp, at a distance of *ca.* 100 mm), whilst being cooled by an electric fan to about 60°C. The Carius tube was opened as before.

9.13 Peroxide initiated reactions

Peroxide initiated reactions were performed in nickel autoclaves (*ca.* 125 ml, fitted with bursting discs, maximum working pressure 220 atm) into which any solid and liquid reagents, together with solvent if used, were charged. The autoclave was then sealed using a copper gasket and, as before, degassed twice by freeze-thawing. HFP was introduced into the cooled (liquid air) as before and the valve closed. The autoclave was then heated, whilst rocking, in a purpose built cell for 20 hours. Subsequently, the autoclave was cooled (liquid air) and opened. Any remaining HFP was recovered as it returned to room temperature and the products were poured out.

9.2 Free Radical Additions of Ethers to Hexafluoropropene

9.21 Oxolane

A Carius tube was charged with acetone (10ml), oxolane (**37**) (8.8 g, 120 mmol) and HFP (**1**) (20.3 g, 135 mmol) was irradiated with UV light for 3 days. The tube was open and no HFP was recovered. A clear, pale brown liquid removed, from which acetone was removed by distillation. Further distillation (137 - 143°C) gave a clear colourless liquid, (2H-hexafluoropropyl)oxolane (**54**) (19.8 g, 72.5%), pure by capillary GLC. IR, NMR and MS spectra agreed with literature;[113] NMR numbers 1 and 2. A further fraction was obtained (4.2 g), also a clear colourless liquid, identified as 2,5-

di(2*H*-hexafluoropropyl)oxolane (**55**). IR, NMR and MS spectra as literature;[113] NMR number 3.

9.22 1,4-Dioxane

A Carius tube was charged with 1,4-dioxane (**38**) (10 g, 110 mmol), HFP (**1**) (21.5 g, 140 mmol) and acetone (10 ml), and irradiated with UV light for 3 days. No HFP was recovered, distillation at 95-98°C/90 mmHg and at 81-84°C/50 mmHg gave two fractions of a colourless liquid (overall; 11.7 g, 50.7%). Smaller amounts of starting material and also higher boiling components were also recovered. The product was identified by NMR as (2*H*-hexafluoropropyl)-1,4-dioxane; IR, MS and NMR data agreed with literature;[113] NMR numbers 4 and 5.

9.23 Diethyl ether

(i) A Carius tube was charged with diethyl ether (**39**) (3.5 g, 48 mmol), acetone (4.0 g) and HFP (**1**) (7.5 g, 50 mmol) and irradiated with UV for 3 days. After reaction no HFP was recovered, a clear pale brown liquid was obtained. This was distilled, the major product fraction boiling at 116 - 118°C, identified as 2,2,3,4,4,4-hexafluoro-1-methylbutyl ethyl ether, (7.2 g, 33.5% yield); IR, MS and NMR agreed with literature;[113] NMR number 6 and 7. The low yield was attributed to the formation of diadduct.

(ii) A Carius tube was charged with diethyl ether (**39**) (7.1 g, 96 mmol), acetone (7.9 g) and HFP (**1**) (22.7 g, 151 mmol) and UV irradiated for 3 days. After reaction no HFP was recovered, and a clear pale brown liquid was obtained that was distilled, the major product fraction boiling at 70 - 71°C/13 mmHg, identified as di(2,2,3,4,4,4-hexafluoro-1-methylbutyl) ether (**40**), (8.5 g, 39.4% yield); IR, MS and NMR data agreed with literature;[113] NMR number 8. Smaller fractions of diethyl ether and acetone, and of monoadduct were also obtained.

9.24 Diethoxy ethane with HFP

Diethoxy ethane (8.4 g, 71 mmol), acetone (10ml) and HFP (**1**) (35.4 g, 236 mmol), in a Carius tube, were irradiated with UV light for 3 days. Upon opening, 7.7 g of HFP was recovered. Acetone was removed by distillation, further distillation at 115-116°C/9 mmHg gave a clear, colourless liquid, 1,2-di(2,2,3,4,4,4-hexafluoro-1-methylbutoxy)-3,3,4,5,5,5-hexafluoropentane (**56**) (14.0 g, 41.0%); IR, MS and NMR agreed with literature;[121] NMR number 9.

9.3 Competition reactions

Competition reactions were performed using γ-initiation in Carius tubes charged in the usual manner. Reactions were followed by the disappearance of the starting materials from capillary GLC traces using a flame ionisation detector, comparing samples taken before and after reaction, obviating the need to correct the GLC figures for different detector responses.

9.31 Competition between oxolane and diethyl ether

A Carius tube was charged with oxolane (**37**) (7.18 g, 100 mmol), diethyl ether (**39**) (7.39 g, 100 mmol) and HFP (**1**) (5.2 g, 35 mmol) and irradiated for 4 days with γ-rays (8Mrad). No HFP was recovered. GLC analysis was performed on samples taken before and after reaction. The diethyl ether peak integration changed from 48.92% to 50.10%, the oxolane peak from 51.07% to 25.73%, implying that the HFP reacted almost exclusively with oxolane.

9.32 Competition between oxane and diethyl ether

A Carius tube was charged with oxane (**41**) (8.61 g, 100 mmol), diethyl ether (**39**) (7.41 g, 100 mmol) and HFP (**1**) (4.8 g, 32 mmol) and irradiated with γ-rays for 4 days (8Mrad). After opening 0.1 g of HFP was recovered. GLC analysis showed the proportion of diethyl ether had dropped from 42.89% to 34.10%, while the oxane proportion had dropped only from 57.11% to 56.09%, showing diethyl ether to be clearly more reactive.

9.33 Competition between 1,4-dioxane and diethyl ether

A Carius tube was charged with 1,4-dioxane (**38**) (8.80 g, 100 mmol), diethyl ether (**39**) (7.36 g, 99 mmol) and HFP (**1**) (5.4 g, 36 mmol) and irradiated with γ-rays for 4 days (8Mrad). No HFP was recovered after opening. GLC analysis showed that the proportion of ether had dropped from 62.50% to 45.79%, while that of 1,4-dioxane had changed from 37.50% to 40.12%, implying that the HFP reacted almost exclusively with diethyl ether.

9.4 1,3,5-Trioxane with HFP

(i) A Carius tube was charged with 1,3,5-trioxane (**42**) (5.5 g, 61 mmol), acetone (15 ml) and HFP (**1**) (18.0 g, 120 mmol), and irradiated with UV light. HFP (14.6 g) was recovered, and remaining 1,3,5-trioxane was sublimed from the reaction mixture. The product distilled in a kugelrohr apparatus at 50°/0.05 mmHg as a clear, colourless liquid , which was identified as (2*H*-hexafluoropropyl)-1,3,5-trioxane (**51**), (4.6 g, 31.4% yield);. (Found: C, 29.7; H, 2.4, F, 47.6. $C_6H_6F_6O_3$ requires C, 30.0; H, 2.5; F, 47.5%); IR number 1; MS number 1; NMR number 10.

(ii) A Carius tube was charged with 1,3,5-trioxane (**42**) (5.85 g, 65 mmol), acetone (15 ml) and HFP (**1**) (20.0 g, 133 mmol) and irradiated with γ-rays for 29 days (59Mrad). 16.0 g of HFP was recovered. NMR showed the composition of the remaining material to be approximately 60% starting material, 40% monoadduct (**51**). No further work up was attempted.

9.5 Attempted reaction of dimethoxy methane with HFP

A Carius tube was charged with dimethoxy methane (**43**) (8.60 g, 113 mmol), acetone (10 ml) and HFP (**1**) (22.9 g, 153 mmol). After 3 days UV irradiation the tube was opened and HFP recovered (3.2 g). All the volatile components (approximately 90% of the remaining mixture) were removed under vacuum, and analysed by GLC/MS, which showed the presence of numerous products. No further work up was performed.

9.6 Attempted reaction of para-*formaldehyde with HFP*

(i) A Carius tube was charged with *para*-formaldehyde (**44**) (1.24 g), acetone (5 ml) and HFP (**1**) (9.5 g). After 3 days UV irradiation the tube was opened and all the HFP was recovered.

(ii) A Carius tube was charged with *para*-formaldehyde (**44**) (0.5 g), 2,2,2-trifluoroethanol (5 ml) and HFP (**1**) (7.3 g)e. The tube was opened after 3 days UV irradiation and all the HFP recovered.

9.7 Oxirane with HFP

A Carius tube was charged with acetone (5 ml) and degassed. Oxirane (**46**) (2.7 g, 61 mmol) and HFP (**1**) (8.2 g, 55 mmol) were condensed in the cooled down (liquid air) tube, which was then sealed. After 3 days UV irradiation the tube was opened. No HFP was recovered. Volatile components were removed under vacuum and analysed by GLC/MS, which showed the presence of numerous products, various oligomers of oxirane being identified, together with HFP adducts of those oligomers. No further work up was performed.

9.8 Oxetane with HFP

A Carius tube was charged with oxetane (**50**) (3.5 g, 60 mmol), acetone (10 ml) and HFP (**1**) (2.7 g, 18 mmol) as before, sealed and irradiated with UV light for 3 days.After opening HFP (0.7 g) was recovered. GLC/MS analysis of the volatile components, which had been removed under vacuum, showed the presence of several oligomers of oxetane and adducts thereof.

CHAPTER TEN
EXPERIMENTAL TO CHAPTER FOUR

10.1 General Procedures

Free radical additions were performed using the general procedures of chapter nine, except where otherwise stated. DBPO was dried under vacuum for several hours prior to use.

The degree of incorporation of HFP (**1**) was estimated from NMR integrations using (trifluoromethyl)benzene as a reference (seen at -64 ppm in the ^{19}F spectrum, and as two peaks at 7.5 ppm in the ^{1}H spectrum), using the general formula below.

$$n = \frac{I_{F,s}}{I_{F,r}} \times \frac{n_{F,r}}{n_{F,s}} \times \frac{I_{H,r}}{I_{H,s}} \times \frac{n_{H,s}}{n_{H,r}}$$

Where $I_{F,s}$ is the integration of the sample in the fluorine spectrum, $I_{F,r}$ for the reference, $n_{F,r}$ is the number of fluorines in the reference, $n_{F,s}$ is the number in the sample. $I_{H,r}$ is the integration of the reference in the proton spectrum, $I_{H,s}$ is the integration of the sample, $n_{H,s}$ is the number of hydrogens in the sample and $n_{F,s}$ is the number in the reference.

The CF_3 peak in the ^{19}F spectrum was compared with the CF_3 peak arising from the reference, dividing the integration of the former by the latter gave the standardised relative number of fluorines (both the sample and reference having the same number of fluorines per mole in the respective peak). In the ^{1}H spectrum, the entire integration for the sample was divided by that of the reference, and this figure adjusted to account for the different number of hydrogens in the reference and sample, to give the standardised relative number of hydrogens. In the case of reactions of DEPEG 600 (**57b**), for instance, this figure was divided by 12.4 (one molecule of DEPEG 600 has an average of 62 molecules of hydrogen, whereas a molecule of (trifluoromethyl)benzene has 5, 62 divided by 5 is 12.4). Other figures used were: DEPEG 400 (**57a**), 8.8; DEPEG 2000 (**57c**), 36.4; poly(ethylene oxide) (**60**), 10.4; DEPTHF (**61**), 22.8; 18-crown-6 (**64**), 4.8; 15-crown-5 (**66**), 4.0.

10.2 Preparation of Starting Materials

10.21 Diethylation of poly(ethylene oxide) 400

Sodium hydride (8.3 g, 207 mmol, 60% dispersion in oil) was washed in petroleum ether (3x100 ml), residual petroleum ether being removed under vacuum. Dried (Dean-Stark) poly(ethylene oxide) 400 (32.7 g, 82 mmol) in toluene (100 ml) was added dropwise and the reaction stirred mechanically, under dry nitrogen, for 5 hours. Diethyl sulphate (15.7 g, 102 mmol) was then added dropwise, and stirring continued a further 18 hours. Solvent and remaining diethyl sulphate were removed under reduced pressure. Dichloromethane (80 ml) was added to the reaction mixture, which was then passed down a column of aluminium oxide (*ca.* 300 g) in dichloromethane. The solution in dichloromethane obtained was dried with magnesium sulphate. Rigorous removal of the dichloromethane gave a viscous, clear liquid, DEPEG 400 (**57a**) (27.1 g, 73.7%); IR and NMR data were consistent with literature values; IR analysis showed no hydroxy groups present.[121]

10.22 Diethylation of poly(ethylene oxide) 600

Using the procedure outlined above a dried solution of poly(ethylene oxide) 600 (**60**) (80.4 g, 134 mmol) in toluene (120 ml) was dripped on to washed sodium hydride (11.6 g of 60% dispersion in oil, 290 mmol) and stirred (5 hours). Diethyl sulphate (22.0 g, 143 mmol) was subsequently added and stirring continued (8 hours). After removal of the volatiles, passing down an alumina column in dichloromethane, drying and removal of solvent a white, waxy solid was obtained, DEPEG 600 (**57b**) (69.2 g, 79.4%); IR and NMR data were consistent with literature values; IR analysis showed no hydroxy groups present.[121]

10.23 Diethylation of poly(ethylene oxide) 2000

Using the procedure outlined above a dried solution of poly(ethylene oxide) 2000 (25.2 g, 12.6 mmol) in toluene (100 ml) was dripped on to washed sodium hydride (1.4 g of 60% dispersion in oil, 35 mmol) and stirred (5 hours). Diethyl sulphate (2.3 g, 15 mmol) was subsequently added and stirring continued (8 hours). Volatile components were removed under vacuum, and the residue passed down an alumina column in dichloromethane. After drying and removal of solvent a white solid was obtained, DEPEG 2000 (**57c**) (19.4 g, 75.3%). IR and NMR data were consistent with literature values; IR analysis showed no hydroxy groups present.[121]

10.24 Diethylation of poly(tetramethylene oxide)

Using the same procedure as before, a dried solution of poly(tetrahydrofuran) of average molecular weight 1000 (46.9 g, 47 mmol) in toluene (90 ml) was dripped onto washed sodium hydride (4.5 g of 60% dispersion in oil, 110 mmol) and stirred (5 hours). Diethyl sulphate (14.7 g, 95 mmol) was subsequently added and stirring continued (8 hours). After removal of the volatiles, this was passed down an alumina column in dichloromethane and solvent removed. A white solid was obtained, α-ethyl-ω-ethoxy poly(tetramethylene oxide) 1000 (DEPTHF) (**61**) (27.0 g, 54.8%); (Found: C, 66.8; H, 11.3. $C_{56}H_{114}O_{14}$ requires C, 66.5; H, 11.4%); IR number 2; NMR number 11.

10.3 Additions of DEPEG to HFP

10.31 Using Chemical Initiation

10.311 Addition of DEPEG 600 to HFP using DBPO

An autoclave was charged with DEPEG 600 (**57b**) (4.3 g, 6.6 mmol), acetone (13.2 g), DBPO (0.58 g, 2.4 mmol) and HFP (**1**) (6.6 g, 44 mmol) and rocked at 80°C for 20 hours. HFP (5.4 g) was recovered, and the resultant solution poured from the autoclave. Removed of acetone under reduced pressure gave a pale brown, viscous liquid, poly(2*H*-hexafluoropropyl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 600 (**58b**), with 13 equivalents of HFP incorporated (16.2 g, 93.4%); (Found: C, 32.1; H, 2.5; F, 56.9. $C_{69}H_{62}F_{78}O_{14}$ requires C, 31.9; H, 2.4; F, 57.1%); IR number 3; NMR number 12.

10.312 Other additions of DEPEG 600

Other reactions using different quantities, and also using TBPO at 130°C were performed, table 9.1, using an identical procedure.

DEPEG 600 (**57b**)/g	Acetone /g	Peroxide	Peroxide /g	HFP (**1**)/g	Temp/°C	Recovered HFP/g	Incorporated HFP
4.5	15.5	DBPO	0.40	17.7	80	12.2	5
12.2	8.0	DBPO	5.6	41.0	80	19.2	7
5.5	15.5	TBPO	0.31	18.0	130	5.0	6
3.58	15.5	TBPO	0.23	19.4	130	11.1	5

Table 9.1

IR and NMR were in each case comparable to that of the first reaction.

10.313 Addition of DEPEG 600 by repeated reaction

Using the same general procedure, an autoclave (500 ml) was charged with DEPEG 600 (**57b**) (14.1 g, 22 mmol), acetone (46.4 g), TBPO (0.61 g, 4.2 mmol) and HFP (**1**) (54.3 g, 362 mmol) and rocked at 140°C for 24 hours. As before, the HFP (37.2 g) and then acetone were removed from the reaction product. NMR showed approximately five equivalents of HFP incorporated in the resultant pale brown liquid (27.0 g). The autoclave was charged again with this material, together with acetone (46.55 g), TBPO (0.56 g, 3.8 mmol) and HFP (53.0 g, 353 mmol). was also added, and the autoclave again heated to 140°C for 20 hours. After removal of HFP (34.7 g) and acetone, NMR showed that the brown liquid contained about ten equivalents of HFP (29.4 g). The autoclave was again charged with this material, acetone (64.4 g), TBPO (0.73 g, 5.0 mmol) and HFP (35.7 g, 238 mmol). After being rocked at 140°C for 20 hours, the autoclave was opened, and HFP (28.4 g) and acetone removed. A dark brown liquid was obtained; poly(2*H*-hexafluoropropyl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 600 (**59**), with 12 equivalents of HFP incorporated (24.5 g, 46.1%); IR and NMR data were identical to values from the first reaction.

10.32 Additions of DEPEG to HFP using γ-initiation

10.321 DEPEG 600

A Carius tube was charged with DEPEG 600 (**57b**) (3.7 g, 5.7 mmol), acetone (9.9 g) and HFP (**1**) (39.7 g, 265 mmol), and then irradiated with γ-rays for 4 days. HFP (34.2 g) was recovered, and acetone removed under vacuum, to leave a pale brown, viscous liquid (9.2 g), poly(2*H*-hexafluoropropyl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 600 (**58b**), with 6 equivalents of HFP incorporated; (Found: C, 35.85; H, 3.5; F, 46.2. $C_{51}H_{62}F_{42}O_{14}$ requires C, 36.0; H, 3.7; F, 47.0%); IR and NMR data were comparable to that of higher adducts.

10.322 DEPEG 2000

A Carius tube was charged with DEPEG 2000 (**57c**) (4.7 g, 2.3 mmol), acetone (13.2 g) and HFP (**1**) (30.3 g, 202 mmol), and then irradiated with γ-rays for 7 days. HFP (23.1 g) was recovered, and acetone removed under vacuum, to leave a pale brown, viscous liquid (8.6 g,), poly(2*H*-hexafluoropropyl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 2000 (**58c**), with 14 equivalents of HFP incorporated; IR and NMR data were consistent with that of lower molecular weight samples; IR number 4.

10.323 Other additions

Other reactions using different DEPEGs, quantities and exposure times were also performed, table 9.2, using an identical procedure.

DEPEG /g	Acetone /g	HFP (**1**)/g	Duration /days	Recovered HFP/g	Incorporated HFP
DEPEG 600 (**57b**)					
4.82	12.2	31.3	4	27.8	3
2.39	10.3	37.2	4	35.7	4
3.67	13.2	28.9	4	24.2	5
3.65	10.1	36.7	4	31.2	6
3.77	9.1	28.8	5	26.0	3
5.85	9.6	27.2	5	23.0	3
5.40	15.5	16.0	6	7.1	6
5.17	12.2	28.8	7	21.3	5
3.76	10.5	33.3	7	27.6	6
5.02	15.5	15.5	12	4.3	8
DEPEG 2000 (**57c**)					
4.90	12.6	28.2	7	23.3	12
4.91	11.6	32.8	7	25.0	17

Table 9.2

IR and NMR data were consistent with previous results.

10.33 Additions of DEPEG to HFP using UV initiation

10.331 DEPEG 400

A Carius tube was charged with DEPEG 400 (**57a**) (4.4 g, 9.8 mmol), acetone (11.9 g) and HFP (**1**) (18.8 g, 125 mmol), and UV irradiated for 3 days. HFP (4.9 g) was recovered and acetone removed under reduced pressure, to leave an almost colourless, viscous liquid, poly(2*H*-hexafluoropropyl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 400 (**58a**), with 8 equivalents of HFP incorporated (10.3 g, 63.8%); IR and NMR data were consistent with literature values.[121]

10.332 DEPEG 600

A Carius tube was charged with DEPEG 600 (**57b**) (1.0 g, 1.5 mmol), acetone (4.0 g) and HFP (**1**) (8.9 g 59 mmol), and UV irradiated for 3 days. HFP (0.2 g) was recovered and acetone removed under reduced pressure, to leave an almost colourless, viscous liquid, poly(2*H*-hexafluoropropyl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 600 (**58b**), with 11 equivalents of HFP incorporated (2.3 g, 65.0%); IR and NMR data were consistent with previous results.

10.333 DEPEG 2000

A Carius tube was charged with DEPEG 2000 (**57c**) (5.3 g, 2.6 mmol), acetone (11.9 g) and HFP (**1**) (18.3 g, 122 mmol), and UV irradiated for 3 days. HFP (4.5 g) was recovered and acetone removed under reduced pressure, to leave an almost colourless, viscous liquid, poly(2*H*-hexafluoropropyl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 2000 (**58c**), with 35 equivalents of HFP incorporated (12.8 g, 67.8%); IR and NMR data were consistent with previous results.

10.334 Other additions

Other reactions using different quantities and DEPEGS were also performed, table 9.3, using an identical procedure.

DEPEG /g	Acetone /g	HFP/g	Recovered HFP/g	Incorporated HFP
DEPEG 400 (**57a**)				
3.2	7.9	10.8		6
DEPEG 600 (**57b**)				
5.6	15.5	20.6	8.2	10
4.0	7.9	12.9	0.1	14
4.5	7.9	15.5	0.7	14

Table 9.3

In each case IR and NMR data were consistent with previous results.

10.34 Addition of DEPEG 600 to HFP using UV initiation in a quartz reactor

A quartz tube (*ca.* 60 ml) was charged with DEPEG 600 (**57b**) (5.2 g, 8.0 mmol), acetone (15.5 g) and HFP (**1**) (18.1 g, 121 mmol) using the same technique as for a Carius tube, and irradiated with UV light for 3 days. HFP was recovered (0.7 g, 5 mmol), and acetone removed under reduced pressure from the resultant brown liquid, poly(2*H*-hexafluoropropyl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 600 (**58b**), with 12 equivalents of HFP incorporated (18.3 g, 93.3); IR and NMR data were in agreement with previous results.

10.4 Alternative Photosensitisers

10.41 General procedure

A quartz tube (*ca.* 60 ml) was charged with 1,4-dioxane (**38**) (10 g, 10 ml, 113 mmol) and photosensitiser (*ca.* 1 g). After degassing, HFP (**1**) (18 - 25 g) was also added in the usual manner, the tube sealed and allowed to reach room temperature. The tube was then irradiated with UV light as before, and the tube opened. The extent of reaction was calculated from the mass of HFP recovered, no further work up being performed.

10.42 Fluorene

A quartz tube was charged with 1,4-dioxane (**38**) (10 g, 113 mmol), fluorene (1.0 g) and HFP (**1**) (24.4 g, 163 mmol), and irradiated with UV light. After reaction HFP (17.8 g, 119 mmol) was recovered, indicating the extent of reaction was 27%.

10.43 m-*Terphenyl*

A quartz tube was charged with 1,4-dioxane (**38**) (10 g, 113 mmol), *m*-terphenyl (1.1 g) and HFP (**1**) (24.4 g, 163 mmol), and irradiated with UV light. After reaction HFP (19.3 g, 128 mmol) was recovered, indicating the extent of reaction was 21%.

10.44 Naphthalene

A quartz tube was charged with 1,4-dioxane (**38**) (10 g, 113 mmol), naphthalene (0.9 g) and HFP (**1**) (21.9 g, 163 mmol), and irradiated with UV light. After reaction HFP (16.9 g, 112 mmol) was recovered, indicating the extent of reaction was 23%.

10.45 Biphenyl

A quartz tube was charged with 1,4-dioxane (**38**) (10 g, 113 mmol), biphenyl (1.0 g) and HFP (**1**) (21.7 g, 145 mmol), and irradiated with UV light. After reaction HFP (21.0 g, 140 mmol) was recovered, indicating the extent of reaction was 3%.

10.46 Anthracene

A quartz tube was charged with 1,4-dioxane (**38**) (10 g, 113 mmol), anthracene (0.7 g) and HFP (**1**) (23.7 g, 158 mmol), and irradiated with UV light. After reaction HFP (14.5 g, 96 mmol) was recovered, indicating the extent of reaction was 39%.

10.47 Benzene

A quartz tube was charged with 1,4-dioxane (10 g, 113 mmol), benzene (0.9 g) and HFP (**1**) (23.0 g, 153 mmol), and irradiated with UV light. After reaction HFP (22.1 g, 147 mmol) was recovered, indicating the extent of reaction was 4%.

10.48 Acetone

As a control reaction, a quartz tube was charged with 1,4-dioxane (**38**) (10 g, 113 mmol), acetone (1.0 g) and HFP (**1**) (24.4 g, 163 mmol), and irradiated with UV light. After reaction HFP (0.2 g, 1.6 mmol) was recovered, indicating the extent of reaction was 99%.

10.49 Acetone and benzene as photosensitiser

A quartz tube was charged with 1,4-dioxane (**38**) (10 g, 113 mmol), benzene (0.9 g), acetone (0.8 g) and HFP (**1**) (18.9 g, 126 mmol), and irradiated with UV light. After reaction HFP (6.3 g, 42 mmol) was recovered, indicating the extent of reaction was 66%.

10.5 Attempted Use of Titanium Dioxide as a γ-Ray Sensitiser

A Carius tube was charged with diethyl ether (**39**) (6.5 g, 88 mmol), titanium dioxide (0.76 g, 8.4 mmol) and HFP (**1**) (8.5 g, 57 mmol), and irradiated with γ-rays for 2 days, while being rotated to ensure good contact with the insoluble titanium dioxide. HFP (2.6 g) was recovered, and the conversion of HFP therefore calculated as 69.4%.

10.51 Control experiment

The previous experiment was repeated without the presence of titanium dioxide. A Carius tube was charged with diethyl ether (**39**) (8.4 g, 113 mmol) and HFP (**1**) (8.8 g, 59 mmol), and irradiated with γ-rays for 2 days, while being rotated. HFP (2.7 g) was recovered, and the conversion of HFP therefore calculated as 69.3%.

10.6 Addition of Hydroxy Terminated Poly(ethylene Oxide) to HFP

(i) A Carius tube was charged with poly(ethylene oxide) 600 (**60**) (3.2 g, 5.3 mmol), acetone (19.0 g) and HFP (**1**) (19.4 g, 129 mmol) and irradiated for 3 days with UV light. After irradiation, the tube was opened, HFP (14.1 g) recovered and acetone removed to leave a light brown liquid, (5.4 g). NMR indicated four molar equivalents of HFP had been incorporated, including some at the hydroxy end groups, due to nucleophilic addition; δ_F (235 MHz; solvent $CDCl_3$; standard $CFCl_3$) -74.8 (3F, s, CF_3), -132 (1F, dd, J_{AB} 380, $^2J_{FH}$ 60, C*F*F'H), -134 (1F, d, J_{AB} 380, $^2J_{FH}$ 60, CF*F'*H), -184.2 (1F, s, CF).

(ii) Poly(ethylene oxide) 600 (**60**) (20.8 g, 34.7 mmol), acetone (41.3 g) and HFP (**1**) (45.8 g, 305 mmol) were charged into a Carius tube, which was irradiated with γ-rays for 4 days. The Carius tube was then opened, HFP (26.0 g) recovered and the solution poured out. Acetone was removed under reduced pressure, to leave the brown liquid product (31.4 g). As before NMR indicated about four molar equivalents of HFP incorporated, including one *via* a nucleophilic addition at the end groups; IR and NMR data were consistent with previous results.

10.7 Addition of PTHF to HFP

(i) PTHF (**61**) (4.4 g, 4.2 mmol), acetone (19.0 g) and HFP (**1**) (20.9 g, 139 mmol) were admitted into a Carius tube, which was then irradiated for 3 days with UV light. HFP (4.6 g) was recovered and acetone removed to leave a light brown liquid (14.3 g, 84.3%), poly(2*H*-hexafluoropropyl)-α-ethyl-ω-ethoxy poly(tetramethylene oxide) 1000 (**62**) with approximately 20 molar equivalents of HFP incorporated (Found: C, 34.25; H, 2.7;. $C_{116}H_{114}F_{120}O_{14}$ requires C, 34.7; H, 2.9%); IR number 5; NMR number 13.

(ii) PTHF (**61**) (3.0 g, 2.9 mmol), acetone (19.0 g) and HFP (**1**) (16.1 g, 107 mmol) were charged into a Carius tube, which was sealed and irradiated with UV light for 3 days. The Carius tube was then opened, HFP (5.7 g) recovered and the solution poured out. Acetone was removed, leaving the brown liquid product, poly(2*H*-hexafluoropropyl)-α-ethyl-ω-ethoxy poly(tetramethylene oxide) (**62**) with 26 equivalents of HFP incorporated; IR and NMR data agreed with the previous experiment.

10.8 Addition of Crown Ethers to Fluoroalkenes

10.81 Addition of 18-crown-6 to HFP

(i) A Carius tube was charged with 18-crown-6 (**64**) (2.1 g, 8.0 mmol), acetone (7.9 g) and HFP (**1**) (2.0 g, 13 mmol) and irradiated with γ-rays for 4 days. No HFP was recovered, acetone was removed under reduced pressure. The resultant liquid was distilled (135°C/0.05 mmHg, kugelrohr apparatus) to provide a viscous, almost colourless liquid, poly(2*H*-hexafluoropropyl)-18-crown-6 (**65**), insoluble in water, which NMR indicated had 4 molar equivalents of HFP incorporated (3.4 g, 49.3%); (Found: C, 33.2; H, 2.8. $C_{24}H_{24}F_{24}O_6$ requires C, 33.35; H, 2.8%); IR number 6; MS number 2; NMR number 14.

(ii) A Carius tube was charged with 18-crown-6 (**64**) (4.4 g, 17 mmol), acetone (7.9 g) and HFP (**1**) (2.0 g, 13 mmol) and irradiated with UV rays for 3 days. No HFP was recovered, acetone was removed under reduced pressure to leave a viscous, light brown liquid, poly(2*H*-hexafluoropropyl)-18-crown-6 (**65**), which NMR indicated had

0.8 molar equivalents of HFP incorporated. Distillation (125°C/0.07 mmHg, kugelrohr) gave, after the starting material had been removed, a clear, colourless liquid, a mixture of adducts, averaging to the diadduct (7.9 g, 84.0%). Further attempts to purify the product by chromatography (alumina, dichloromethane), recrystallisation (ethyl acetate and chloroform) and further distillation failed. Attempts to remove 18-crown-6 completely from the product by extraction into water failed; (Found: C, 39.9; H, 5.0. $C_{18}H_{24}F_{12}O_6$ requires C, 38.3; H, 4.3%); IR and NMR consistent with the previous reaction. The material formed complexes with potassium nitrate; MS number 3. Attempts to form crystals of the potassium complex (crystallisation from ethyl acetate and chloroform) failed.

(iii) A Carius tube was charged with 18-crown-6 (**64**) (4.2 g, 16 mmol), acetone (11.9 g) and HFP (**1**) (17.9 g, 120 mmol) and irradiated with UV rays for 3 days. HFP (0.4 g) was recovered and acetone removed under reduced pressure to leave a viscous, light brown liquid, poly(2*H*-hexafluoropropyl)-18-crown-6 (**65**), which NMR indicated had 5 molar equivalents of HFP incorporated (11.6 g, 71.9%); (Found: C, 32.3; H, 2.5. $C_{27}H_{24}F_{30}O_6$ requires C, 32.0; H, 2.4%); IR and NMR were consistent with those of the previous reactions.

10.83 Addition of 15-crown-5 to HFP

A Carius tube was charged with 15-crown-5 (**66**) (3.9 g, 18 mmol), acetone (7.9 g) and HFP (**1**) (1.9 g, 13 mmol) and irradiated with UV rays for 3 days. HFP (0.4 g) was recovered and acetone removed under reduced pressure to leave a viscous, light brown liquid, poly(2*H*-hexafluoropropyl)-15-crown-5 (**67**), which NMR indicated had 0.6 molar equivalents of HFP incorporated (5.2 g); IR number 7; MS number 4; NMR number 15.

10.84 Addition of 18-crown-6 to PFP

(i) A Carius tube was charged with 18-crown-6 (**65**) (4.4 g, 17 mmol), acetone (7.9 g) and PFP (1.5 g, 11 mmol) and irradiated with UV rays for 3 days. No PFP was recovered and acetone was removed under reduced pressure to leave a viscous, light brown liquid, poly(1,1,3,3,3-pentafluoropropyl)-18-crown-6 (**68**), which NMR indicated had 0.6 molar equivalents of PFP incorporated (5.5 g); GLC showed numerable components present; ν_{max}/cm^{-1} 2930 and 2890 (CH), 1470 (CH_2-O scissoring), 1400s, 1280s, 1170vs, 890, 830, 820; δ_H (400 MHz; solvent $CDCl_3$; standard TMS) 1.328 (1H, t, *J* 12, unassigned), 2.87 (2H, broad multiplet, unassigned), 3.83 (4H, broad s, unassigned); δ_F (376 MHz; solvent $CDCl_3$; standard $CFCl_3$) -60.70 (3F, p, $^3J_{FH}$ and $^4J_{FF}$ 9.7, $-CF_3$), 114.43 (2F, m, $-CF_2-$). No further purification was performed.

(ii) A Carius tube was charged with 18-crown-6 (**64**) (1.5 g, 5.7 mmol), acetone (4.0 g) and PFP (5.5 g, 42 mmol) and irradiated with UV rays for 3 days. PFP (0.1) was recovered and acetone removed under reduced pressure to leave a viscous, light brown liquid, poly(1,1,3,3,3-pentafluoropropyl)-18-crown-6 (**68**), which NMR indicated had 7 molar equivalents of PFP incorporated (6.1 g). As before, several components were present (GLC). No further analysis was performed.

CHAPTER ELEVEN
EXPERIMENTAL TO CHAPTER FIVE

11.1 General Procedures

Free radical additions were performed using the general procedures of chapter nine, except where otherwise stated. The degree of incorporation of HFP (**1**) was estimated from the ^{1}H and ^{19}F NMR spectra integrations, using (trifluoromethyl)benzene as a reference. DEPEG 600 (57b) was prepared using the procedure described in chapter ten. Determination of the degree of incorporation of HFCB (**17**) and OFCP (**69**) was performed using the general method described in chapter four, using (trifluoromethyl)benzene as a reference. The CF_2 and CF peaks of the sample in the ^{19}F spectrum were used for integrations (*i.e.*, not the CFH peak), thus when calculating the standardised relative number of fluorines the figure was multipled by 0.6 (HFCB) or 0.43 (OCFB).

11.2 Additions of DEPEG 600 to Hexafluorocyclobutane

(i) A Carius tube was charged with DEPEG 600 (**57b**) (2.5 g, 3.8 mmol), acetone (4 g) and HFCB (**17**) (13.9 g, 86 mmol) and γ-irradiated for 4 days. HFCB (2.8 g) was recovered, acetone removed under reduced pressure, and a viscous brown liquid recovered (1.9 g), which NMR indicated had negligible HFCB incorporated.

(ii) A Carius tube was charged with DEPEG 600 (**57b**) (1.3 g, 2.0 mmol), acetone (3.1 g) and HFCB (**17**) (13.9 g, 86 mmol) and UV irradiated for 3 days. HFCB (5.9 g) was recovered, acetone removed under reduced pressure, and a viscous brown liquid recovered (1.2 g), which NMR indicated had 10 equivalents of HFCB incorporated, as well as about 4 molar equivalents of of acetone (indicated by the occurance of peaks at 0.9 ppm in the ^{1}H NMR spectrum). No further analysis was performed.

(iii) A UV reactor (Pyrex tube, 45 mm internal diameter, with a quartz thimble, 37 mm outside diameter, within, containing a 100W medium pressure mercury lamp, air cooled), suitable for low temperature reactions, was charged with DEPEG 600 (**57b**) (5.4 g, 8.3 mmol) and acetone (7.9 g), and degassed. HFCB (**17**) (12.2 g, 75 mmol) was condensed into the cooled (liquid air) reactor, which was then allowed to reach -30°C (cryostat). The reactor was irradiated with UV light for 5 days, and HFCB (4.6 g) recovered. Acetone was removed under reduced pressure to leave a material which NMR indicated had 6 molar equivalents of HFCB incorporated, and about 2 equivalents of acetone. No further analysis was performed. A second material was recovered from the reactor wall, that was gel-like, involatile and insoluble in common solvents (water, acetone, diethyl ether, dichloromethane, chloroform), no analysis was performed.

(iv) As in the previous reaction, a UV reactor (Pyrex tube, 45 mm internal diameter, with a quartz thimble, 37 mm outside diameter, within, containing a 100W medium pressure mercury lamp, air cooled) was charged with DEPEG 600 (**57b**) (6.7 g, 10 mmol) and acetone (7.9 g), and degassed. HFCB (**17**) (11.6 g, 72 mmol) was condensed into the cooled (liquid air) reactor, which was then allowed to reach 0°C (cryostat). The reactor was irradiated with UV light for 5 days, and no HFCB was recovered. Acetone was removed under reduced pressure to leave a material which NMR indicated had 4 molar equivalents of HFCB incorporated, as well as about one equivalent of acetone. No further analysis was performed. Again a second gel-like material was recovered from the reactor wall.

(v) A UV reactor (Pyrex tube, 45 mm internal diameter, with a *Pyrex* thimble, 37 mm outside diameter, within, containing a 100W medium pressure mercury lamp, air cooled) was charged with DEPEG 600 (**57b**) (5.4 g, 8.3 mmol) and acetone (15.8 g), and degassed. HFCB (**17**) (9.6 g, 59 mmol) was condensed into the cooled (liquid air) reactor, which was then allowed to reach -15°C (cryostat). The reactor was irradiated with UV light for 5 days, and HFCB (4.2 g) recovered. Acetone was removed under reduced pressure to leave a material which NMR indicated had 3 molar equivalents of HFCB incorporated and some acetone as well. No other material was recovered from the reactor.

(vi) A Carius tube was charged with DEPEG 600 (**57b**) (3.0 g, 4.6 mmol), 2,2,2-trifluoroethanol (7.3 g), benzophenone (0.79 g) and HFCB (**17**) (15.4 g, 95 mmol) and UV-irradiated for 3 days. HFCB (12.3 g) was recovered, 2,2,2-trifluoroethanol removed under reduced pressure, and a viscous brown liquid recovered (6.3 g), which NMR indicated had 10 equivalents of HFCB incorporated, as well as 2 equivalents of benzophenone. No further analysis was performed.

11.21 Without photosensitiser

A Carius tube was charged with DEPEG 600 (**57b**) (2.0 g, 3.1 mmol), 2,2,2-trifluoroethanol (6.85 g) and HFCB (**17**) (13.7 g, 85 mmol) and UV irradiated for 3 days. HFCB (10.3 g) was recovered, 2,2,2-trifluoroethanol removed under reduced pressure, and a viscous brown liquid recovered, which NMR indicated had 4 equivalents of HFCB incorporated, poly(2*H*-hexafluorocyclobutyl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 600 (**71a**) (1.8 g, 44.9%); (Found: C, 42.9; H, 4.9. $C_{46}H_{62}F_{24}O_{14}$ requires C, 42.7; H, 4.8%); IR number 8; NMR number 16.

11.3 Additions of DEPEG 600 to OFCP

(i) A Carius tube was charged with DEPEG 600 (**57b**) (2.6 g, 4.0 mmol), acetone (4 g) and OFCP (**69**) (11.4 g, 54 mmol) and γ-irradiated for 4 days. OFCP (0.3 g) was recovered, acetone removed under reduced pressure, and a viscous brown liquid recovered (1.8 g), which NMR indicated had negligible OFCP incorporated.

(ii) A Carius tube was charged with DEPEG 600 (**57b**) (1.1 g, 1.7 mmol), acetone (3.1 g) and OFCP (**69**) (7.2 g, 34 mmol) and UV irradiated for 4 days. OFCP (1.6 g) was recovered, acetone removed under reduced pressure, and a viscous brown liquid recovered (3.0 g), which NMR indicated had 5 equivalents of OFCP incorporated as well as two to three equivalents of acetone. No further analysis was performed.

(iii) A Carius tube was charged with DEPEG 600 (**57b**) (2.9 g, 4.5 mmol), 2,2,2-trifluoroethanol (7.3 g), benzophenone (0.79 g) and OFCP (**69**) (12.3 g, 58 mmol) and UV irradiated for 3 days. OFCP (6.5 g) was recovered, 2,2,2-trifluoroethanol removed under reduced pressure, and a viscous brown liquid recovered (3.9 g), which NMR indicated had 10 equivalents of OFCP incorporated, as well as about two equivalents of benzophenone. No further analysis was performed.

11.31 Without photosensitiser

A Carius tube was charged with DEPEG 600 (**57b**) (2.2 g, 3.4 mmol), 2,2,2-trifluoroethanol (6.9 g) and OFCP (**69**) (15.5 g, 73 mmol) and UV irradiated for 3 days. OFCP (14.1 g) was recovered, 2,2,2-trifluoroethanol removed under reduced pressure, and a viscous brown liquid recovered, which NMR indicated had 5 equivalents of OFCP incorporated, poly(2*H*-hexafluorocyclopentyl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 600 (**71b**) (2.1 g, 36.1%); (Found: C, 38.6; H, 3.9. $C_{55}H_{62}O_{14}F_{40}$ requires C, 38.7; H, 3.7%); IR number 9; NMR number 17.

11.4 Reaction between HFCB and acetone.

A quartz tube (*ca.* 60ml) was charged with acetone (4.0 g, 69 mmol), degassed and cooled (liquid air). HFCB (**17**) (8.3 g, 51 mmol) was condensed in the tube, which was then sealed, and irradiated with UV light (1000W, medium pressure, mercury lamp) for 3 days. HFCB (2.4 g) was recovered, and, after removal of acetone under reduced pressure, a gel-like material was recovered; ν_{max}/cm^{-1} 3400 (OH), 2980 and 2940 (CH), 1740s (C=O), 1370, 1200br (CF), 880, 860, 720s. Attempts to dissolve this material (water, ethanol, acetone, ether, dichloromethane, chloroform) were unsuccessful. No further attempts at analysis were performed.

11.5 Attempted additions to decafluoro-3,4-bis(trifluoromethyl)hex-3-ene

Decafluoro-3,4-bis(trifluoromethyl)hex-3-ene (**74**) is a liquid, and was added to the Carius tube with the other liquid components before degassing [5 ml of decafluoro-3,4-bis(trifluoromethyl)hex-3-ene weighs 9.7 g].

11.51 Oxetane

(i) A Carius tube was charged with oxetane (**50**) (1.8 g, 31 mmol), acetone (4.0 g) and decafluoro-3,4-bis(trifluoromethyl)hex-3-ene (**74**) (9.7 g, 49 mmol), degassed and sealed. It was observed that the fluoroalkene was immiscible with the other components and, after 3 days UV irradiation, all the starting materials were recovered.

(ii) A Carius tube was charged with oxetane (**50**) (1.8 g, 31 mmol), 2,2,2-trifluoroethanol (6.9 g) and decafluoro-3,4-bis(trifluoromethyl)hex-3-ene (**74**) (9.7 g, 49 mmol), degassed and sealed. It was observed that the fluoroalkene was immiscible with the oxetane and, after 3 days UV irradiation, all the starting materials were recovered.

(iii) A Carius tube was charged with oxetane (**50**) (1.8 g, 31 mmol), 2,2,2-trifluoroethanol (6.9 g), acetone (0.4 g) and decafluoro-3,4-bis(trifluoromethyl)hex-3-ene (**74**) (9.7 g, 49 mmol), degassed and sealed. It was observed that the fluoroalkene was immiscible with other components and, after 3 days UV irradiation, all the starting materials were recovered.

11.52 1,4-Dioxane

A Carius tube was charged with 1,4-dioxane (**38**) (2.0 g, 23 mmol), acetone (4.0 g) and decafluoro-3,4-bis(trifluoromethyl)hex-3-ene (**74**) (9.7 g, 49 mmol), degassed and sealed. It was observed that the fluoroalkene was immiscible with the oxetane and, after 3 days UV irradiation, all the starting materials were recovered.

*11.53 2-(*2H*-Hexafluoropropyl)oxolane*

A Carius tube was charged with 2-(2*H*-hexafluoropropyl)oxolane (**54**) (3.4 g, 8.8 mmol), acetone (0.2 g) and decafluoro-3,4-bis(trifluoromethyl)hex-3-ene (**74**) (5.8 g, 29 mmol), degassed and sealed. After 3 days UV irradiation of this homogeneous solution, all the starting materials were recovered.

*11.54 2-(*2H*-Hexafluoropropyl)-1,4-dioxane*

A Carius tube was charged with 2-(2*H*-hexafluoropropyl)-1,4-dioxane (3.4 g, 8.8 mmol), acetone (0.2 g) and decafluoro-3,4-bis(trifluoromethyl)hex-3-ene (**74**) (5.8

g, 29 mmol), degassed and sealed. After 3 days UV irradiation of this homogeneous solution, all the starting materials were recovered.

11.6 Attempted Addition of DEPEG 600 to Chlorotrifluoroethene

(i) A Carius tube was charged with DEPEG 600 (**57b**) (3.6 g, 5.5 mmol), acetone (4.0 g) and CTFE (**75**) (9.3 g, 80 mmol), and γ-irradiated for 4 days. CTFE (3.5 g) was recovered. Acetone was removed under reduced pressure to leave a white solid, which NMR (run as a suspension in d_6-acetone) indicated was a mixture of poly(CTFE) and DEPEG 600. Addition of acetone gave a white suspension, attempts to extract DEPEG 600 into the acetone were unsuccessful. Elemental analysis suggested a 9:1 molar ratio of CTFE to DEPEG 600 (Found: C, 33.9; H, 3.8. $C_{48}H_{62}Cl_9F_{27}O_{14}$ requires C, 34.0; H, 3.7%); ν_{max}/cm^{-1} 2930w and 2860 (CH), 1460 (CH_2-O scissoring), 1350, 1290, 1200 (CF), 1130br (CF and C-O), 970, 850; the insolubility in common solvents (water, acetone, chloroform) as well as in di-2,5-(2*H*-hexafluoropropyl)oxolane and intractability of the material precluded further analysis.

(ii) A Carius tube was charged with DEPEG 600 (**57b**) (3.3 g, 5.1 mmol), 2,2,2-trifluoroethanol (6.9 g) and CTFE (**75**) (10.9 g, 94 mmol), and γ-irradiated for 4 days. No CTFE was recovered. Solvent was removed under reduced pressure to leave a white solid as before. Addition of acetone gave a white suspension, but attempts to extract DEPEG 600 into the acetone were again unsuccessful. The material was insoluble in common solvents (water, acetone, chloroform); no further analysis was performed.

11.7 Attempted Additions to 1,1-Difluoroethene

11.71 1,4-Dioxane

A Carius tube was charged with 1,4-dioxane (**38**) (5 g, 57 mmol), acetone (4.0 g) and 1,1-difluoroethene (VDF) (**76**) (8.9 g, 140 mmol), degassed and γ-irradiated for 4 days. VDF (0.3 g) was recovered, and after removal of solvent an off-white solid was obtained (7.9 g), sparingly soluble in acetone, insoluble in chloroform. Elemental analysis suggested this consisted of approximately 250 molar equivalents of 1,1-difluoroethene to one DEPEG 600; (Found: C, 38.2; H, 3.4. $C_{530}H_{562}F_{500}O_{14}$ requires C, 38.2; H, 3.4%); ν_{max}/cm^{-1} 2920 and 2840 (CH), 1460 (CH_2-O scissoring), 1410 (CH_2-CF_2 scissoring), 1380, 1210 (CF), 1180 (CF), 1070, 970, 870, 790, 760.

11.72 DEPEG 600

A Carius tube was charged with DEPEG 600 (**57b**) (2.5 g, 3.8 mmol), acetone (4.0 g) and VDF (**76**) (6.8 g, 106 mmol), degassed and γ-irradiated for 4 days. VDF (0.3 g) was recovered, and after removal of solvent an off white solid was obtained, insoluble in common solvents (ethanol, acetone, diethyl ether, chloroform), precluding further analysis.

CHAPTER TWELVE

EXPERIMENTAL TO CHAPTER SIX

12.1 General Procedures

Free radical additions were performed using the general procedures of chapter nine, except where otherwise stated. The degree of incorporation of HFA (77) was estimated from the ^1H and ^{19}F NMR spectra integrations, using (trifluoromethyl)benzene as a reference. DEPEG 600 (**57b**) was prepared using the procedure described in chapter ten.

12.2 Additions to Hexafluoroacetone

12.21 Cyclohexane

A Carius tube was charged with cyclohexane (**82**) (2.7 g, 32 mmol) and HFA (77) (8.3 g, 50 mmol), and γ-irradiated for 4 days. HFA (0.1) was recovered, and a brown liquid recovered. NMR analysis indicated 1.7 molar equivalents of HFA had reacted, giving a mixture of products. IR and NMR of the mixture was consistent with the literature.[154]

12.22 Oxolane

(i) An autoclave was charged with oxolane (**37**) (10.8 g, 150 mmol), DBPO (0.31 g, 2.2 mmol) and HFA (**77**) (10.6, 64 mmol), and rocked at 80°C for 20 hours. HFA (2.9 g) was recovered, and a brown liquid obtained, from which the volatile components were removed under reduced pressure (*ca.* 1 mmHg). The latter provided a clear, colourless liquid (9.8 g); GLC/MS indicated that this was composed as; starting material (87.9%), 2-(hexafluoro-2-hydroxyprop-2-yl)oxolane (**92a**) (8.7%) and 2-(2*H*-hexafluoroprop-2-oxy)oxolane (**92b**) (3.4%). Attempts to distil the mixture (36°C/44 mmHg) led to a rapid darkening indicative of decomposition, no products were isolated.

(ii) A Carius tube was charged with oxolane (**37**) (10.5 g, 146 mmol) and HFA (77) (10.5 g, 63 mmol), and γ-irradiated for 4 days. HFA (5.6 g) was recovered, and a brown liquid obtained, from which the volatile components (10.6 g) were removed under reduced pressure (*ca.* 1 mmHg). The latter provided a clear, colourless liquid that GLC/MS indicated was of 2-(hexafluoro-2-hydroxyprop-2-yl)oxolane (**92a**) (17.8% of the mixture) from which starting material could not be separated. No further attempt at analysis was performed and no product was isolated.

(iii) A Carius tube was charged with oxolane (**37**) (10.6 g, 147 mmol), acetone (5.1 g) and HFA (77) (11.7 g, 70 mmol), and γ-irradiated for 4 days. HFA (6.3 g) was recovered, and a brown liquid obtained, from which the volatile components (10.1 g) were removed under reduced pressure (*ca.* 1 mmHg). The latter provided a clear, colourless liquid that GLC/MS indicated that this was 6.7% 2-(hexafluoro-2-

hydroxyprop-2-yl)oxolane (**92a**) from which starting material could not be separated. No further attempt at analysis was performed and no product was isolated.

(iv) A Carius tube was charged with oxolane (**37**) (4.4 g, 62 mmol; dried over molecular sieve), acetone (4.0 g; dried over molecular sieve) and HFA (**77**) (18.2 g, 110 mmol) (all glassware thoroughly carefully dried, FEP tubing used in place of rubber), and UV irradiated for 3 days. HFA (0.6 g) was recovered, and a light brown liquid obtained, from which the volatile components were removed under reduced pressure (*ca.* 1 mmHg). Distillation (50 - 65°C/2 mmHg) of the latter gave a liquid (3.4 g), which GLC showed was composed of about 12 components, determined to be a mixture of mono- and di-adducts by GLC/MS. Attempts to separate these by further distillation were unsuccessful, a mixture only being obtained (2.8 g); IR number 10; MS number 5.

12.23 Diethyl ether

A Carius tube was charged with diethyl ether (**39**) (3.9 g, 53 mmol), acetone (7.9 g) and HFA (**77**) (12.5 g, 75 mmol), and UV irradiated for 3 days. HFA (0.3 g) was recovered, and acetone and diethyl ether removed under reduced pressure. The resultant material was distilled (100°C/0.07 mmHg, kugelrohr apparatus) to provide a clear, colourless liquid (5.2 g). GLC showed several components still present and inseparable, of which 2-(1-ethoxy ethoxy)-2*H*-hexafluoropropane (**93b**), 3-ethoxy-1,1,1-trifluoro-2-hydroxy-2-(trifluoromethyl)butane (**93a**), 4-ethoxy-1,1,1-trifluoro-2-hydroxy-2-(trifluoromethyl)butane and 2-(2-ethoxy ethoxy)-2*H*-hexafluoropropane were tentatively identified (see chapter six, section 6.23), some diadduct was also present; IR number 11; MS number 6; δ_H (400 MHz; solvent d_6-acetone; standard TMS) 0.8 - 1.7 (20H, m, CH_3CH_2O-), 1.96 - 2.23 (5 - 6H, m, CH_3CHR_fO-), 3.42 (10H, s, $CH_3CH_2OCH_2$-), 2.8 - 3.9 (4H, m, $CH_3CH_2OCHR_f$-), 7.20 [3H, s, -$OC(CF_3)_2H$], 8.045 [1H, broad s, -$C(CF_3)_2OH$]; δ_F (376 MHz; solvent d_6-acetone; standard $CFCl_3$) -69.7 - -77.8 (several peaks, CF_3).

12.24 Diethoxy ethane

A Carius tube was charged with diethoxy ethane (**94**) (5.5 g, 47 mmol), acetone (7.9 g) and HFA (**77**) (4.5 g, 27 mmol), and UV irradiated for 3 days. HFA (0.1 g) was recovered, and acetone removed under reduced pressure. Diethoxy ethane (3.1 g) was distilled from the resultant liquid (up to 50°C/0.1 mmHg, kugelrohr apparatus) and further distillation (75°C/0.01 mmHg, kugelrohr apparatus) gave a clear, colourless liquid, an inseparable mixture of the mono- (**95** and **96**) and di-adducts of diethoxy ethane with HFA (1.1 g); IR number 12; MS number 7; δ_H (250 MHz; solvent $CDCl_3$; standard TMS) 1.12 (14H, m, CH_3CHR_fO-), 1.26 (1H, t, $^3J_{HH}$ 10.7, $CH_3CH_2OCH_2$-), 1.46 (2H, m, CH_3CHR_fO-), 3.23 [1H, heptet, $^3J_{HF}$ 6.5, -$OC(CF_3)_2H$], 3.6 (5H, broad m, $-CH_2-$), 3.8 (5H, broad m, $-CHR_f-$), 8.21 [1H, s, $-C(CF_3)_2OH$]; δ_F (235 MHz; solvent $CDCl_3$; standard $CFCl_3$) -69.3 - -82.0 (several peaks, CF_3). Further distillation (100 - 125°C/0.01 mmHg, kugelrohr apparatus) gave further fractions of higher adduct mixtures (0.9 g total), no further analysis was performed.

12.25 1,4-Dioxane

A Carius tube was charged with 1,4-dioxane (**38**) (5.0 g, 57 mmol; dried over molecular sieve), acetone (4.0 g; dried over molecular sieve) and HFA (**77**) (17.3), all glassware having been carefully dried, FEP tubing being used in place of rubber, and UV irradiated for 3 days, during which a white solid precipitated out of the solution. No HFA was recovered, and acetone and 1,4-dioxane were removed under reduced pressure. The resultant solid (7.6 g) was recrystallised from petroleum ether (60 - 80°C boiling fraction), and sublimed, to afford white crystals, an inseparable mixture of 1,4-dioxane, 2-(2*H*-hexafluoroprop-2-oxy)-6-(hexafluoro-2-hydroxyprop-2-yl)-1,4-dioxane (**98**) and di-2,6-(hexafluoro-2-hydroxyprop-2-yl)-1,4-dioxane (**99**) (2.6 g) (assignments are discussed in chapter six, section 6.24); IR number 13; MS number 8; NMR number 18.

12.26 DEPEG 600

(i) A Carius tube was charged with DEPEG 600 (**57b**) (3.8 g, 5.8 mmol), acetone (8.0 g) and HFA (**77**) (28.3 g, 170 mmol), and irradiated with γ-rays for 4 days. HFA (23.9 g) was recovered, and acetone removed under reduced pressure, to afford a viscous brown material that NMR indicated had 4 molar equivalents of HFA incorporated. Heating this material under reduced pressure (200°C/0.4 mmHg, kugelrohr apparatus) removed dissolved HFA, NMR now indicated 1.1 molar equivalents of HFA incorporated, no further analysis was performed.

(ii) A Carius tube was charged with DEPEG 600 (4.1 g, 6.3 mmol), acetone (11.9 g) and HFA (13.8 g, 83 mmol), and irradiated with UV light for 3 days. HFA (0.1 g) was recovered, and acetone removed under reduced pressure, to afford a viscous brown material that NMR indicated had 13 molar equivalents of HFA incorporated. Heating this material under reduced pressure (200°C/0.4 mmHg, kugelrohr apparatus) removed dissolved HFA, NMR now indicated 5 molar equivalents of HFA incorporated, poly(2*H*-hexafluoroprop-2-oxy)-poly(hexafluoro-2-hydroxyprop-2-yl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 600 (2.6 g, 27.9%); (Found: C, 36.9; H, 4.2; F, 38.3%. $C_{45}H_{62}F_{30}O_{19}$ requires C, 36.6; H, 4.2; F, 38.6%); IR number 14; NMR number 19.

CHAPTER THIRTEEN
EXPERIMENTAL TO CHAPTER SEVEN

13.1 General Procedure

Solutions were made up of PMMA (**101**) (5.75 g) dissolved in acetone (57.65 g) and fluorinated polyether [2.53 g; dodecaadduct of HFP with DEPEG 600 (**58b**), prepared using peroxide initiation as described in chapter ten] dissolved in acetone (9.77 g). Samples (approximately 7 ml) were then prepared by mixing these two solutions. From these were drawn approximately 1 ml aliquots which were placed on glass slides with raised edges, giving films of about 800 mm^2. The acetone was then allowed to evaporate, firstly at atmospheric pressure (6 hours), then under reduced pressure (2 hours). The films were removed from the glass and cut in to suitable sections for ESCA.

13.21 50% adduct in PMMA

PMMA (**101**) solution (8.30 g; 0.753 g of PMMA) and fluorinated polyether (**58b**) solution (4.46 g; 0.917 g of fluorinated polyether) were mixed (54.9% fluorinated polyether in PMMA), and a sample of this solution applied to a glass slide. The surface of the film resultant after evaporation of acetone was analysed (ESCA) with the following counts detected for each element; carbon (9203), oxygen (2346), fluorine (7754) and silicon (522). This implied a composition of $CF_{0.84}O_{0.29}Si_{0.06}$, which corresponded to $CF_{0.92}O_{0.28}$ when the silicon dioxide signal from the glass was allowed for. Deconvolution of the C_{1s} spectrum was presented in chapter 7, a figure of 15.4 was established for the percentage of trifluorinated carbons on the surface compared with the total number of carbons.

13.22 20% fluorinated polyether in PMMA

PMMA (**101**) solution (8.33 g; 0.755 g of PMMA) and fluorinated polyether (**58b**) solution (1.12 g; 0.230 g of fluorinated polyether) were mixed (23.4% fluorinated polyether in PMMA), and a sample of this solution applied to a glass slide and, after evaporation of acetone, the carbon content of the surface analysed by ESCA. After deconvolution of the C_{1s} spectrum it was found that 15.5% of the surface was composed of trifluorinated carbons compared with the total number of carbons.

13.23 10% fluorinated polyether in PMMA

PMMA (**101**) solution (8.50 g; 0.771 g of PMMA) and fluorinated polyether (**58b**) solution (0.48 g; 0.099 g of fluorinated polyether) were mixed (11.4% fluorinated polyether in PMMA), and a sample of this solution applied to a glass slide and, after evaporation of acetone, the carbon content of the surface analysed by ESCA. After deconvolution of the C_{1s} spectrum it was found that 16.8% of the surface was composed of trifluorinated carbons compared with the total number of carbons.

13.24 5% fluorinated polyether in PMMA

PMMA (**101**) solution (8.53 g; 0.774 g of PMMA) and fluorinated polyether (**58b**) solution (0.24 g; 0.049 g of fluorinated polyether) were mixed (6.0% fluorinated polyether in PMMA), and a sample of this solution applied to a glass slide and, after evaporation of acetone, the carbon content of the surface analysed by ESCA. After deconvolution of the C_{1s} spectrum it was found that 15.0% of the surface was composed of trifluorinated carbons compared with the total number of carbons.

13.25 2.5% fluorinated polyether in PMMA

PMMA (**101**) solution (8.62 g; 0.782 g of PMMA) and fluorinated polyether (**58b**) solution (0.14 g; 0.029 g of fluorinated polyether) were mixed (3.5% fluorinated polyether in PMMA), and a sample of this solution applied to a glass slide and, after evaporation of acetone, the carbon content of the surface analysed by ESCA. After deconvolution of the C_{1s} spectrum it was found that 16.2% of the surface was composed of trifluorinated carbons compared with the total number of carbons.

13.26 1% fluorinated polyether in PMMA

PMMA (**101**) solution (8.96 g; 0.813 g PMMA) and fluorinated polyether (**58b**) solution (0.04 g; 0.008 g of fluorinated polyether) were mixed (1.0% fluorinated polyether in PMMA), and a sample of this solution applied to a glass slide and, after evaporation of acetone, the carbon content of the surface analysed by ESCA. After deconvolution of the C_{1s} spectrum it was found that 8.6% of the surface was composed of trifluorinated carbons compared with the total number of carbons.

CHAPTER FOURTEEN
EXPERIMENTAL TO CHAPTER EIGHT

Unless stated otherwise, fluorinations were performed in FEP tubing (4.76 mm internal diameter, sealed at one end). Tubing lengths were chosen so that the FEP vessel was about a third full of substrate. Fluorine was admitted *via* a PTFE capillary tube (0.30 mm internal diameter, 1.59 mm external diameter), in nitrogen from an 800 ml nickel cylinder, charged to a total of 10 atm. The gas flow was regulated to provide separate small bubbles to pass through the substrate, lasting about 20 hours. Due to the very corrosive and toxic nature of fluorine precautions were taken to ensure no leakage could occur. All waste gases were scrubbed using soda lime. When required, UV irradiation was achieved using a 1000W medium pressure mercury lamp, the reaction vessel being cooled by an electric fan. The extent of fluorination was judged by ^{1}H NMR.

Elemental fluorine was obtained commercially, diluted 50% in nitrogen. Starting materials were prepared by the techniques described in chapters nine and ten.

*14.11 Fluorination of 2,5-di(2*H*-hexafluoropropyl)oxolane*

2,5-Di(2*H*-hexafluoropropyl)oxolane (**55**) (3.4 g, 3.0 ml, 9 mmol) was fluorinated using the technique described above (10% fluorine in nitrogen for 1 day, 20% for 1 day, 30% for 1 day and 50% for 1 day). The reaction vessel was then irradiated with UV light, as more fluorine was passed through (50% fluorine in nitrogen for 2 days), after which ^{1}H NMR showed no hydrogen present. A clear, colourless, mobile liquid was recovered, perfluoro-2,5-dipropyloxolane (**106**) (3.2 g, 67% yield); NMR and IR in agreement with literature;[104] for NMR analysis see chapter eight, section 8.71.

14.12 Fluorination of 1,2-di(2,2,3,4,4,4-hexafluoro-1-methylbutoxy)-3,3,4,5,5,5-hexafluoropentane

1,2-Di(2,2,3,4,4,4-hexafluoro-1-methylbutoxy)-3,3,4,5,5,5-hexafluoropentane (**56**) (3.5 g, 3 ml, 6 mmol) was fluorinated as before (10% fluorine in nitrogen for 1 day, 20% for 1 day, 30% for 1 day and 50% for 1 day). The reaction vessel was then irradiated with UV light, as more fluorine was passed through (50% fluorine in nitrogen for 2 days), after which ^{1}H NMR showed no hydrogen present. A clear, colourless, mobile liquid was recovered, perfluoro[1,2-di(1-methylbutoxy)pentane] (**107**) (3.7 g, 73% yield); NMR and IR in agreement with literature;[104] for NMR analysis see chapter eight, section 8.72.

*14.13 Fluorination of 2-(2*H*-hexafluoropropyl)oxolane*

2-(2*H*-Hexafluoropropyl)oxolane (**54**) (3.1 g, 3.0 ml, 13 mmol) was fluorinated using the technique described above (10% fluorine in nitrogen for 1 day, 20% for 1 day, 30% for 1 day and 50% for 1 day). The reaction vessel was then irradiated with UV light, as more fluorine was passed through (50% fluorine in nitrogen for 2 days). ^1H NMR showed the resultant material to contain no hydrogen and a clear, colourless, mobile liquid was obtained, perfluoro-2-propyloxolane (0.92 g, 18% yield); NMR and IR in agreement with literature.[104] The low yield was attributed to the volatility of the reaction mixture.

14.21 Use of a hydrogen fluoride scavenger

2,5-Di(2*H*-hexafluoropropyl)oxolane (**55**) (3.4 g, 3.0 ml, 9 mmol) was fluorinated in an FEP tube also containing potassium fluoride, and otherwise using the technique described above (10% fluorine in nitrogen for 1 day, 20% for 1 day, 30% for 1 day and 50% for 1 day). The reaction vessel was then irradiated with UV light, as more fluorine was passed through (50% fluorine in nitrogen for 2 days), after which ^1H NMR showed no hydrogen present. Although the expected product, perfluoro-2,5-dipropyloxolane (**106**), was recovered, MS showed the additional presence of higher molecular weight products. No further analysis was performed.

14.22 Attempted perfluorination by addition of starting material

2,5-Di(2*H*-hexafluoropropyl)oxolane (**55**) (3.4 g, 3.0 ml, 9 mmol) was fluorinated in an FEP tube as described above. The sample was treated with fluorine (10% fluorine in nitrogen for 1 day, 20% for 1 day, 30% for 1 day and 50% for 1 day) and a sample submitted for elemental analysis. As further fluorine was passed through (50% fluorine in nitrogen for 2 days), additional 2,5-di(2*H*-hexafluoropropyl)oxolane was added (a couple of drops on five occasions over two days). ^1H NMR showed hydrogen present still present, and elemental analysis showed no significant change in the material's composition had occurred over the last two days. The experiment was abandoned.

14.23 Perfluorination by addition of hydrocarbon

2,5-Di(2*H*-hexafluoropropyl)oxolane (**55**) (3.4 g, 3.0 ml, 9 mmol) was fluorinated in an FEP tube as described above (10% fluorine in nitrogen for 1 day, 20% for 1 day, 30% for 1 day and 50% for 1 day) and a sample taken and submitted for elemental analysis. As further fluorine was passed through (50% fluorine in nitrogen for 2 days), benzene was added (a couple of drops on five occasions over two days). ^1H NMR showed hydrogen present still present, but the elemental analysis showed the material had become more fluorinated over the last two days. Passing more fluorine through, with the addition of more benzene, (same conditions) provided material which ^1H NMR showed had no hydrogens present. NMR and IR showed this to be predominantly perfluoro-2,5-dipropyloxolane (**106**),[104] though MS showed the presence of some higher molecular weight materials.

light, as more fluorine was passed through (50% fluorine in nitrogen for 2 days). ^1H NMR showed the resultant material to contain no hydrogen and a clear, colourless, mobile liquid was obtained, perfluoro-2-propyloxolane (0.92 g, 18% yield); NMR and IR in agreement with literature.[104] The low yield was attributed to the volatility of the reaction mixture.

14.21 Use of a hydrogen fluoride scavenger

2,5-Di(2*H*-hexafluoropropyl)oxolane (**55**) (3.4 g, 3.0 ml, 9 mmol) was fluorinated in an FEP tube also containing potassium fluoride, and otherwise using the technique described above (10% fluorine in nitrogen for 1 day, 20% for 1 day, 30% for 1 day and 50% for 1 day). The reaction vessel was then irradiated with UV light, as more fluorine was passed through (50% fluorine in nitrogen for 2 days), after which ^1H NMR showed no hydrogen present. Although the expected product, perfluoro-2,5-dipropyloxolane (**106**), was recovered, MS showed the additional presence of higher molecular weight products. No further analysis was performed.

14.22 Attempted perfluorination by addition of starting material

2,5-Di(2*H*-hexafluoropropyl)oxolane (**55**) (3.4 g, 3.0 ml, 9 mmol) was fluorinated in an FEP tube as described above. The sample was treated with fluorine (10% fluorine in nitrogen for 1 day, 20% for 1 day, 30% for 1 day and 50% for 1 day) and a sample submitted for elemental analysis. As further fluorine was passed through (50% fluorine in nitrogen for 2 days), additional 2,5-di(2*H*-hexafluoropropyl)oxolane was added (a couple of drops on five occasions over two days). ^1H NMR showed hydrogen present still present, and elemental analysis showed no significant change in the material's composition had occurred over the last two days. The experiment was abandoned.

14.23 Perfluorination by addition of hydrocarbon

2,5-Di(2*H*-hexafluoropropyl)oxolane (**55**) (3.4 g, 3.0 ml, 9 mmol) was fluorinated in an FEP tube as described above (10% fluorine in nitrogen for 1 day, 20% for 1 day, 30% for 1 day and 50% for 1 day) and a sample taken and submitted for elemental analysis. As further fluorine was passed through (50% fluorine in nitrogen for 2 days), benzene was added (a couple of drops on five occasions over two days). ^1H NMR showed hydrogen present still present, but the elemental analysis showed the material had become more fluorinated over the last two days. Passing more fluorine through, with the addition of more benzene, (same conditions) provided material which ^1H NMR showed had no hydrogens present. NMR and IR showed this to be predominantly perfluoro-2,5-dipropyloxolane (**106**),[104] though MS showed the presence of some higher molecular weight materials.

14.3 Fluorination of the Adduct of HFP with DEPEG 600

An FEP tube was charged with the adduct of HFP with DEPEG 600 (**58b**) (4.1 g, material with 11 molar equivalents of HFP incorporated, 1.8 mmol) and treated with fluorine (5% fluorine in nitrogen for 1 day, 10% for 1 day and 15% for 1 day) as above. During the course of reaction the material darkened and thickened until it was black, and too viscous for further gas to pass through. The experiment was abandoned.

14.31 At elevated temperature

An FEP tube was charged with the adduct of HFP with DEPEG 600 (**58b**) (3.9 g, material with 12 molar equivalents of HFP incorporated, 1.6 mmol). The tube was placed in a glass test tube in an oil bath and fluorine (5% in nitrogen) passed through for 1 day. The tube was heated to 50°C and more fluorine passed through (5% in nitrogen for 1 day, 10% for 1 day and 15% for 1 day).During the course of reaction the material darkened and thickened until it was black, and too viscous for further gas to pass through. The experiment was abandoned.

14.32 In a sealed system

A nickel vessel (approximately 100 by 8 mm, 5 mm deep, open top) was charged with the adduct of HFP with DEPEG 600 (**58b**) (1.3 g, material with 13 molar equivalents of HFP incorporated, 0.5 mmol) and placed in an autoclave (80 ml, sealed with a PTFE gasket). The tube was placed in a glass test tube in an oil bath and fluorine (5% in nitrogen) passed through for 1 day. The tube was heated to 50°C and more fluorine passed through (5% in nitrogen for 1 day, 10% for 1 day and 15% for 1 day).During the course of reaction the material darkened and thickened until it was black, and too viscous for further gas to pass through. The experiment was abandoned.

14.33 In a solvent

(i) An FEP tube was charged with the adduct of HFP with DEPEG 600 (**58b**) (2.2 g, material with 13 molar equivalents of HFP incorporated, 0.8 mmol) and 1,2-di(2,2,3,4,4,4-hexafluoro-1-methylbutoxy)-3,3,4,5,5,5-hexafluoropentane (**56**) (7.8 g). This solution was treated with fluorine (5% fluorine in nitrogen for 4 days, 10% 2 day, 15% 1 day, 20% 1 day, 25% 1 day, 30% 1 day and 50% 1 day, then 50% 7 days with UV irradiation) as above, during which the solution lost colour. After the solution was perfluorinated (^{1}H NMR) the solvent, perfluoro[1,2-di(1-methylbutoxy)pentane], was removed under reduced pressure (100°C/1 mmHg) to give a clear colourless liquid, perfluoro[polypropyl-α-ethyl-ω-ethoxy poly(ethylene oxide) 600] (**103**) (1.5 g, 48%); (Found: C, 22.7; F, 67.9. $C_{69}O_{14}F_{114}$ requires C, 25.75; F, 67.3%); IR number 15; for

NMR analysis see chapter eight, section 8.64. Low yields were attributed to handling losses, due to the viscous nature of the product.

(ii) An FEP tube was charged with the adduct of HFP with DEPEG 600 (**58b**) (7.6 g, material with 12 molar equivalents of HFP incorporated, 3.1 mmol) and 2,5-di(2*H*-hexafluoropropyl)oxolane (**55**) (11.0 g). This solution was treated with fluorine (5% fluorine in nitrogen for 4 days, 10% 2 day, 15% 1 day, 20% 1 day, 30% 1 day and 50% 1 day, then 50% 7 days with UV irradiation) as above, during which time the solution lost colour. After the solution was perfluorinated (^{1}H NMR) the solvent, perfluoro-2,5-dipropyloxolane, was removed under reduced pressure (50°C/1 mmHg) to give a clear, colourless liquid, perfluoro[polypropyl-α-ethyl-ω-ethoxy poly(ethylene oxide) 600] (**103**) (6.0 g, 54%); NMR and IR in agreement with the previous reaction.

14.4 Fluorination of Other Polyfluoropolyethers

14.41 Fluorination of the adduct of HFP with DEPEG 400

An FEP tube was charged with the adduct of HFP with DEPEG 400 (**58a**) (3.6 g, material with 8 molar equivalents of HFP incorporated, 2.2 mmol) and 2,5-di(2*H*-hexafluoropropyl)oxolane (**55**) (2.5 g). This solution was treated with fluorine (5% fluorine in nitrogen for 6 days, 10% 2 day, 15% 2 day, 20% 2 day, 25% 2 days, 30% 2 days and 50% 2 days, then 50% 4 days with UV irradiation) as above, during which time the solution lost colour. After the solution was perfluorinated (^{1}H NMR), the solvent, perfluoro-2,5-dipropyloxolane (**106**), was removed under reduced pressure (80°C at 0.02mmHg) and the liquid distilled (200°C/0.05mmHg, Kugelrohr apparatus) to give a clear, colourless liquid, perfluoro[polypropyl-α-ethyl-ω-ethoxy poly(ethylene oxide) 400] (**102**) (5.4 g, 64%); NMR and IR agreed with literature.[121]

14.42 Fluorination of the adduct of HFP with DEPEG 2000

An FEP tube was charged with the adduct of HFP with DEPEG 2000 (**58c**) (1.2 g, material with 35 molar equivalents of HFP incorporated, 0.16 mmol) and 2,5-di(2*H*-hexafluoropropyl)oxolane (**55**) (9.3 g). This solution was treated with fluorine (5% fluorine in nitrogen for 6 days, 10% 2 days, 15% 2 days, 20% 2 days) as above, during which time the solution became darker and more viscous. The experiment was abandoned.

14.43 Fluorination of the adduct of HFP with PTHF

An FEP tube was charged with the adduct of HFP with PTHF (**62**) (6.9 g, material with 25 molar equivalents of HFP incorporated, 1.4 mmol) and 2,5-di(2*H*-hexafluoropropyl)oxolane (**55**) (12.4 g). This solution was treated with fluorine (5%

fluorine in nitrogen for 6 days, 10% 2 day, 15% 2 day, 20% 2 day, 25% 2 days, 30% 2 days and 50% 2 days, then 50% 4 days with UV irradiation) as above, during which time the solution lost colour. After the solution was perfluorinated (^{1}H NMR), the solvent, perfluoro-2,5-dipropyloxolane (**106**), was removed under reduced pressure (80°C at 0.02mmHg) and the liquid distilled (200°C/0.05mmHg, Kugelrohr apparatus) to give a clear, colourless liquid, perfluoro[polypropyl-α-ethyl-ω-ethoxy poly(tetramethylene oxide) 1000] (**104**) (5.4 g, 64%); (Found: C, 23.3; F, 74.8. $C_{131}O_{14}F_{264}$ requires C, 23.1; F, 73.6%.); IR number 16; for NMR analysis see chapter eight, section 8.64.

14.42 Fluorination of the adduct of HFP with 18-crown-6

An FEP tube was charged with the adduct of HFP with 18-crown-6 (**65**) (6.9 g, material with 5 molar equivalents of HFP incorporated, 6.8 mmol) and 2,5-di(2*H*-hexafluoropropyl)oxolane (**55**) (12.4 g). This solution was treated with fluorine (5% fluorine in nitrogen for 6 days, 10% 2 day, 15% 2 day, 20% 2 day, 25% 2 days, 30% 2 days and 50% 2 days, then 50% 4 days with UV irradiation) as above, during which time the solution lost colour. After the solution was perfluorinated (^{1}H NMR), the solvent, perfluoro-2,5-dipropyloxolane (**106**), was removed under reduced pressure (80°C at 0.02mmHg) and the remaining liquid distilled (150°C/0.03, Kugelrohr) to give a clear, colourless liquid, perfluoro(pentapropyl-18-crown-6) (**105**) (3.2 g, 53%); (Found: C, 22.6; F, 70.65. $C_{27}O_6F_{54}$ requires C, 22.4; F, 70.9%); IR number 17; MS number 9; for NMR analysis see chapter eight, section 8.64.

14.5 Attempted Fluorination of DEPEG

An FEP tube was charged with DEPEG 600 (**57b**) (1.4 g, 2.1 mmol) and 2,5-di(2*H*-hexafluoropropyl)oxolane (**55**) (8.5 g) to give a white suspension. This was treated with fluorine (2.5% fluorine in nitrogen for 3 days, 5% 2 days, 10% 2 day, 15% 2 days) as above, during which time the reaction mixture went clear, then a steadily darker brown. The experiment was abandoned.

APPENDICES AND REFERENCES

Appendix One

NMR Data

1. 2-(2*H*-Hexafluoropropyl)-oxolane (RS isomer, 53%)
2. 2-(2*H*-Hexafluoropropyl)-oxolane (RR isomer, 47%)
3. 2,5-Di(2*H*-hexafluoropropyl)oxolane (8 isomers)
4. (2*H*-Hexafluoropropyl)-1,4-dioxane (RS isomer, 52%)
5. (2*H*-Hexafluoropropyl)-1,4-dioxane (RR isomer, 48%)
6. 2,2,3,4,4,4-Hexafluoro-1-methylbutyl ethyl ether (RS isomer, 57%)
7. 2,2,3,4,4,4-Hexafluoro-1-methylbutyl ethyl ether (RR isomer, 43%)
8. Di(2,2,3,4,4,4-hexafluoro-1-methylbutyl) ether (8 isomers)
9. 1,2-Di(2,2,3,4,4,4-hexafluoro-1-methylbutoxy)-3,3,4,5,5,5-hexafluoropentane
10. (2*H*-Hexafluoropropyl)-1,3,5-trioxane
11. α-Ethyl-ω-ethoxy poly(tetramethylene oxide) 1000
12. Poly(2*H*-hexafluoropropyl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 600
13. Poly(2*H*-hexafluoropropyl)-α-ethyl-ω-ethoxy poly(tetramethylene oxide) 1000
14. Poly(2*H*-hexafluoropropyl)-18-crown-6
15. Poly(2*H*-hexafluoropropyl)-15-crown-5
16. Poly(2*H*-hexafluorocyclobutyl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 600
17. Poly(2*H*-hexafluorocyclopentyl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 600
18. Mixture of 2-(2*H*-hexafluoroprop-2-oxy)-6-(hexafluoro-2-hydroxyprop-2-yl)-1,4-dioxane and di-2,6-(hexafluoro-2-hydroxyprop-2-yl)-1,4-dioxane
19. Poly(2*H*-hexafluoroprop-2-oxy)-poly(hexafluoro-2-hydroxyprop-2-yl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 600

All spectra were run in deuterochloroform with the following exceptions: numbers 10, 12, 13, 14, 15, 16, 17 and 19 which were run in d_6-acetone.

Chemical shifts are quoted in ppm relative to an internal tetramethylsilane reference (^{1}H and ^{13}C spectra) or an external trichlorofluoromethane reference (^{19}F spectra) with downfield shifts positive.

For an AB system , chemical shifts are quoted as the 'centre of gravity,' calculated from:

$$\delta_1 - \delta_3 = \delta_2 - \delta_4 = \sqrt{\Delta v^2 + J^2}$$

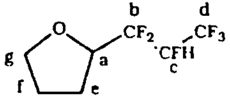
Where δ_n is the chemical shift of the *n*th peak, Δv is the difference in chemical shifts between the two resonances of the nucleii and *J* is the coupling constant.

The following abrieviations are used:

s	singlet
d	doublet
t	triplet
q	quartet
m	multiplet

All ^{13}C NMR spectra were recorded broad band proton decoupled.

1. 2-(2*H*-Hexafluoropropyl)-oxolane (RS isomer, 53%)



Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^{1}H				
1.9	d	$^{2}J_{HH}$ = 20.0	4	f
	t	$^{3}J_{HH}$ = 5.6		
2.0		$^{2}J_{HH}$ = 20.0		f
	t	$^{3}J_{HH}$ = 5.6		
2.069 or 2.085	d	$^{2}J_{HH}$ = 13.6		e (*cis* to R_f)
	d	$^{3}J_{HH}$ = 5.6		
2.174 or 2.156	d	$^{2}J_{HH}$ = 13.6		e (*trans* to R_f)
	d	$^{3}J_{HH}$ = 13.2		
	d	$^{3}J_{HH}$ = 5.6		
3.882 or 3.837	d	$^{2}J_{HH}$ = 6.9	1	g
3.912 or 3.868	d	$^{2}J_{HH}$ = 6.9	1	g
4.305	d	$^{3}J_{HH}$ = 13.2	1	a
	t	$^{3}J_{HF}$ = 12.8		
		$^{3}J_{HF}$ = 4.4		
5.082	d	$^{2}J_{HF}$ = 42.8	1	c
	d	$^{3}J_{HF}$ = 20.8		
	q	$^{3}J_{HF}$ = 6.4		
^{13}C				
24.12	d	$^{3}J_{CF}$ = 4.2		e
25.74	s			f
69.80	s			g
75.34	d	$^{2}J_{CF}$ = 33.9		a
	d	$^{2}J_{CF}$ = 22.8		
83.58	d	$^{1}J_{CF}$ = 192.2		c
	d	$^{2}J_{CF}$ = 39.7		
	q	$^{2}J_{CF}$ = 34.4		
	d	$^{2}J_{CF}$ = 23.7		
117.86	t	$^{1}J_{CF}$ = 253.6		b
	d	$^{2}J_{CF}$ = 25.5		
121.19	q	$^{1}J_{CF}$ = 282.3		d
	d	$^{2}J_{CF}$ = 24.4		

1. 2-(2*H*-Hexafluoropropyl)-oxolane (RS isomer, continued)

Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^{19}F				
-74.19	d	$^{3}J_{FH}$ = 22.2	3	d
	d	$^{3}J_{FF}$ = 10.5		
	d	$^{4}J_{FF}$ = 6.4		
	d	$^{4}J_{FF}$ = 0.8		
-120.10	d	$^{2}J_{FF}$ = 269.8	1	b
		$^{3}J_{FF}$ = 9.0		
	q	$^{4}J_{FF}$ = 9.0		
		$^{3}J_{FF}$ = 4.5		
-124.26	d	$^{2}J_{FF}$ = 269.8	1	b
		$^{3}J_{FF}$ = 12.5		
	q	$^{4}J_{FF}$ = 12.5		
		$^{3}J_{FH}$ = 12.5		
		$^{3}J_{FH}$ = 12.5		
213.29	d	$^{2}J_{FH}$ = 42.8	1	c
	d	$^{3}J_{FF}$ = 14.3		
	q	$^{3}J_{FF}$ = 10.5		
	d	$^{3}J_{FF}$ = 10.5		
	d	$^{4}J_{FH}$ = 3.8		

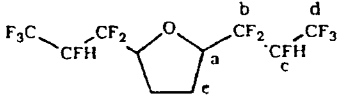
2. 2-(2*H*-Hexafluoropropyl)-oxolane (RR isomer, 47%)

Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^{1}H				
1.9	d	$^{2}J_{HH}$ = 20.0	4	f
	t	$^{3}J_{HH}$ = 5.6		
2.0		$^{2}J_{HH}$ = 20.0		f
	t	$^{3}J_{HH}$ = 5.6		
2.085 or 2.069	d	$^{2}J_{HH}$ = 13.6		e (*cis* to R_f)
	d	$^{3}J_{HH}$ = 5.6		
2.156 or 2.174	d	$^{2}J_{HH}$ = 13.6		e (*trans* to R_f)
	d	$^{3}J_{HH}$ = 13.2		
	d	$^{3}J_{HH}$ = 5.6		
3.837 or 3.882	d	$^{2}J_{HH}$ = 6.9	1	g
3.868 or 3.912	d	$^{2}J_{HH}$ = 6.9	1	g
4.210	d	$^{3}J_{HF}$ = 13.6	1	a
	t	$^{3}J_{HH}$ = 13.2		
	d	$^{3}J_{HF}$ = 6.0		
5.083	d	$^{2}J_{HF}$ = 42.8	1	c
	d	$^{3}J_{HF}$ = 20.8		
	q	$^{3}J_{HF}$ = 6.4		

2. 2-(2*H*-Hexafluoropropyl)-oxolane (RR isomer, continued)

Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^{13}C				
24.16	d	$^3J_{CF}$ = 42.1		e
25.74	s			f
69.94	s			g
76.88	d	$^2J_{CF}$ = 29.8		a
	d	$^2J_{CF}$ = 24.8		
85.02	d	$^1J_{CF}$ = 197.6		c
	d	$^2J_{CF}$ = 34.7		
	q	$^2J_{CF}$ = 27.5		
	d	$^2J_{CF}$ = 27.5		
117.58	t	$^1J_{CF}$ = 252.5		b
	d	$^2J_{CF}$ = 19.9		
120.79	q	$^1J_{CF}$ = 281.9		d
	d	$^2J_{CF}$ = 25.9		
	d	$^3J_{CF}$ = 7.6		
^{19}F				
-74.70	d	$^3J_{FF}$ = 10.5	3	d
		$^4J_{FF}$ = 10.5		
	d	$^3J_{FF}$ = 6.4		
	d	$^4J_{FF}$ = 6.4		
-124.85	d	$^2J_{FF}$ = 270.2	1	b
	d	$^3J_{FF}$ = 10.7		
	d	$^3J_{FH}$ = 10.7		
	d	$^3J_{FH}$ = 10.7		
	q	$^4J_{FF}$ = 10.7		
-130.32	d	$^2J_{FF}$ = 270.2	1	b
	d	$^3J_{FF}$ = 12.1		
	q	$^4J_{FF}$ = 12.1		
	d	$^3J_{FH}$ = 12.1		
	d	$^3J_{FH}$ = 12.1		
-218.59	d	$^2J_{FH}$ = 41.0	1	c
	q	$^3J_{FF}$ = 10.8		
	t	$^3J_{FF}$ = 10.8		

3. 2,5-Di(2*H*-hexafluoropropyl)oxolane (8 isomers)

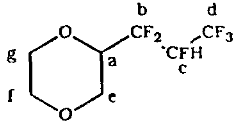


Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^1H				
2.29	m		2	e
4.44, 4.50 and 4.57	m		1	a
5.011	m		1	c
^{13}C				
24.01	d	$^3J_{CF}$ = 3.4		e (major)
24.37	d	$^3J_{CF}$ = 4.2		e (major)
24.41	d	$^3J_{CF}$ = 5.3		e (minor)
24.57	d	$^3J_{CF}$ = 3.4		e (minor)
25.16	d	(*J* negligible)		e (major)
25.34	d	(*J* negligible)		e (major)
25.36	d	(*J* negligible)		e (minor)
25.55	d	(*J* negligible)		e (minor)
77.81	d	$^2J_{CF}$ = 36.9		a (RS, minor)
	d	$^2J_{CF}$ = 3.6		
77.97	d	$^2J_{CF}$ = 34.8		a (RS, major)
	d	$^2J_{CF}$ = 23.3		
79.14	d	$^2J_{CF}$ = 30.9		a (RR, minor)
	d	$^2J_{CF}$ = 24.8		
79.24	d	$^2J_{CF}$ = 32.0		a (RR, major)
	d	$^2J_{CF}$ = 24.7		
83.83	d	$^2J_{CF}$ = 191.8		c (RS)
	d	$^3J_{CF}$ = 40.1		
	q	$^3J_{CF}$ = 35.1		
	d	$^3J_{CF}$ = 24.4		
85.48	d	$^2J_{CF}$ = 200.2		c (RR)
	q	$^3J_{CF}$ = 35.1		
	d	$^3J_{CF}$ = 27.9		
	d	$^3J_{CF}$ = 27.9		
117.27	t	$^2J_{CF}$ = 253.0		b (RS)
	d	$^3J_{CF}$ = 19.1		
117.67	d	$^2J_{CF}$ = 253.7		b (RR)
	d	$^3J_{CF}$ = 28.3		
121.04	q	$^2J_{CF}$ = 283.4		d (RR)
	d	$^3J_{CF}$ = 25.5		
	d	$^3J_{CF}$ = 8.1		
121.41	q	$^2J_{CF}$ = 282.3		d (RS)
	d	$^3J_{CF}$ = 25.7		

3. 2,5-Di(2*H*-hexafluoropropyl)oxolane (8 isomers, continued)

Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^{19}F				
-74.27	m			d (RS)
-74.81	m			d (RR)
-116.80	d of m	$^{2}J_{FF}$ = 270.7		b (RR)
-117.00	d of m	$^{2}J_{FF}$ = 270.7		b (RR)
-120.25	d of m	$^{2}J_{FF}$ = 270.7		b (RR)
-120.25	d of m	$^{2}J_{FF}$ = 270.7		b (RR)
-121.14	d of m	$^{2}J_{FF}$ = 270.7		b (RS)
-121.26	d of m	$^{2}J_{FF}$ = 272.6		b (RS)
-125.46	d of m	$^{2}J_{FF}$ = 270.7		b (RS)
-125.79	d of m	$^{2}J_{FF}$ = 272.6		b (RS)
-212.98	d of m	$^{2}J_{FH}$ = 32.7		c
-216.22	d of m	$^{2}J_{FH}$ = 41		c (minor)
-217.16	d of m	$^{2}J_{FH}$ = 45		c (minor)
-218.50	d of m	$^{2}J_{FH}$ = 43.6		c

4. (2*H*-Hexafluoropropyl)-1,4-dioxane (RS isomer, 52%)



Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^{1}H				
3.61	m		7	f
3.67	m			e
3.70	m			f
3.73	m			g
3.84	m			g
3.94	m			e
4.01	d	$^{3}J_{HF}$ = 20.8		a
	d of m	$^{3}J_{HF}$ = 2.4		
5.09	d	$^{2}J_{HF}$ = 42.3	1	c
	d	$^{3}J_{HF}$ = 20.4		
	q	$^{3}J_{HF}$ = 6.4		
	d	$^{3}J_{HF}$ = 0.7		
^{13}C				
63.68	t	$^{1}J_{CH}$ = 146.5		e
	t	$^{3}J_{CF}$ = 2.3		
66.10	t	$^{1}J_{CH}$ = 145.0		f
66.94	t	$^{1}J_{CH}$ = 144.6		g
71.50	d	$^{1}J_{CH}$ = 146.1		a
	d	$^{2}J_{CF}$ = 34.4		
	d	$^{2}J_{CF'}$ = 22.1		
82.22	d	$^{1}J_{CF}$ = 193.4		c
	d	$^{1}J_{CH}$ = 159.4		
	d	$^{2}J_{CF}$ = 38.1		
	q	$^{2}J_{CF}$ = 34.7		
	d	$^{2}J_{CF}$ = 23.6		
120.44	t	$^{1}J_{CF}$ = 252.6		b
	d	$^{2}J_{CF}$ = 25.6		
120.92	q	$^{1}J_{CF}$ = 282.3		d
	d	$^{2}J_{CF}$ = 25.5		
	d	$^{2}J_{CH}$ = 5.3		
	d	$^{3}J_{CF}$ = 1.1		

4. (2*H*-Hexafluoropropyl)-1,4-dioxane (RS isomer, continued)

^{19}F				
-73.95	d	$^{3}J_{FF}$ = 11.3	3	d
	d	$^{4}J_{FF}$ = 11.3		
	d	$^{4}J_{FF'}$ = 10.9		
	d	$^{3}J_{FH}$ = 6.0		
-125.87	d	$^{2}J_{FF'}$ = 294.1	1	b
	q	$^{4}J_{FF}$ = 12.0		
	d	$^{3}J_{FF}$ = 8.6		
	d	$^{3}J_{FH}$ = 3.8		
-128.13	d	$^{2}J_{FF'}$ = 294.1	1	b
	d	$^{3}J_{FH}$ = 20.3		
	d	$^{3}J_{FH}$ = 20.3		
	q	$^{4}J_{FF}$ = 10.7		
	d	$^{3}J_{FF}$ = 8.3		
-218.53	d	$^{2}J_{HF}$ = 43.6	1	c
	q	$^{3}J_{FF}$ = 10.2		
	d	$^{3}J_{FF}$ = 10.2		
	d	$^{3}J_{FF}$ = 10.2		

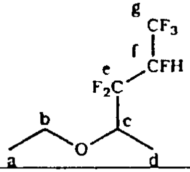
5. (2*H*-Hexafluoropropyl)-1,4-dioxane (RR isomer, 48%)

Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^{1}H				
3.61	m		7	f
3.67	m			e
3.70	m			f
3.73	m			g
3.84	m			g
3.90	m			e
3.97	d	$^{3}J_{HF}$ = 12.1		a
	d of m	$^{3}J_{HF}$ = 6.4		
5.15	d	$^{2}J_{HF}$ = 48.8	1	c
	d	$^{3}J_{HF}$ = 15.4		
	d	$^{3}J_{HF}$ = 10.4		
	q	$^{3}J_{HF}$ = 5.3		

5. (2*H*-Hexafluoropropyl)-1,4-dioxane (RR isomer, continued)

^{13}C				
64.35	t	$^{1}J_{CH}$ = 145.7		e
	d	$^{3}J_{CF}$ = 2.4		
66.10	t	$^{1}J_{CH}$ = 145.0		f
66.91	t	$^{1}J_{CH}$ = 144.6		g
74.27	d	$^{1}J_{CH}$ = 145.4		a
	d	$^{2}J_{CF}$ = 29.3		
	d	$^{2}J_{CF'}$ = 26.2		
	d	$^{3}J_{CF}$ = 1.1		
83.74	d	$^{1}J_{CF}$ = 197.3		c
	d	$^{1}J_{CH}$ = 155.6		
	q	$^{2}J_{CF}$ = 34.7		
	d	$^{2}J_{CF}$ = 29.0		
	d	$^{2}J_{CF}$ = 26.0		
115.93	d	$^{1}J_{CF}$ = 253.7		b
	d	$^{1}J_{CF}$ = 249.5		
	d	$^{2}J_{CF}$ = 0.7		
120.59	q	$^{1}J_{CF}$ = 282.0		d
	d	$^{2}J_{CF}$ = 25.6		
	d	$^{2}J_{CH}$ = 5.7		
^{19}F				
-73.95	d	$^{3}J_{FF}$ = 11.3	3	d
	d	$^{4}J_{FF}$ = 11.3		
	d	$^{4}J_{FF'}$ = 10.9		
	d	$^{3}J_{FH}$ = 6.0		
-120.44	d	$^{2}J_{FF'}$ = 276.4	1	b
	d	$^{3}J_{FF}$ = 10.1		
	d	$^{3}J_{FH}$ = 10.1		
	d	$^{3}J_{FH}$ = 10.1		
	q	$^{4}J_{FF}$ = 10.1		
-123.44	d	$^{2}J_{FF'}$ = 276.4	1	b
	d	$^{3}J_{FH}$ = 5.6		
	q	$^{4}J_{FF}$ = 5.6		
	d	$^{3}J_{FF}$ = 4.5		
	d	$^{3}J_{FH}$ = 4.5		
-213.56	d	$^{2}J_{FH}$ = 41.8	1	c
	d	$^{3}J_{FF}$ = 15.0		
	q	$^{3}J_{FF}$ = 11.3		
	d	$^{3}J_{FF'}$ = 3.8		
	d	$^{4}J_{FH}$ = 3.8		

6. 2,2,3,4,4,4-Hexafluoro-1-methylbutyl ethyl ether (RS isomer, 57%)

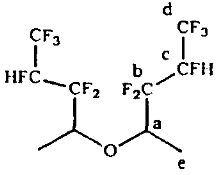


Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^{1}H				
1.31	a	$^{3}J_{HH}$ = 6.8	3	a
1.32	d	$^{3}J_{HH}$ = 6.8	3	d
3.49	d	$^{2}J_{HH}$ = 9.2	1	b
	q	$^{3}J_{HH}$ = 7.1		
3.72	d	$^{2}J_{HH}$ = 9.2	1	b
	q	$^{3}J_{HH}$ = 7.1		
3.85	d	$^{3}J_{HF}$ = 21.8	1	c
	q	$^{3}J_{HH}$ = 6.4		
	d	$^{3}J_{HF}$ = 3.7		
	d	$^{4}J_{HF}$ = 2.4		
5.12	d	$^{2}J_{HF}$ = 42.8	1	f
	q	$^{3}J_{HF}$ = 6.0		
^{13}C				
10.5	d	$^{3}J_{CF}$ = 5.0		d
15.27	s			a
65.54	s			b
72.49	d	$^{2}J_{CF}$ = 32.1		c
	d	$^{2}J_{CF}$ = 22.9		
83.27	d	$^{1}J_{CF}$ = 192.2		f
	q	$^{2}J_{CF}$ = 34.3		
	d	$^{2}J_{CF}$ = 24.3		
117.93	d	$^{1}J_{CF}$ = 253.8		c
	d	$^{1}J_{CF}$ = 253.8		
	d	$^{2}J_{CF}$ = 25.9		
121.40	q	$^{1}J_{CF}$ = 282.6		g
	d	$^{2}J_{CF}$ = 25.9		
^{19}F				
-74.07	m		3	g
-124.72	d of m	$^{2}J_{FF'}$ = 273.8	1	e
-129.38	d of m	$^{2}J_{FF'}$ = 273.8	1	e
-213.55	d of m	$^{2}J_{HF}$ = 42.1	1	f

7. 2,2,3,4,4,4-Hexafluoro-1-methylbutyl ethyl ether (RR isomer, 43%)

Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^{1}H				
1.31	a	$^{3}J_{HH}$ = 6.8	3	a
1.34	d	$^{3}J_{HH}$ = 6.8	3	d
3.49	d	$^{2}J_{HH}$ = 9.2	1	b
	q	$^{3}J_{HH}$ = 7.1		
3.71	d	$^{2}J_{HH}$ = 9.3	1	b
	q	$^{3}J_{HH}$ = 7.1		
3.80	d	$^{3}J_{HF}$ = 21.8	1	c
	q	$^{3}J_{HH}$ = 6.4		
	d	$^{3}J_{HF}$ = 3.7		
	d	$^{4}J_{HF}$ = 2.4		
5.22	d	$^{2}J_{HF}$ = 42.8	1	f
	q	$^{3}J_{HF}$ = 6.4		
^{13}C				
12.84	d	$^{3}J_{CF}$ = 3.5		d
15.29	s			a
65.94	s			b
75.00	d	$^{2}J_{CF}$ = 26.9		c
	d	$^{2}J_{CF}$ = 26.9		
83.39	d	$^{1}J_{CF}$ = 196.1		f
	q	$^{2}J_{CF}$ = 34.3		
	d	$^{2}J_{CF}$ = 30.5		
	d	$^{2}J_{CF}$ = 26.3		
117.69	d	$^{1}J_{CF}$ = 253.4		e
	d	$^{1}J_{CF}$ = 253.4		
	d	$^{2}J_{CF}$ = 19.8		
121.15	q	$^{1}J_{CF}$ = 282.3		g
	d	$^{2}J_{CF}$ = 25.9		
	d	$^{2}J_{CH}$ = 5.3		
^{19}F				
-74.68	m		3	g
-119.10	d of m	$^{2}J_{FF'}$ = 279.0	1	e
-123.61	d of m	$^{2}J_{FF'}$ = 279.0	1	e
-216.59	d of m	$^{2}J_{HF}$ = 44.0	1	f

8. Di(2,2,3,4,4,4-hexafluoro-1-methylbutyl) ether (8 isomers)

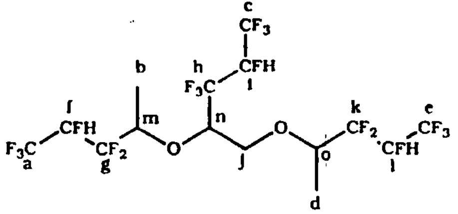


Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^1H				
1.344	d	$^3J_{HH}$ = 6.4	3	e (RS)
1.390	d	$^3J_{HH}$ = 6.4		e (RR)
	d	$^4J_{HF}$ = 1.2		
4.07	m		1	a
5.045	d of m	$^2J_{HF}$ = 43.2	1	c
^{13}C				
9.51	d	$^3J_{CF}$ = 5.0		e (RSSR)
10.32	d	$^3J_{CF}$ = 4.5		e (RRRS)
11.87	d	$^3J_{CF}$ = 5.0		e (RRSR)
12.22	d	$^3J_{CF}$ = 3.8		e (RRRS)
12.46	d	$^3J_{CF}$ = 4.5		e (RSRS)
13.32	m			e (RRRR)
14.27	m			e (RRSS)
14.98	m	$^3J_{CF}$ = 3.4		e (RRSR)
70.02	d	$^2J_{CF}$ = 33.8		a (RSSR)
	d	$^2J_{CF}$ = 23.2		
72.07	d	$^2J_{CF}$ = 33.0		a (RRRS)
	d	$^2J_{CF}$ = 23.9		
72.83	d	$^2J_{CF}$ = 32.3		a (RRRS)
	d	$^2J_{CF}$ = 23.9		
73.87	d	$^2J_{CF}$ = 32.6		a (RRSR)
	d	$^2J_{CF}$ = 23.9		
74.30	d	$^2J_{CF}$ = 27.7		a (RSRS)
	d	$^2J_{CF}$ = 27.7		
74.97	d	$^2J_{CF}$ = 34.4		a (RRRR)
	d	$^2J_{CF}$ = 30.5		
75.76	d	$^2J_{CF}$ = 33.3		a (RRSS)
	d	$^2J_{CF}$ = 33.3		
76.62	d	$^2J_{CF}$ = 31.9		a (RRSR)
	d	$^2J_{CF}$ = 31.9		
83.62	d of m	$^1J_{CF}$ = 190.8		c

8. Di(2,2,3,4,4,4-hexafluoro-1-methylbutyl) ether (8 isomers, continued)

Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^{13}C *(continued)*				
117.24	t	$^1J_{CF}$ = 250.7		b (RS)
	d	$^2J_{CF}$ = 24.7		
117.31	t	$^1J_{CF}$ = 250.0		b (RR)
	d	$^2J_{CF}$ = 30.7		
121.08	q	$^2J_{CF}$ = 281.1		d (RR)
	d	$^2J_{CF}$ = 25.8		
121.21	q	$^2J_{CF}$ = 279.9		d (RS)
	d	$^2J_{CF}$ = 25.4		
^{19}F				
-74.26	m			d (RS)
-74.517	m			d (RR)
-117.94	d of m	$^2J_{FF}$ = 273.9		b (RRRS)
-118.15	d of m	$^2J_{FF}$ = 275.8		b (RRSS)
-119.04	d of m	$^2J_{FF}$ = 275.8		b (RRSR)
-119.24	d of m	$^2J_{FF}$ = 275.8		b (RRRR)
-122.39	d of m	$^2J_{FF}$ = 275.8		b (RRSR)
-123.10	d of m	$^2J_{FF}$ = 275.8		b (RRSS)
-123.12	d of m	$^2J_{FF}$ = 275.8		b (RRRR)
-123.19	d of m	$^2J_{FF}$ = 275.1		b (RSRS)
-123.62	d of m	$^2J_{FF}$ = 273.9		b (RRRS)
-123.68	d of m	$^2J_{FF}$ = 276.2		b (RRSR)
-123.88	d of m	$^2J_{FF}$ = 274.3		b (RRRS)
-124.28	d of m	$^2J_{FF}$ = 275.4		b (RSSR)
-126.59	d of m	$^2J_{FF}$ = 275.1		b (RSRS)
-128.00	d of m	$^2J_{FF}$ = 274.3		b (RRRS)
-128.61	d of m	$^2J_{FF}$ = 276.2		b (RRSR)
-129.20	d of m	$^2J_{FF}$ = 275.4		b (RSSR)
-212.2	d of m	$^2J_{FH}$ = 41		c (RRSR)
-212.7	m			c (RSRS RRSR, and RRSS)
-213.0	d of m	$^2J_{FH}$ = 41		c (RRRR)
-213.4	d of m	$^2J_{FH}$ = 41		c (RRRS)
-213.7	d of m	$^2J_{FH}$ = 41		c (RSSR)
-214.8	d of m	$^2J_{FH}$ = 41		c (RRRS)

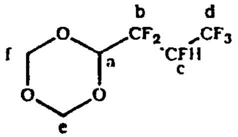
9. 1,2-Di(2,2,3,4,4,4-hexafluoro-1-methylbutoxy)-3,3,4,5,5,5-hexafluoropentane



Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^{1}H				
1.4	m		6	b, d
3.5 to 4.4	series of peaks		5	j, m, n, o
5.0	broad m		3	f, i, k
^{13}C				
10 to 16	series of s			b
11.3	s			d (RS)
12.7 or 13.4	s			d (RR)
67 to 70	series of s			j
70.5	d			m, n, o
	d			
74.5	broad m			
76.5	broad m			
78.0	broad m			
84.0	d of m	$^{1}J_{CF}$ = 175.6		f, i, l
118.6	t	$^{1}J_{CF}$ = 257.2		g, h, k
	d	$^{1}J_{CF}$ = 26.1		
122.1	q	$^{1}J_{CF}$ = 280.3		a, c, e
	d	$^{2}J_{CF}$ = 27.0		
122.1	q	$^{1}J_{CF}$ = 279.9		a, c, e
	d	$^{2}J_{CF}$ = 25.8		
122.2	q	$^{1}J_{CF}$ = 280.3		a, c, e
	d	$^{2}J_{CF}$ = 25.8		
122.4	q	$^{1}J_{CF}$ = 279.9		a, c, e
	d	$^{2}J_{CF}$ = 25.8		
^{19}F				
-73.5			6	a, c, e
-73.7				
-73.9				
-74.2				
-120.7 to -125.4	series of d		1	g, h, k (RR)
-125.4 to 129.8	series of d		2	g, h, k
-129.8 to -135.2	series of d		1	g, h, k (RS)
-210.5 to -215.0	series of m		2	f, h, i

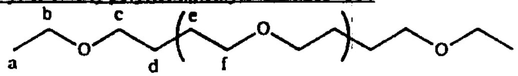
(2*H*-Hexafluoropropyl)-1,3,5-trioxane

(in d_6-acetone)



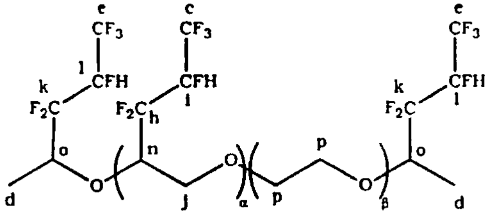
Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
5.302	d	$^{2}J_{HH}$ = 5.2		e
5.326	d	$^{2}J_{HH}$ = 5.2		e
5.331	d	$^{2}J_{HH}$ = 2.0		f
5.346	d	$^{2}J_{HH}$ = 2.0		f
5.53	d	$^{2}J_{HF}$ = 42.4		c
	d	$^{3}J_{HF}$ = 9.0		
	q	$^{3}J_{HF}$ = 6.2		
	d	$^{3}J_{HF}$ = 4.6		
5.56	d	$^{3}J_{HF}$ = 8.8		a
	d	$^{3}J_{HF}$ = 4.0		
83.98	d	$^{1}J_{CF}$ = 194.2		c
	d	$^{2}J_{CF}$ = 34.7		
	q	$^{2}J_{CF}$ = 34.5		
	d	$^{2}J_{CF}$ = 23.6		
93.87	s			e or f
93.93	s			f or e
96.57	d	$^{2}J_{CF}$ = 31.5		a
	d	$^{2}J_{CF}$ = 26.2		
114.51	d	$^{1}J_{CF}$ = 254.6		b
	d	$^{1}J_{CF}$ = 254.6		
	d	$^{2}J_{CF}$ = 22.8		
122.10	q	$^{1}J_{CF}$ = 281.9		d
	d	$^{1}J_{CF}$ = 25.3		
-74.50	m		3	d
-128.206	d of m	$^{2}J_{FF}$ = 278.1	1	b
-130.03	d of m	$^{2}J_{FF}$ = 278.1	1	b
-216.16	d of m	$^{2}J_{HF}$ = 42.1	1	c

11. α-Ethyl-ω-ethoxy poly(tetramethylene oxide) 1000



Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^{1}H				
1.18	t	$^{3}J_{HH}$ = 7.5		a
1.62	s			d, e
3.41	broad m			c, f
^{13}C				
15.22	s			a
26.59	s			d, e
66.00	s			b
70.62	s			c, f

12. Poly(2*H*-hexafluoropropyl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 600
(in d_6-acetone)

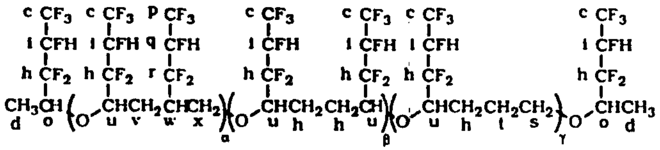


Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^{1}H				
1.15	t	$^{3}J_{HH}$ = 6.8	3	$C\mathit{H}_3CH_2O$
1.34	m		4	d (RS)
1.38	m			d (RR)
3.47	q	$^{3}J_{HH}$ = 6.4	2	$CH_3C\mathit{H}_2O$
3.54	m		8	j, p ($C\mathit{H}H'OCHR_f$)
3.64	s		15	p
3.65	m		8	j, p ($CH\mathit{H}'OCHR_f$)
3.9	broad s		16	n, o ($C\mathit{H}R_fOCH_2$)
4.1	broad s			n, o (CHR_fOCHR_f)
5.59	very broad s		8	i, l

12. Poly(2*H*-hexafluoropropyl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 600

Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^{13}C				
10 to 14	series of m			d
15.6	s			$\mathit{C}H_3CH_2O$
67.0	s			$CH_3\mathit{C}H_2O$
67.8	m			j ($\mathit{C}H_2OCHR_f$)
69.6	broad m			j, p ($CH_2CH_2OCHR_f$)
70.8	s			p (CH_2OEt)
71.2	s			p (CH_2OEt)
71.4	s			p
72.6	m			n, o ($\mathit{C}HR_fOCH_2$)
72.8	m			n, o ($\mathit{C}HR_fOCH_2$)
73.0	m			n, o ($\mathit{C}HR_fOCH_2$)
73.7	m			n, o ($\mathit{C}HR_fOCH_2$)
78	broad s			n, o (CHR_fOCHR_f)
80	broad s			n, o (CHR_fOCHR_f)
84.4	d of m	$^{1}J_{CF}$ = 192.0		h, k
118.7	t of m	$^{1}J_{CF}$ = 262.1		i, l
122.2	q of m	$^{1}J_{CF}$ = 283.7		c, e
^{19}F				
-75.2	broad s		3	c, e
-75.3	m		3	c, e
-116 to -123	series of peaks		4	h, k
-208.8	d	$^{2}J_{HF}$ = 42.1	2	i, l
	m	$^{3}J_{FF}$ = 3.4		
-214.0	broad s			i, l
-216.3	broad s		(negligible)	i, l

13. **Poly(2*H*-hexafluoropropyl)-α-ethyl-ω-ethoxy poly(tetramethylene oxide) 1000**
(in d_6-acetone)

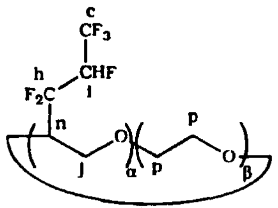


Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz		Relative Intensity	Assignment
^1H					
1.14	t	$^3J_{HH}$ =	8		CH_3CH_2O
1.35	m				d (RS)
1.38	m				d (RR)
1.43	broad s				v
1.60	broad s				h
1.72	broad s				t
3.17	broad s				w
3.42	broad s				s
3.76	broad s			(negligible)	x or s $(CHR_fOCH_2CH_2)$
3.88	broad s			(negligible)	s $(CHR_fOCH_2CH_2)$ or x
4.36	broad s				o, u
5.67	very broad s				i, q
^{13}C					
15.6	s				CH_3CH_2O
18.6	broad s				v
21.4	t	$^3J_{CF}$ =	4.5		h (γ)
23.1	d	$^3J_{CF}$ =	5.3		h (γ)
23.9	t	$^3J_{CF}$ =	4.9		h (γ)
23 to 28	series of peaks				h (β), t
33.7	t	$^2J_{CF}$ =	22.4		w
66.8	s				s (-$CH_2OCH_2CH_2$-
71.2	s				s, x
72.8					u $(CH_2OCHR_fCH_2)$
75 to 82	series of peaks				o, u, s
84.5	d of m	$^1J_{CF}$ =	207.1		i, q
119.5	t of m	$^1J_{CF}$ =	252.9		h, r
122.3	q	$^1J_{CF}$ =	279.5		c, p
	d of m	$^2J_{CF}$ =	25.4		

13. **Poly(2*H*-hexafluoropropyl)-α-ethyl-ω-ethoxy poly(tetramethylene oxide) 1000 (continued)**

Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz		Relative Intensity	Assignment
^{19}F					
-75.1	s				c, p
-75.2	s				c, p
-75.4	m				c, p
-75.7	m				c, p
111.0	d	$^2J_{FF}$ =	263.2		r
113.0	d	$^2J_{FF}$ =	263.2		r
-115 to -128	series of peaks				h
208.7	d			(negligible)	i, q
212.9	broad s				i, q
213.3	m				i, q
214.0	broad s				i, q
215.1	broad s				i, q
217.2	broad s			(negligible)	i, q

14. **Poly(2*H*-hexafluoropropyl)-18-crown-6**
(in d_6-acetone)



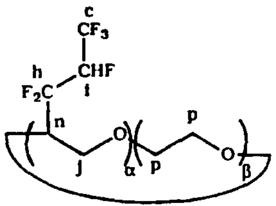
α + β = 6

Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz		Relative Intensity	Assignment
^1H					
2.92	m				j
3.59	s			~10	p
3.80	d	$^3J_{HF}$ =	11.2	2	n
	d	$^3J_{HF}$ =	4.8		
	d	$^4J_{HF}$ =	4.0		
4.00	d	$^3J_{HF}$ =	11.2	2	n
	d	$^3J_{HF}$ =	6.4		
	d	$^4J_{HF}$ =	4.8		
5.70	d of m	$^2J_{HF}$ ~	40	2	i

14. Poly(2*H*-hexafluoropropyl)-18-crown-6 (continued)

Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^{13}C				
69.64	d	$^{3}J_{CF} =$ 4.5		j
70.05	d	$^{3}J_{CF} =$ 4.9		j
71.25	s			p
77.34	d	$^{2}J_{CF} =$ 28.5		n
	d	$^{2}J_{CF} =$ 21.6		
79.14	t	$^{2}J_{CF} =$ 23.5		n
84.22	d of m	$^{1}J_{CF} =$ 190.4		i
118.78	d	$^{1}J_{CF} =$ 252.8		h
	d	$^{1}J_{CF} =$ 252.8		
	d	$^{2}J_{CF} =$ 35.7		
119.30	d	$^{1}J_{CF} =$ 252.8		h
	d	$^{1}J_{CF} =$ 252.8		
	d	$^{2}J_{CF} =$ 39.4		
121.72	q	$^{1}J_{CF} =$ 281.1		c
	d	$^{2}J_{CF} =$ 26.1		
122.38	q	$^{1}J_{CF} =$ 281.4		c
	d	$^{2}J_{CF} =$ 26.9		
^{19}F				
-73.63	d	$^{3}J_{FF} =$ 16.5	3	c
	d	$^{3}J_{FF} =$ 10.9		
	d	$^{4}J_{FF} =$ 10.9		
-73.84	d	$^{3}J_{FF} =$ 19.2	3	c
	d	$^{3}J_{FF} =$ 9.4		
	d	$^{4}J_{FF} =$ 9.4		
-119.7	d of m	$^{2}J_{FF} =$ 267.0	1	h
-121.7	d of m	$^{2}J_{FF} =$ 267.0	1	h
-122.1	d of m	$^{2}J_{FF} =$ 267.0	1	h
-125.1	d of m	$^{2}J_{FF} =$ 267.0	1	h
-212.74	d of m	$^{2}J_{FH} =$ 42.3	1	i
-214.25	d of m	$^{2}J_{FH} =$ 41.4	1	i

15. Poly(2*H*-hexafluoropropyl)-15-crown-5
(in d_6-acetone)

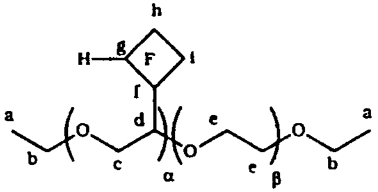


$\alpha + \beta = 5, \alpha \approx 0.6$ (mean)

Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^{1}H				
2.93	m			j
3.60	s		≈35	p
3.81	d of m	$^{3}J_{HF} =$ 11.2	1	n
4.00	d of m	$^{3}J_{HF} =$ 11.2	1	n
5.69	d of m	$^{2}J_{HF} \approx$ 40	2	i
^{13}C				
69.61	d	$^{3}J_{CF} =$ 4.4		j
70.08	d	$^{3}J_{CF} =$ 4.9		j
71.26	s			p
77.37	d	$^{2}J_{CF} =$ 29.1		n
	d	$^{2}J_{CF} =$ 22.4		
79.16	t	$^{2}J_{CF} =$ 22.5		n
84.20	d of m	$^{1}J_{CF} =$ 193.2		i
118.78	d	$^{1}J_{CF} =$ 254.2		h
	d of m	$^{1}J_{CF} =$ 252.1		
119.29	d	$^{1}J_{CF} =$ 255.9		h
	d of m	$^{1}J_{CF} =$ 249.9		
121.69	q of m	$^{1}J_{CF} =$ 280.8		c
122.37	q of m	$^{1}J_{CF} =$ 280.6		c
^{19}F				
-73.55	m		3	c
-73.76	d of m	$^{3}J_{FF} =$ 19.2	3	c
-118.9	d of m	$^{2}J_{FF} =$ 267.0	1	h
-120.8	d of m	$^{2}J_{FF} =$ 267.0	1	h
-122.4	d of m	$^{2}J_{FF} =$ 267.0	1	h
-124.4	d of m	$^{2}J_{FF} =$ 263.2	1	h
-213.24	d of m	$^{2}J_{FH} =$ 42.5	1	i
-215.10	d of m	$^{2}J_{FH} =$ 40.9	1	i

16. Poly(2*H*-hexafluorocyclobutyl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 600

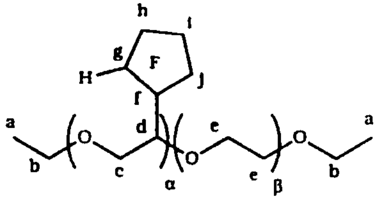
(in d_6-acetone)



Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^1H				
1.10	t	$^3J_{HH}$ = 7.0		a
3.3	broad s			c
3.56	m			b
3.66	m			e
3.78	m			d
3.92	m			d
5.22	broad s			g
^{19}F				
-137 to -114	m			h, i
-212	m			g
-221	m			g
		(f not identified)		

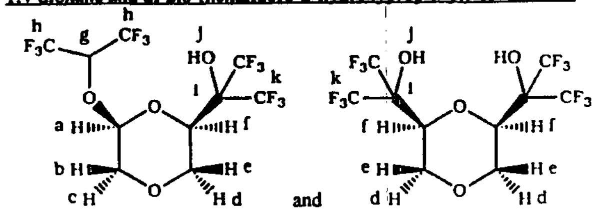
17. Poly(2*H*-hexafluorocyclopentyl)-α-ethyl-ω-ethoxy-poly(ethylene oxide) 600

(in d_6-acetone)



Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^1H				
1.13	t	$^3J_{HH}$ = 7.1		a
3.3	broad s			c
3.44	q	$^3J_{HH}$ = 6.8		b
3.52	s			e
3.6 to 4.1	m			d
5.18	m			g
^{19}F				
-117.4	m			h, i, j
-124.4	m			
-127.5	m			
-131.9	m			
-193.9	m			f
-207.7	m			g
-227.9	m			g

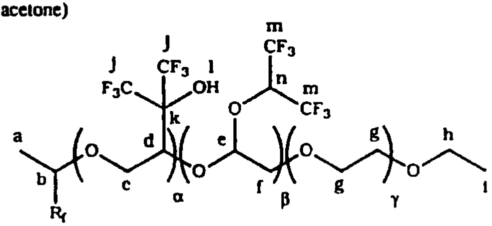
18. Mixture of 2-(2*H*-hexafluoroprop-2-oxy)-6-(hexafluoro-2-hydroxyprop-2-yl)-1,4-dioxane and di-2,6-(hexafluoro-2-hydroxyprop-2-yl)-1,4-dioxane



Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^{1}H				
3.701	d	$^{2}J_{HH}$ = 11.1		b
	d	$^{3}J_{HH}$ = 11.1		
3.963	d	$^{2}J_{HH}$ = 10.0		c e
	d	$^{3}J_{HH}$ = 10.0		
4.008	d	$^{2}J_{HH}$ = 11.7		c
	d	$^{3}J_{HH}$ = 2.6		
4.401	d	$^{3}J_{HH}$ = 10.3		a
4.405	d of t	$^{3}J_{HH}$ = 8.7		f
4.572	d	$^{2}J_{HH}$ = 11.3		d
	d	$^{3}J_{HH}$ = 2.0		
6.780	s			g
7.215 or 7.283 or 7.689	s			j
^{13}C				
64.54	s			d
66.46	s			b
74.24	s			f
77.07	s			a
123.35	q	$^{1}J_{CF}$ = 286.4		h or k
123.80	q	$^{1}J_{CF}$ = 286.7		h or k
123.73	q	$^{1}J_{CF}$ = 286.6		h or k
123.74	q	$^{1}J_{CF}$ = 287.2		h or k
130.38	s			i
131.03	s			g
^{19}F				
-76.83	q	$^{4}J_{FF}$ = 9.0	1	j
-77.13	q	$^{4}J_{FF}$ = 9.0	1	j
-79.83	q	$^{4}J_{FF}$ = 9.0	1	j
-80.05	q	$^{4}J_{FF}$ = 9.0	1	j
-80.43	q	$^{4}J_{FF}$ = 8.6	1	h
-80.64	q	$^{4}J_{FF}$ = 8.6	1	h

19. Poly(2*H*-hexafluoroprop-2-oxy)-poly(hexafluoro-2-hydroxyprop-2-yl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 600

(in d_6-acetone)



Rf = -C(CF$_3$)$_2$OH or -OC(CF$_3$)$_2$H

Chemical Shift/ppm	Multiplicity	Coupling Constant/Hz	Relative Intensity	Assignment
^{1}H				
1.0	t	$^{3}J_{HH}$ = 7.3	1	i
1.4	m		1	a
3.4	q	$^{3}J_{HH}$ = 7.3		h
3.6	m		15	c, g
~4	broad m		2	b, d, e
5.4	broad m		2	l, n
^{19}F				
-73.6	s			m or j
-76.5	m			j or m

Appendix Two
Selected NMR spectra

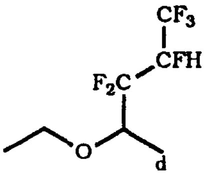
1. (2,2,3,4,4,4-Hexafluoro-2-methyl) ethyl ether
   2D $^1H^{13}C$ HETCOR NMR spectrum
2. (2,2,3,4,4,4-Hexafluoro-2-methyl) ethyl ether
   2D $^1H^{13}C$ HETCOR NMR spectrum (expansion)
3. 2-(2*H*-Hexafluoropropyl)-1,4-dioxane
   2D $^1H^{13}C$ HETCOR NMR spectrum
4. 2-(2*H*-Hexafluoropropyl)-1,4-dioxane
   2D ^1H COSY NMR spectrum
5. Di(2,2,3,4,4,4-hexafluoro-2-methylbutyl) ether
   ^{19}F NMR spectrum (expansion)
6. Di(2,2,3,4,4,4-hexafluoro-2-methylbutyl) ether
   2D ^{19}F COSY NMR spectrum (expansion)

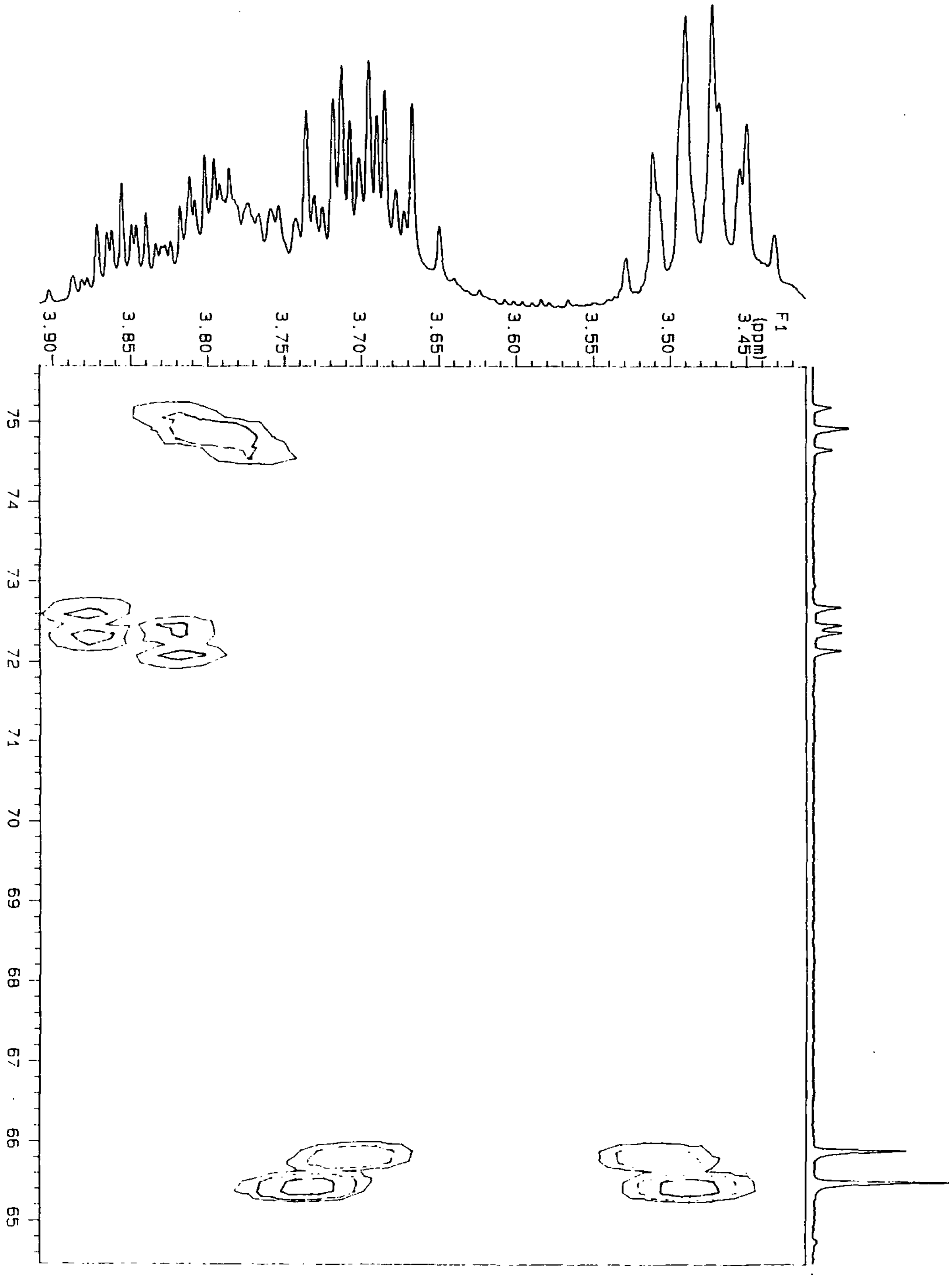
1. (2,2,3,4,4,4-Hexafluoro-2-methyl) ethyl ether.

2D $^1H^{13}C$ HETCOR NMR spectrum.

2. (2,2,3,4,4,4-Hexafluoro-2-methyl) ethyl ether.

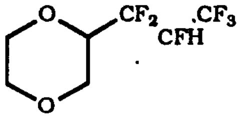
2D $^1H^{13}C$ HETCOR NMR spectrum (expansion).

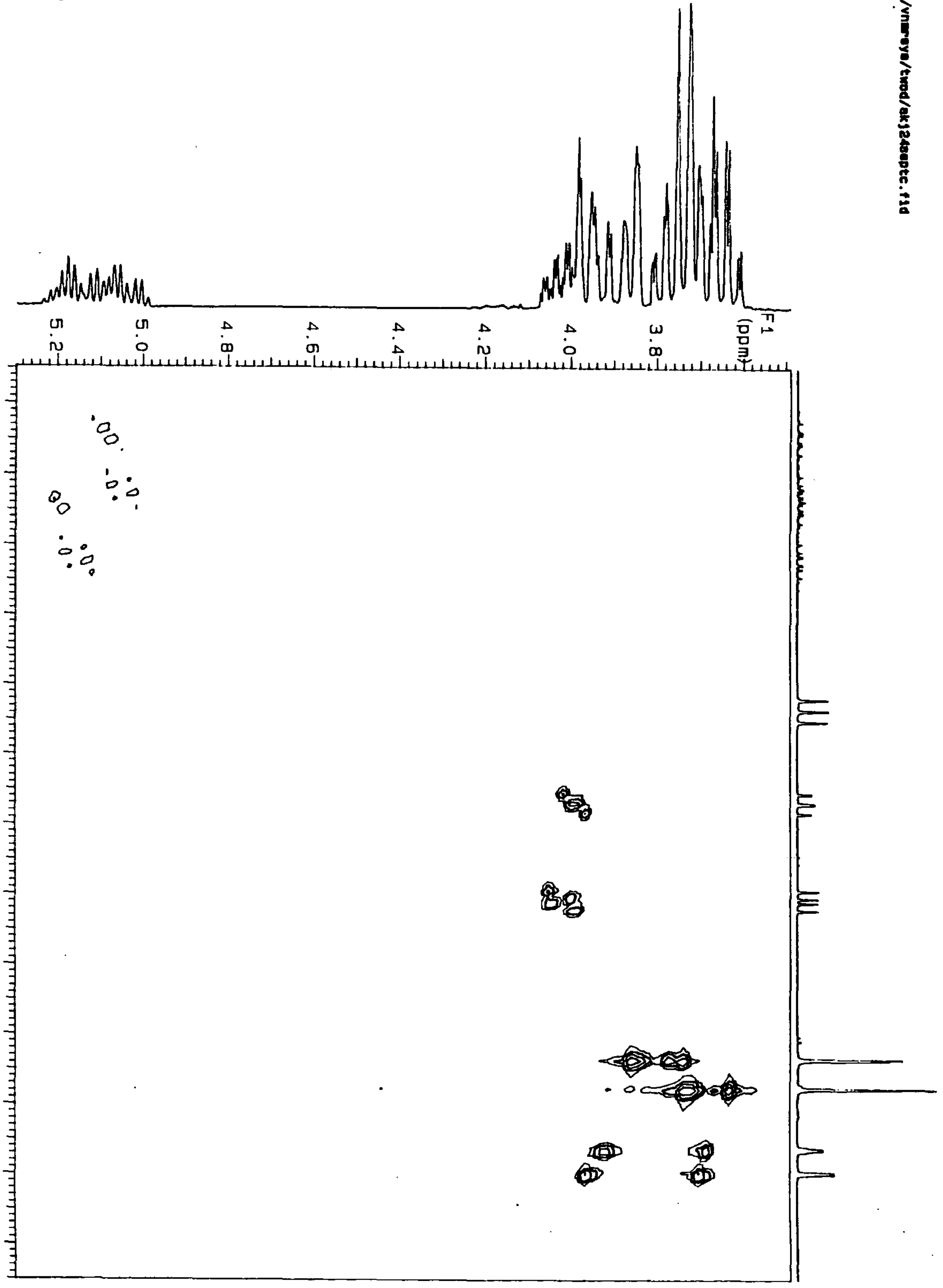




3. 2-(2*H*-Hexafluoropropyl)-1,4-dioxane.

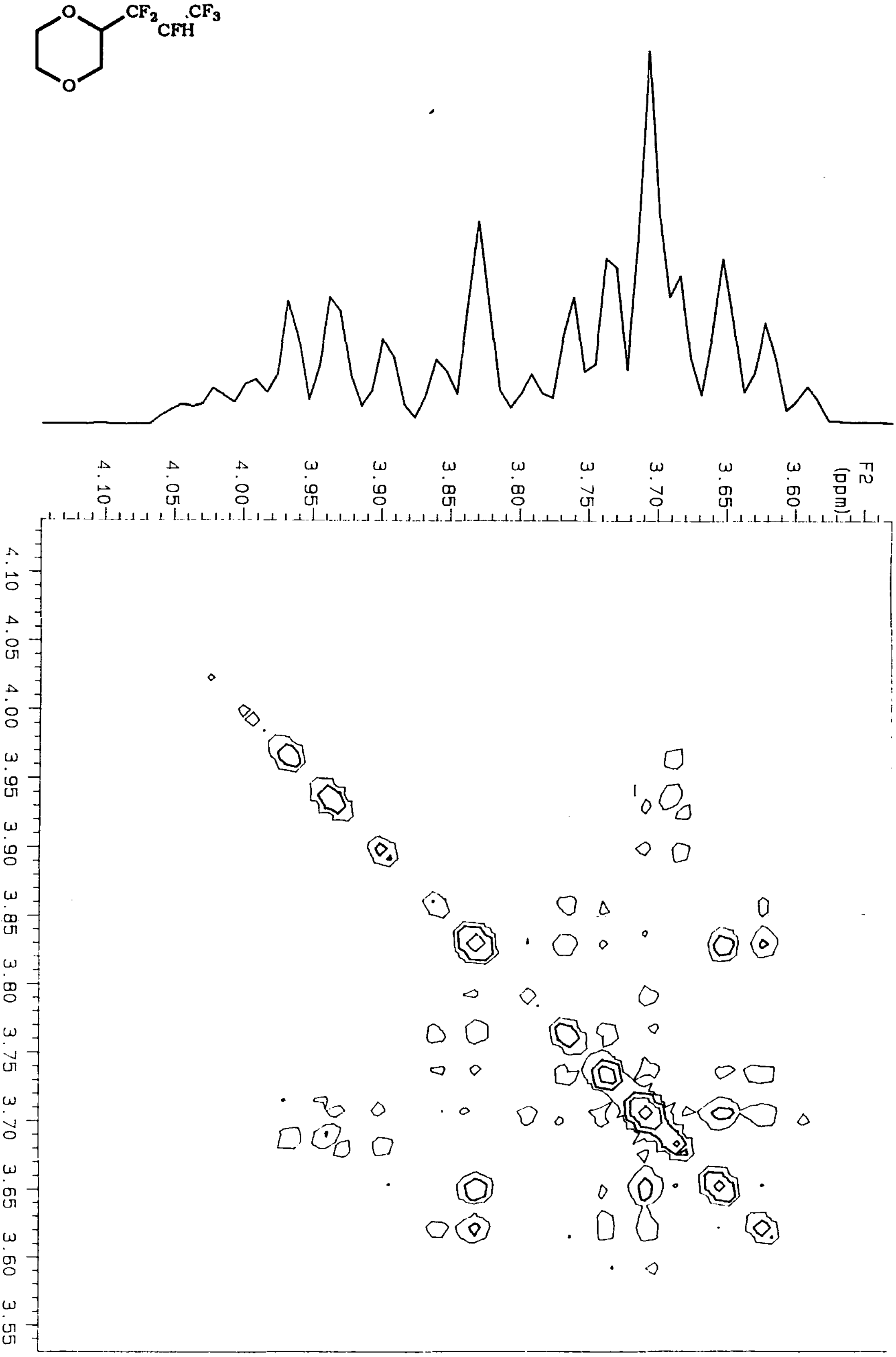
2D $^1H^{13}C$ HETCOR NMR spectrum.





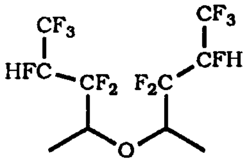
4. 2-(2*H*-Hexafluoropropyl)-1,4-dioxane.

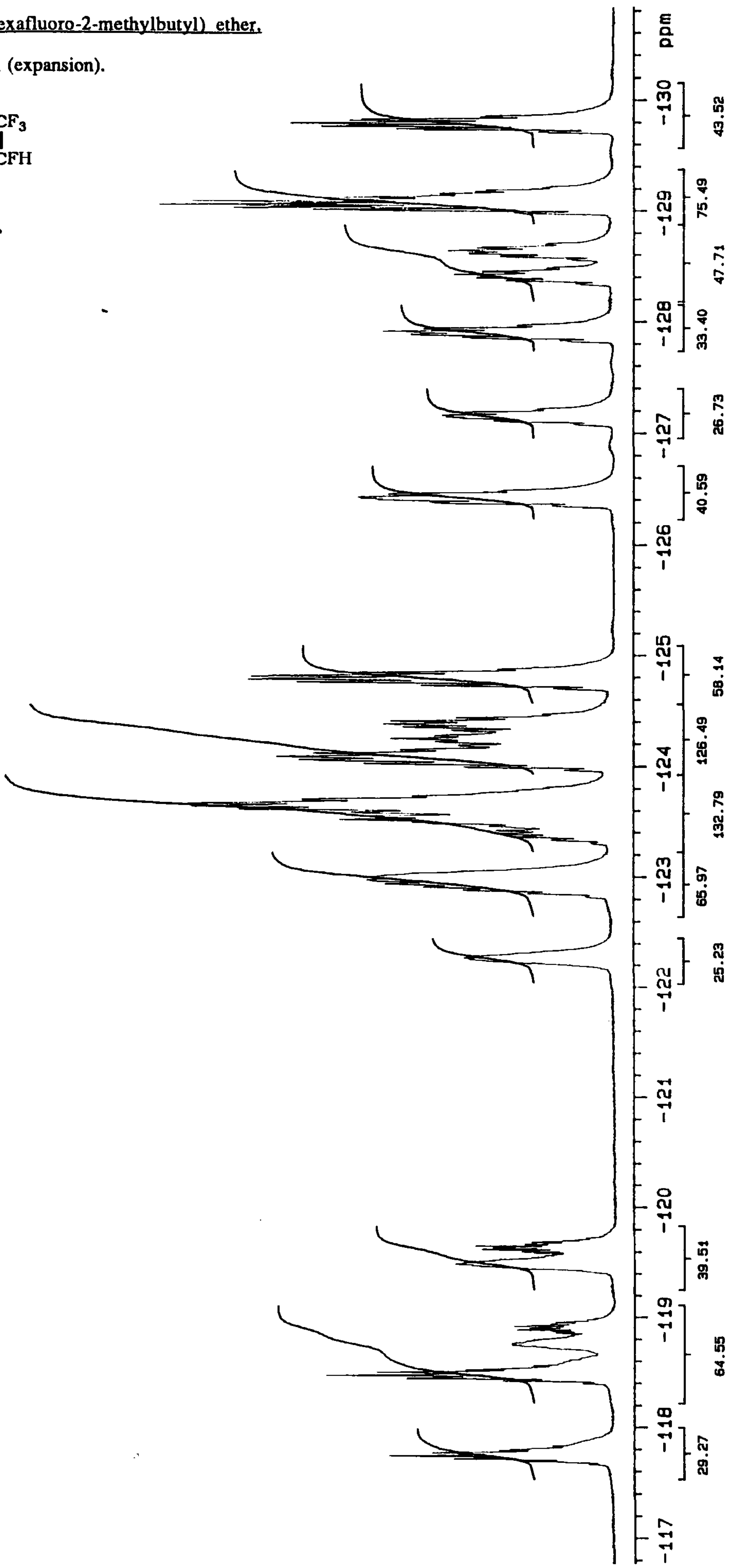
2D ^{1}H COSY NMR spectrum.



5. Di(2,2,3,4,4,4-hexafluoro-2-methylbutyl) ether.

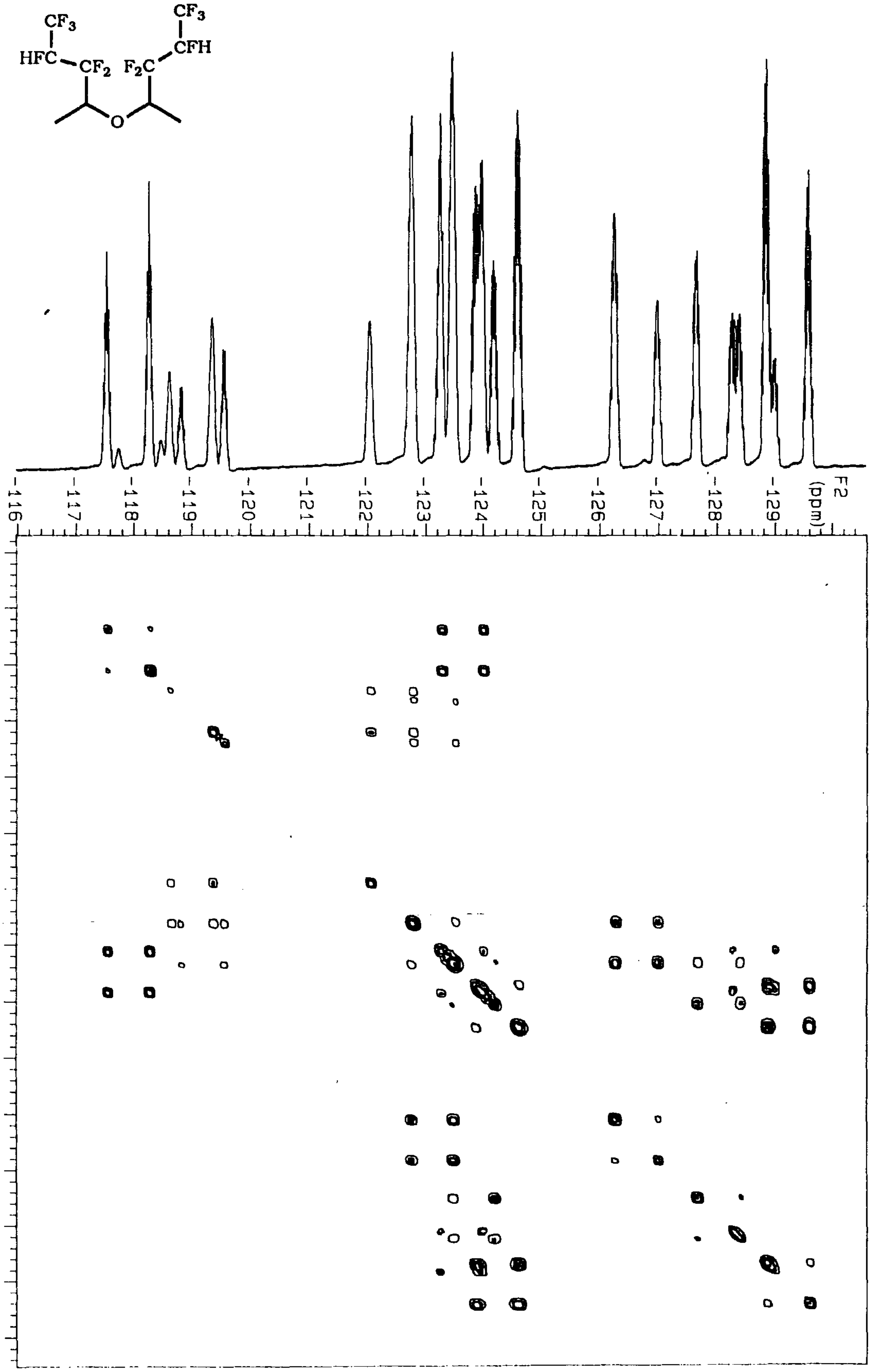
^{19}F NMR spectrum (expansion).





6. Di(2,2,3,4,4,4-hexafluoro-2-methylbutyl) ether.

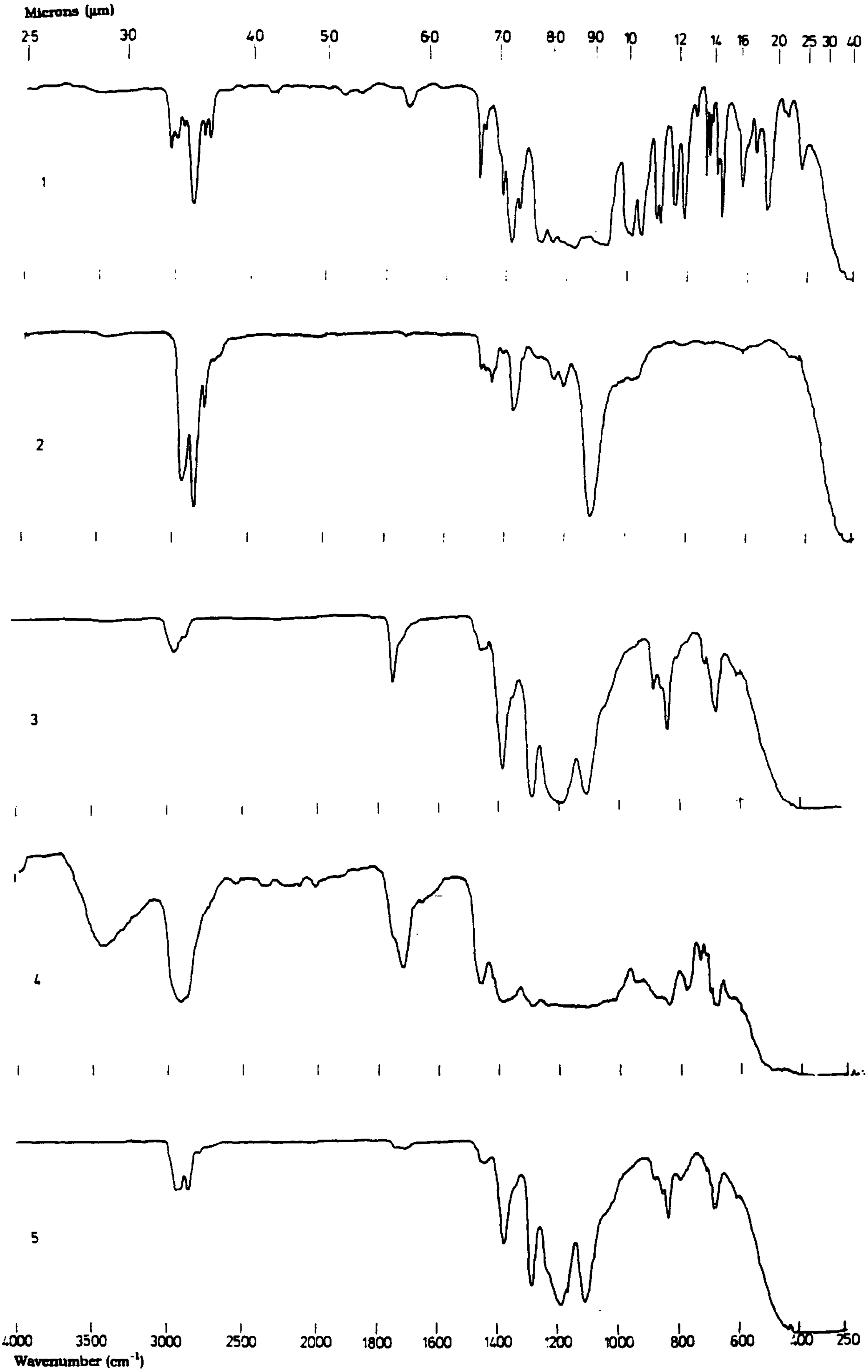
2D ^{19}F COSY NMR spectrum (expansion).

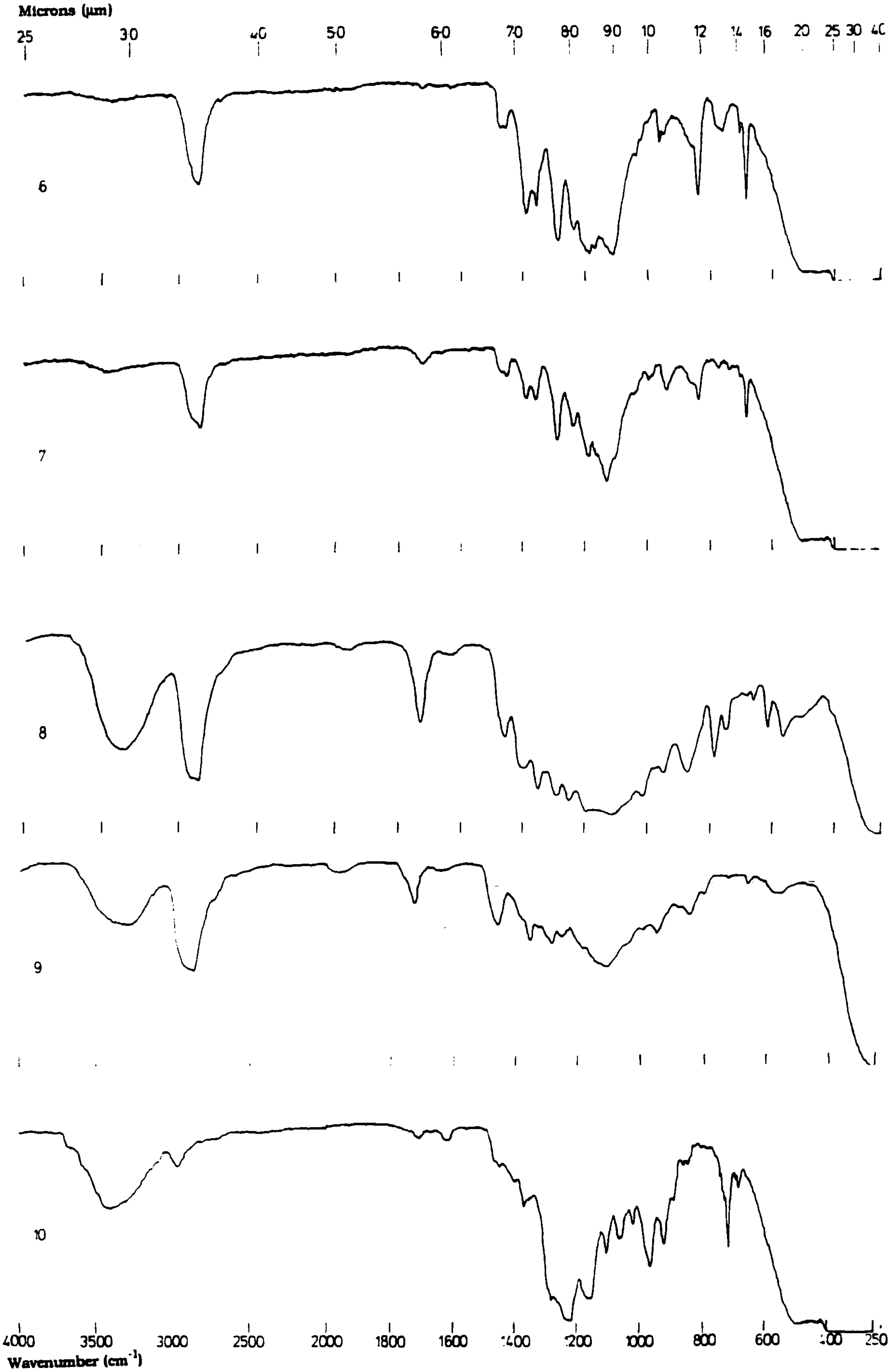


Appendix Three

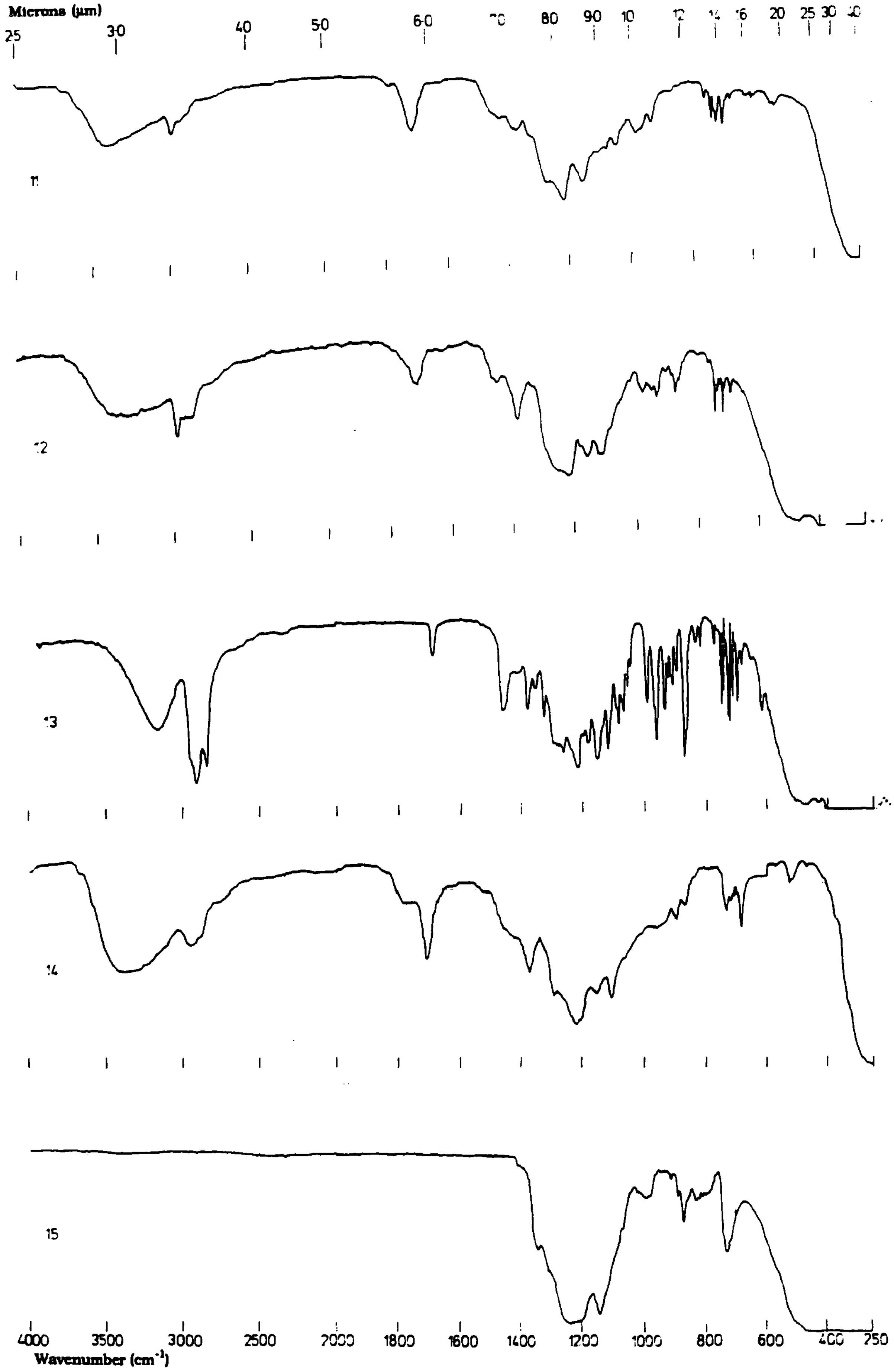
IR spectra

1. (2*H*-Hexafluoropropyl)-1,3,5-trioxane (**51**)
2. α-Ethyl-ω-ethoxy poly(tetramethylene oxide) 1000 (**61**)
3. Poly(2*H*-hexafluoropropyl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 600 (**58b**)
4. Poly(2*H*-hexafluoropropyl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 2000 (**58c**)
5. Poly(2*H*-hexafluoropropyl)-α-ethyl-ω-ethoxy poly(tetramethylene oxide) 1000 (**62**)
6. Poly(2*H*-hexafluoropropyl)-18-crown-6 (**65**)
7. Poly(2*H*-hexafluoropropyl)-15-crown-5 (**67**)
8. Poly(2*H*-hexafluorocyclobutyl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 600 (**71a**)
9. Poly(2*H*-octafluorocyclopentyl)-α-ethyl-ω-ethoxy poly(ethylene oxide) 600 (**71b**)
10. Addition product of oxolane to HFA (**92**)
11. Addition product of diethyl ether to HFA (**93**)
12. Addition product of 1,2-diethoxy ethane to HFA (**95**) & (**96**)
13. Addition product of 1,4-dioxane to HFA (**98**) & (**99**)
14. Addition product of α-ethyl-ω-ethoxy poly(ethylene oxide) 600 to HFA
15. Perfluoro[polypropyl-α-ethyl-ω-ethoxy poly(ethylene oxide) 600] (**103**)
16. Perfluoro[polypropyl-α-ethyl-ω-ethoxy poly(tetramethylene oxide) 1000] (**104**)
17. Perfluoro(polypropyl-18-crown-6) (**105**)


Microns (µm)
2·5
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10
12
14
16
20
25
30
40
1
2
3
4
5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm^{-1})



Microns (µm)
2·5
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10
12
14
16
20
25
30
40
6
7
8
9
10
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm⁻¹)


Microns (μm)
2·5
3·0
4·0
5·0
6·0
7·0
8·0
9·0
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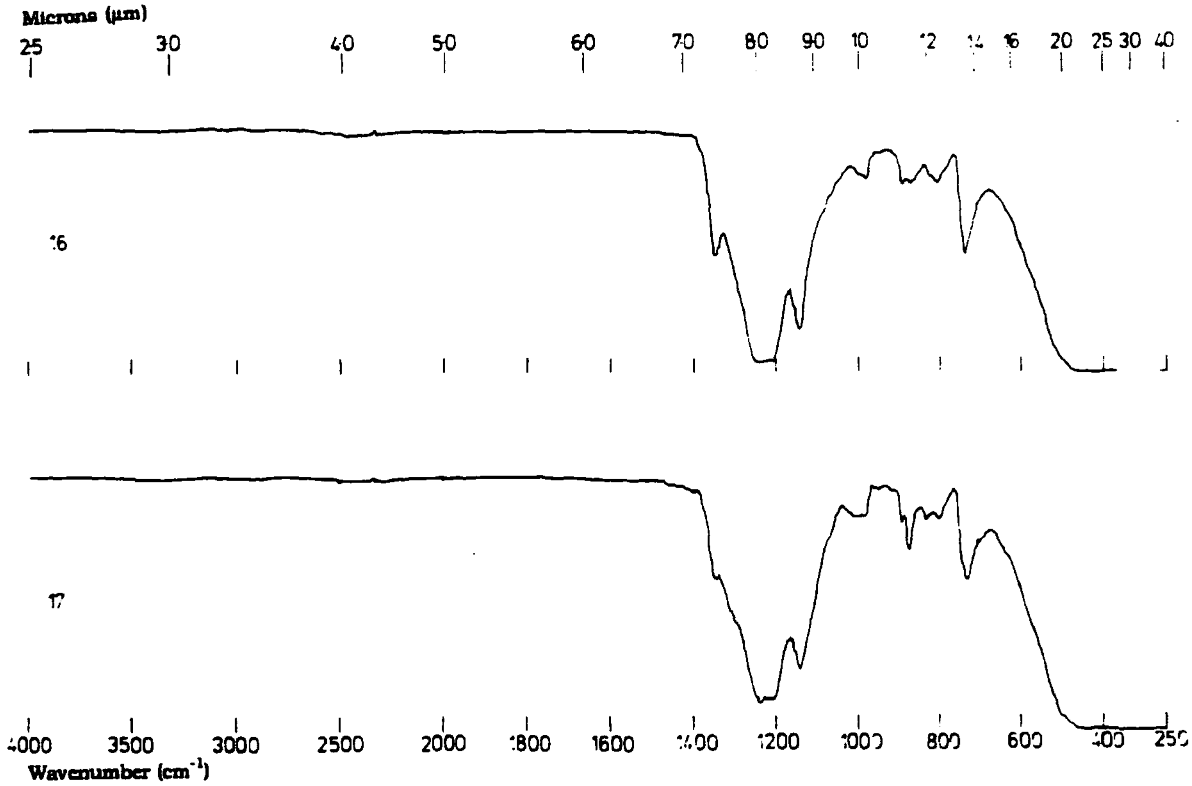
30
40
11
12
13
14
15
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm^{-1})


Microns (µm)
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4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
20
25
30
40
16
17
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm^{-1})

Appendix Four

MS spectra

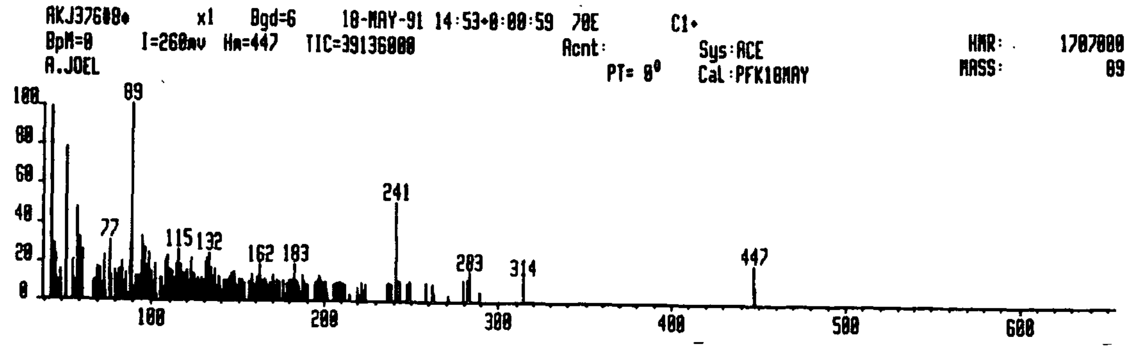
1. (2*H*-Hexafluoropropyl)-1,3,5-trioxane (**51**)
2. Poly(2*H*-hexafluoropropyl)-18-crown-6 (**65**)
3. Poly(2*H*-hexafluoropropyl)-18-crown-6 complex with potassium nitrate
4. Poly(2*H*-hexafluoropropyl)-15-crown-5 (**67**)
5. Addition product of oxolane to HFA (**92**)
6. Addition product of diethyl ether to HFA (**93**)
7. Addition product of 1,2-diethoxy ethane to HFA (**95**) & (**96**)
8. Addition product of 1,4-dioxane to HFA (**98**) & (**99**)
9. Perfluoro(polypropyl-18-crown-6) (**105**)

PDMS spectra

10. Poly(2*H*-hexafluoropropyl)-18-crown-6 (**65**)
11. Poly(2*H*-hexafluoropropyl)-18-crown-6 washed with lithium chloride
12. Poly(2*H*-hexafluoropropyl)-18-crown-6 washed with sodium acetate
13. Poly(2*H*-hexafluoropropyl)-18-crown-6 washed with potassium acetate
14. Poly(2*H*-hexafluoropropyl)-18-crown-6 washed with 1:1:1 lithium chloride, sodium acetate and potassium acetate

1. (2*H*-Hexafluoropropyl)-1,3,5-trioxane (51)

EI+ Mass Spectrum

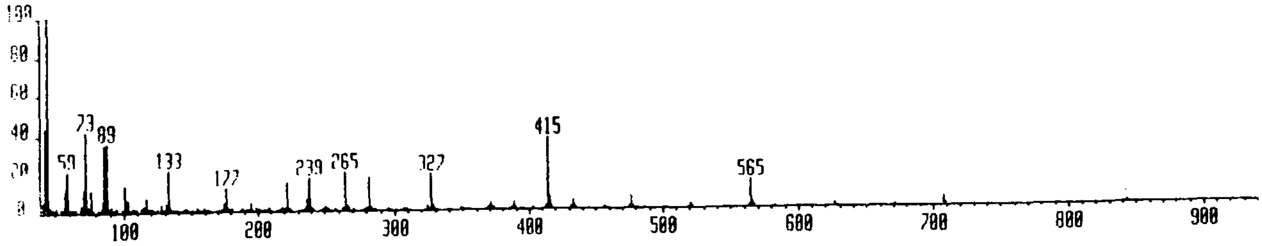


Mass	% Base
44.02	98.07
45.01	28.18
46.03	22.61
47.03	10.37
48.01	8.67
49.03	15.00
52.05	77.33
56.01	20.15
57.01	9.20
58.02	46.57
59.02	11.60
60.01	31.63
61.00	24.90
68.00	8.90
68.99	10.37
70.01	16.46
71.01	4.10
72.03	16.05
73.02	8.49
74.02	22.14
75.03	3.16
77.01	29.99
78.01	12.48
79.99	14.94
80.99	12.42
82.01	15.29
83.00	14.47
84.01	19.21
85.01	9.26
86.03	13.65
87.01	2.81
88.01	28.18
88.96	100.00
89.98	5.68
91.01	11.25
91.97	8.32
92.99	11.72
94.00	31.87
95.00	18.92
96.00	26.07
97.00	17.57
98.01	23.55
99.01	12.36
100.03	14.29
101.01	8.73
102.03	17.75
103.02	2.05
105.02	11.13
105.99	10.95
106.99	6.39
108.01	20.62
108.99	22.67
109.98	15.41
110.99	14.06
112.02	13.88
112.96	11.07
114.02	17.69
115.00	25.95
116.02	17.63
117.04	11.07
118.00	13.30
119.00	13.12
119.99	14.53
121.00	9.02
122.00	21.32
123.01	9.67
124.02	13.12
125.01	9.78
126.00	10.78
127.01	9.20
128.00	10.66
128.98	8.73
130.03	9.84
130.97	21.03
132.01	23.67
133.00	12.01
134.00	16.11
135.00	11.42
136.00	15.17
137.00	6.68
138.01	11.54
139.01	6.62
140.01	4.28
140.91	9.37
141.00	8.79
142.03	9.14
143.00	9.67
144.00	10.43
144.98	11.42
145.98	13.47
146.98	14.18
148.00	7.85
148.98	6.74
149.99	10.25
150.98	3.75
152.00	10.13
153.01	8.03
156.05	8.73
156.94	3.46
158.00	12.60
158.97	7.50
159.98	5.45
160.98	11.66
161.99	17.75
162.99	9.37
164.01	9.49
164.99	10.25
165.99	8.55
166.99	7.21
168.04	8.61
168.98	3.57
170.04	12.36
170.98	8.26
171.99	9.49
173.01	9.14
173.97	8.67
176.00	9.43
176.98	2.99
178.00	8.44
180.01	10.25
180.98	9.96
181.99	10.78
182.97	18.75
183.97	9.90
185.00	7.26
186.00	3.93
186.98	13.01
187.97	9.31
188.96	7.62
190.04	7.44
194.98	8.96
195.97	10.54
196.97	12.30
197.98	11.66
198.95	9.14
200.01	8.73
200.93	9.14
201.92	2.93
205.02	7.79
205.93	8.03
207.94	8.67
208.97	8.96
209.98	4.04
211.00	8.20
212.03	7.56
215.01	2.87
219.91	6.15
220.97	2.46
222.01	9.20
222.97	5.27
223.96	8.44
235.99	8.14
237.06	8.67
238.00	7.26
238.90	8.44
240.93	50.50
241.95	10.31
243.10	9.84
247.97	8.32
248.95	9.72
257.98	8.79
261.98	8.03
262.96	4.10
270.95	2.58
279.01	10.02
281.95	11.13
282.94	14.94
288.95	4.22
313.94	11.95
446.97	19.74
447.94	8.55

2. Poly(2*H*-hexafluoropropyl)-18-crown-6 (**65**)

EI+ Mass Spectrum

```
AKJ505J#33+     x1    Bgd=5     29-JUL-92 11:44+0:03:12  70E        EI+
BpM=0      I=2.4v   Hm=842   TIC=125073000            Acnt:      Sys:ACE              HMR:       15563000
A.K.JOEL                                            PI= 0°     Cal:PFK20JUL             MASS:            45
```



Mass	% Base
41.00	4.66
42.00	5.69
42.99	42.77
43.99	23.76
45.00	100.00
46.00	2.36
46.99	2.19
48.97	1.23
50.97	1.77
55.01	1.27
56.02	1.41
56.99	8.62
58.00	11.94
59.01	20.90
60.00	1.00
60.98	1.21
62.98	0.98
64.98	1.41
68.96	3.37
69.99	3.29
71.00	3.55
72.01	11.61
72.99	40.81
73.99	1.71
74.99	3.29
75.98	0.34
76.97	10.63
77.97	0.38
81.95	0.44
82.99	0.75
85.00	1.63
85.98	6.01
86.99	34.46
87.99	12.38
89.00	35.15
90.00	1.81
90.99	2.50
92.95	1.28
94.95	1.63
97.00	0.31
98.98	1.51
99.99	0.94
100.99	13.25
102.00	3.29
103.01	5.56
103.99	0.52
104.97	0.85
106.96	0.98
108.96	0.51
112.96	1.81
113.99	0.72
115.00	2.36
116.00	1.12
117.00	6.56
118.00	0.60
118.97	1.40
120.98	1.50
124.94	0.76
126.94	3.37
128.98	0.42

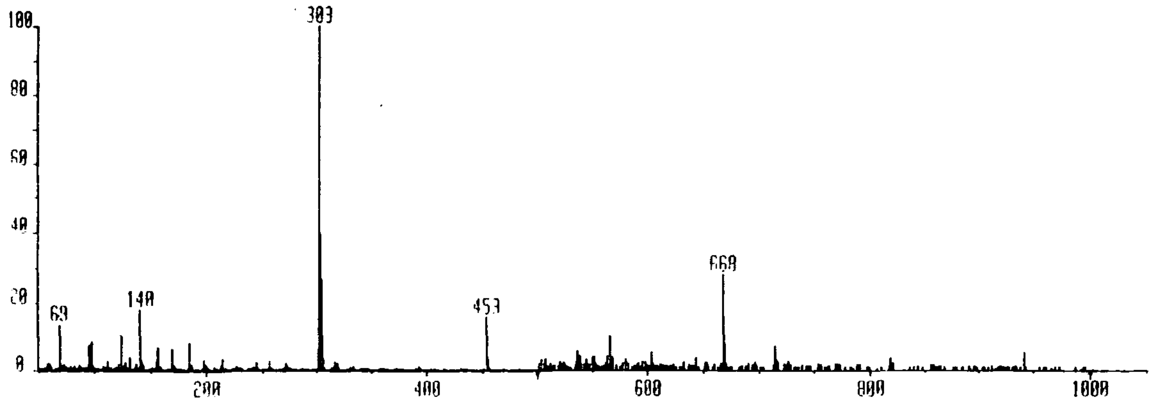
Mass	% Base
130.99	4.07
131.98	0.58
133.00	21.01
134.00	1.39
134.98	0.82
136.95	0.37
138.94	0.35
140.93	0.31
144.97	1.20
145.99	0.36
146.97	1.16
150.93	0.80
154.92	2.14
156.95	0.44
158.94	1.84
160.98	0.54
162.95	0.41
170.94	0.31
172.92	0.72
174.94	3.85
175.95	0.35
177.00	11.62
178.01	1.05
178.99	0.35
180.91	0.39
188.93	1.17
192.90	0.38
193.90	0.84
194.91	3.92
198.92	0.97
200.92	0.33
204.97	0.44
207 91	0.57
208.92	1.27
216.90	0.71
218.92	1.90
219.91	0.46
220.95	1.32
221.92	1.33
222.89	14.45
223.90	0.96
224.90	0.33
232.93	0.31
234.93	0.35
235.90	0.98
236.90	5.69
237 90	1.18
238.92	16.43
239.92	1.27
240.91	0.64
248.92	0.37
250.92	1.73
251.92	0.37
252.93	0.90
257 49	0.40
262.93	1.29
263.95	0.32
265.01	19.89
266.01	2.76
266 94	1.97

Mass	% Base
270 90	0.36
278.97	0.40
280.89	1 68
281.91	0.31
282.90	17.25
283.91	1.70
284.91	0.46
286.90	0.39
294.92	0.64
304.93	0.31
306.92	0.49
308.93	0.89
324.92	1.73
325.92	0.31
326.93	18.61
327.93	2.26
328.94	0.43
338.90	0.31
348.86	0.57
368.88	1 45
370.95	3.29
371.95	0.48
372.85	0.62
386.84	0.40
388.86	3.29
389.87	0.32
402.87	0.34
412.92	1.18
413.96	0.80
414.96	36.64
415.97	6.13
416.94	1.23
430.86	0.39
432.87	3.95
433.87	0.52
456.86	0.32
458.87	0.31
474.87	0.48
476.88	5.71
477.88	0.89
520.90	2.13
521.91	0.34
562.89	0.79
563.92	0 73
564.92	13.92
565.92	2.78
566.93	0.44
626.84	1.16
670.88	0.69
707.90	0.31
708.23	4 36
708.55	1.00
842.67	0.58

3. Poly(2*H*-hexafluoropropyl)-18-crown-6 complex with potassium nitrate

FAB Mass Spectrum

```
AKJ505E#3+       x1    Bgd=2     21-JUL-92 12:01+0:00:53  70E         FB+
BpM=0     I=10v     Hm=1014  TIC=394810016               Acnt:          Sys:FABHI               HMR:       65534000
A.K..INFL                                                      PT= 0°    Cal PFKB.JULS           MASS:           303
                                                      ·X20·0
```



Mass	% Base	
40.16	0.17	
41.08	24.39	F
41.16	2.34	F
42.15	1.00	
43.14	7.07	
44.14	2.52	
45.15	15.35	
46.15	0.54	
47.14	0.20	
50.11	0.12	
51.12	0.20	
53.13	0.37	
54.12	0.14	
55.12	0.43	
56.09	0.26	
57.05	0.79	F
57.12	1.85	F
58.11	0.50	
59.11	1.67	
60.09	0.46	
61.09	1.21	
65.07	1.25	
68.02	0.19	
69.00	13.42	
70.02	0.20	
70.99	1.10	F
71.07	0.75	F
72.07	0.29	
73.05	1.61	
74.04	0.14	
75.05	0.92	
77.04	0.46	
77.93	0.63	
78.93	0.94	
80.93	0.21	
81.04	0.11	
81.98	1.20	
83.01	0.14	
84.00	0.30	
86.04	0.23	
87.04	1.59	
88.04	0.21	
89.05	0.78	
90.05	0.13	
91.04	0.19	
93.04	0.78	
93.92	0.32	
94.04	0.10	
94.17	0.10	
94.93	7.23	
95.99	0.35	
96.92	3.38	
98.01	0.15	
98.94	1.07	
99.99	0.19	
101.04	0.32	
102.97	0.45	
103.92	0.52	
107.06	0.15	
107.93	0.93	
108.93	0.30	
109.92	0.41	
110.02	0.11	
111.00	0.78	
111.98	2.42	
112.99	0.39	
113.99	0.82	
115.01	0.12	
117.06	0.21	
118.93	0.64	
119.92	0.41	
120.93	1.80	
121.92	0.39	
122.94	0.81	
123.91	10.01	
124.94	0.22	
125.90	1.46	F
126.01	1.44	F

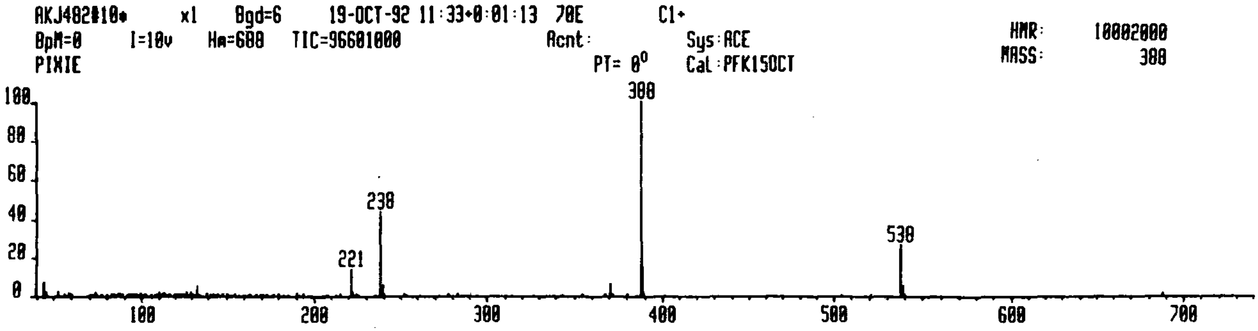
Mass	% Base	
127.01	2.34	
128.00	0.59	
129.02	0.42	
130.01	0.26	
131.00	3.57	
133.00	0.29	
135.93	0.78	
136.93	1.98	
137.93	0.18	
138.97	0.78	
139.92	17.67	
140.99	0.86	
141.30	2.63	F
142.02	1.43	F
143.00	0.19	
143.99	0.16	
148.97	0.38	
149.93	0.12	
150.93	0.58	
151.97	0.20	
152.99	0.31	
154.03	2.57	
155.00	0.87	
156.01	6.54	
157.01	0.61	
158.01	1.07	
158.99	0.23	
161.07	0.14	
162.93	0.18	
164.96	0.27	
165.93	0.14	
166.97	0.18	
168.02	0.14	
168.97	5.98	
170.01	1.56	
170.98	1.02	
172.01	0.38	
173.04	0.12	
174.90	0.48	
176.86	0.22	
178.89	0.29	
179.67	0.18	
180.95	0.18	
181.88	0.11	
182.05	0.15	
182.97	0.22	
184.04	7.88	
185.03	1.46	
186.04	1.33	
187.04	0.27	
188.00	0.13	
188.96	0.14	
190.90	0.28	
194.98	0.11	
195.88	0.21	
197.04	2.78	
197.99	0.52	
199.03	0.78	
200.02	1.45	
201.03	0.28	
202.03	0.29	
204.89	0.10	
206.90	0.55	
208.94	0.27	
210.97	0.12	
212.03	0.23	
213.03	1.31	
214.04	3.20	
215.03	0.52	
216.04	0.47	
223.01	0.23	
224.86	0.52	
227.02	1.17	
228.01	0.18	
229.03	0.42	
230.01	0.28	
231.02	0.24	
232.03	0.11	
237.00	0.20	

Mass	% Base	
239.02	0.24	
240.92	0.56	
242.07	0.29	
243.03	0.78	
244.05	2.11	
245.02	0.48	
245.40	0.11	
246.06	0.37	
252.94	0.15	
255.02	0.29	
257.06	2.38	
258.07	0.31	
259.06	0.43	
259.95	0.14	
261.05	0.17	
265.19	0.12	
269.04	0.11	
269.90	0.19	
271.01	0.33	
272.07	1.90	
273.07	1.05	
274.06	0.28	
277.03	0.25	
283.00	0.12	
285.06	0.14	
287.07	0.38	
289.08	0.18	
291.04	0.11	
297.02	0.20	
299.02	0.31	
300.08	0.16	
301.07	6.07	
302.06	4.99	F
303.07	100.00	FC
304.08	39.26	F
305.09	26.37	F
306.09	3.19	
307.10	0.50	
307.93	0.14	
313.03	0.14	
315.06	0.78	
316.08	0.24	
317.08	2.18	
318.08	0.47	
319.08	1.82	
320.07	0.28	
321.08	0.25	
327.07	0.12	
329.07	0.42	
330.13	0.17	
331.07	0.60	
332.08	0.16	
333.09	1.20	
334.07	0.31	
335.02	0.15	
341.04	0.48	
343.09	0.28	
344.08	0.10	
345.08	0.36	
346.10	0.18	
347.10	0.36	
348.09	0.15	
349.05	0.15	
354.93	0.13	
357.02	0.32	
358.09	0.11	
359.08	0.34	
360.07	0.18	
361.08	0.35	
363.11	0.46	
364.07	0.16	
371.09	0.20	
373.13	0.22	
374.07	0.10	
375.10	0.41	
377.05	0.43	
378.12	0.15	
387.11	0.13	
389.08	0.23	

Mass	% Base	
394.11	0.27	
395.07	0.15	
399.07	0.13	
401.13	0.14	
403.11	0.21	
404.03	0.14	
405.11	0.15	
407.09	0.19	
415.08	0.32	
417.06	0.11	
419.10	0.14	
422.06	0.12	
423.09	0.14	
431.03	0.19	
433.12	0.41	
435.08	0.27	
449.10	0.13	
451.10	0.45	
453.04	15.61	F
454.07	3.00	F
455.08	1.61	
455.97	0.23	
461.15	0.11	
465.09	0.15	
467.11	0.15	
469.03	0.24	
477.05	0.13	
479.14	0.16	
481.13	0.11	
483.11	0.19	
493.13	0.12	
495.15	0.15	
503.13	0.15	
507.09	0.16	
520.08	0.12	
523.17	0.10	
535.14	0.27	
536.21	0.13	
537.18	0.20	
543.14	0.14	
549.10	0.18	
551.16	0.18	
563.19	0.19	
565.18	0.48	
566.19	0.17	
567.19	0.16	
579.20	0.14	
595.08	0.11	
597.19	0.10	
603.09	0.25	
633.06	0.11	
643.16	0.17	
653.20	0.11	
668.12	1.39	
669.59	0.38	
697.26	0.12	
715.08	0.34	
716.27	0.15	
717.14	0.12	
726.19	0.13	
818.27	0.17	
841.24	0.25	
1003.18	0.03	
1014.31	0.03	

4. Poly(2*H*-hexafluoropropyl)-15-crown-5 (**67**)

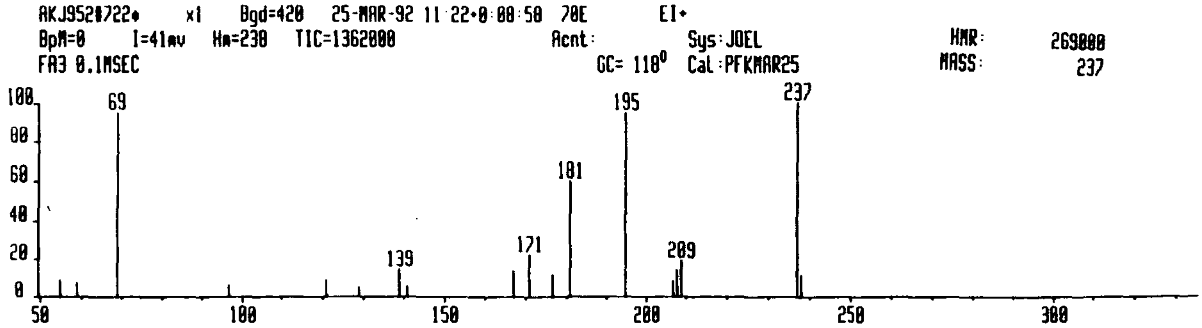
CI+ Mass Spectrum



Mass	% Base	
43.99	1.07	
44.99	0.34	
52.03	0.32	
109.99	0.33	
128.97	0.32	
132.97	0.82	
220.97	2.09	
237.99	6.69	
238.99	0.81	
370.92	0.88	
387.92	15.26	F
388.95	2.27	F
389.95	0.33	
537.92	3.98	
538.93	0.77	

5. Addition product of oxolane to HFA (92)

EI+ Mass Spectrum



Mass	% Base
55.00	8.18
59.01	7.06
68.99	95.17
96.99	5.58
121.01	8.55
128.98	4.46
139.04	14.13
141.04	5.20
141.08	5.20
167.00	13.75
171.04	21.93
177.00	11.15
180.99	59.85
195.04	95.17
207.04	7.81
208.03	13.38
209.06	18.59
236.99	100.00
238.02	11.15

6. Addition product of diethyl ether to HFA (93)

EI+ Mass Spectrum

```
AKJ35415+      x1    Bgd=1     13-MAY-91 15:53+0:00:44  70E         EI+                              HMR:      11532000
BpM=0     I=1.0v   Hm=414   TIC=66090000              Acnt:          Sys:ACE                         MASS:           43
A.K.JOEL                                                      PT= 0°    Cal:PFK13MAY
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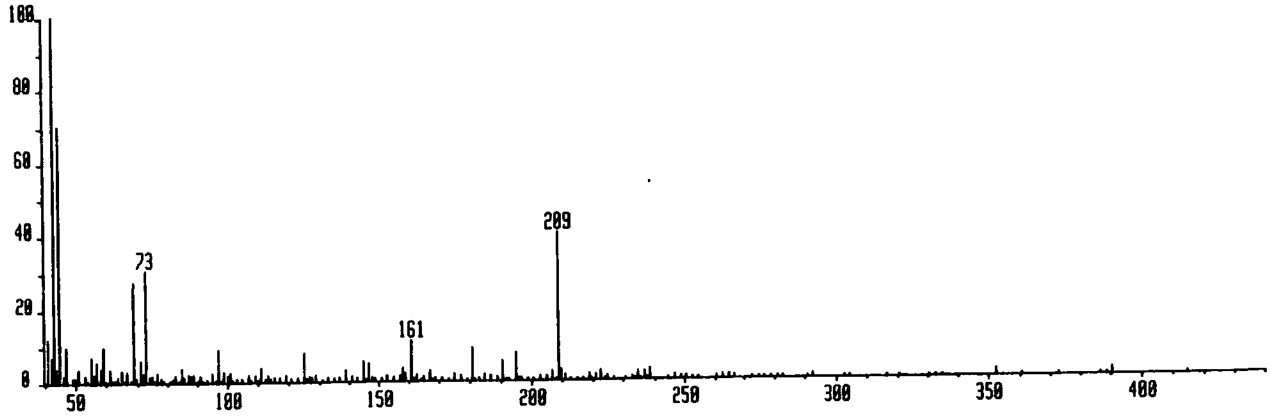


Mass	% Base	
40.97	12.02	
41.94	6.74	
42.94	100.00	F
42.98	3.66	F
43.95	3.86	
44.96	70.08	
45.96	1.86	
46.95	9.61	
48.93	1.06	
49.92	0.95	
50.92	3.50	
52.95	1.63	
53.95	0.49	
54.95	6.94	
55.96	1.97	
56.95	5.32	
57.95	3.85	
58.95	9.61	
59.94	0.49	
60.93	3.36	
62.92	0.42	
63.91	1.22	
64.92	3.15	
66.91	2.68	
67.93	0.50	
68.88	27.46	F
68.96	3.43	F
69.93	0.98	
70.93	5.94	
71.94	2.48	
72.94	30.42	
73.94	1.36	
74.89	1.58	
76.89	2.56	
77.86	1.15	
78.89	0.48	
80.91	0.51	
81.93	0.82	
82.91	1.59	
83.92	0.37	
84.91	3.62	
85.93	1.23	
86.91	2.21	
87.90	1.55	
88.88	2.19	
89.88	0.30	
90.86	1.58	
91.85	0.41	
92.86	0.65	
94.87	2.40	
95.89	0.45	
96.84	8.95	
97.88	0.37	
98.89	2.74	
99.90	1.65	
100.91	2.25	
102.88	0.58	
104.85	0.68	
106.86	1.83	
108.86	1.86	

Mass	% Base
109.89	0.39
110.84	3.62
111.85	0.68
112.86	1.84
113.90	0.73
114.88	1.12
116.84	1.08
118.81	1.56
120.83	0.69
122.83	1.20
124.83	7.75
125.83	0.57
126.85	1.21
127.78	0.98
128.82	1.73
130.83	0.34
132.80	0.95
134.82	0.85
136.81	1.02
138.81	3.11
140.80	1.23
142.84	0.90
144.78	5.48
145.78	0.35
146.75	4.63
147.76	0.95
148.78	0.55
150.78	0.69
152.81	1.23
154.77	1.09
156.76	1.27
157.76	3.41
158.76	2.13
160.75	10.94
161.75	0.55
162.74	1.83
164.77	1.20
166.75	2.64
168.75	0.76
170.76	0.62
172.74	0.38
174.75	1.77
176.74	1.35
180.73	8.99
181.73	0.51
182.75	0.55
184.74	1.79
186.72	1.22
188.71	0.97
190.70	5.53
191.70	0.43
192.72	0.41
194.72	7.58
195.72	0.53
196.70	0.57
198.71	0.40
202.73	0.96
204.71	1.08
206.70	2.25
207.70	0.40

Mass	% Base
208.68	40.18
209.68	2.74
210.69	1.23
212.69	0.46
216.70	0.34
218.69	1.55
219.69	0.30
220.69	1.28
222.70	2.49
223.69	0.39
224.68	0.91
230.68	0.34
232.68	0.69
233.68	0.33
234.66	2.19
235.68	0.41
236.67	2.09
237.68	0.39
238.68	2.81
246.67	1.08
248.67	0.70
250.65	0.58
252.65	0.35
254.63	0.42
260.65	0.69
262.65	1.00
264.65	0.97
266.65	0.66
272.62	0.40
274.63	0.49
276.64	0.51
278.64	0.39
280.64	0.48
282.62	0.35
290.62	0.42
292.59	1.14
302.59	0.46
316.58	0.40
320.57	0.42
330.54	0.42
334.53	0.40
352.45	1.60
360.49	0.48
372.47	0.36
386.47	0.37
388.47	0.43
390.44	1.66
414.44	0.30

7. Addition product of 1,2-diethoxy ethane to HFA (95) & (96)

EI+ Mass Spectrum

```
AKJ375#14•      x1    Bgd=11    14-MAY-91 11:30+0:01:27  70E        C1-                          HMR:       8360000
BpM=0    I=1.3v   Hm=700   TIC=42354000                 Acnt:            Sys:ACE             MASS:          166
A.K.JOEL                                                       PT= 0°     Cal:PFK14MAY
```

Mass	% Base
41.96	0.78
42.98	0.67
45.00	0.55
45.96	0.60
57.00	0.86
58.00	2.16
58.98	2.53
61.00	1.09
62.04	0.61
68.97	0.68
71.02	0.67
72.02	0.42
72.96	0.60
78.89	0.74
80.89	0.90
85.01	2.20
86.02	0.57
87.01	0.50
92.99	0.54
101.02	0.57
112.97	1.40
116.97	0.82
126.86	2.23
127.03	0.38
127.95	3.04
129.01	0.54
130.96	0.55
134.97	1.66
136.95	3.00
137.95	4.19
138.96	5.70
139.97	0.54
143.95	0.68
146.95	17.87
147.95	5.71
150.95	0.44
152.97	1.25
154.96	2.59
159.06	0.68
159.96	1.11
162.95	0.62
165.94	100.00
166.95	27.33
167.95	1.40
168.98	0.48
169.97	0.45
177.94	3.59
178.95	6.75
180.99	0.60
183.01	0.67
184.97	0.93
186.96	1.21
187.95	0.87
189.95	0.84
191.95	0.61
192.97	1.39
195.00	0.91
205.98	0.72
206.95	3.88
208.96	2.99

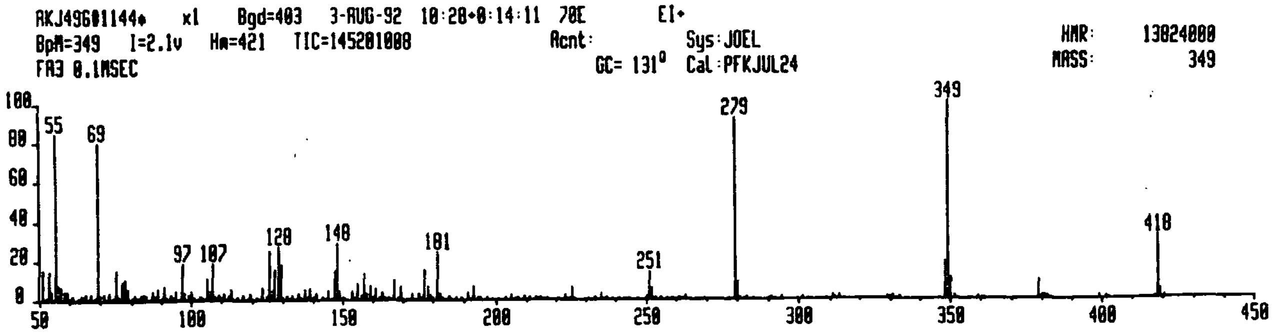
Mass	% Base
209.99	0.66
210.98	1.76
211.95	0.76
213.01	0.59
218.96	1.16
221.97	0.36
222.98	18.63
223.97	2.13
224.97	1.73
227.94	1.28
228.96	0.86
230.95	3.41
231.97	0.60
232.98	0.48
233.98	0.53
234.99	1.35
235.98	0.41
236.99	0.74
239.02	0.63
242.96	0.61
246.94	13.66
247.94	1.02
248.98	0.91
249.96	1.09
250.98	1.67
251.97	0.44
253.00	1.37
255.00	0.99
256.95	0.71
261.94	2.58
262.93	7.86
263.96	0.76
265.02	0.38
267.97	0.57
268.96	1.42
270.00	0.96
272.96	0.59
273.95	1.03
274.94	0.69
277.95	1.33
279.03	1.28
280.85	7.16
281.95	0.69
283.04	0.74
285.95	0.97
292.97	1.17
296.97	1.05
299.95	0.84
301.96	0.82
304.94	42.87
305.94	4.17
306.94	0.65
308.94	1.29
311.94	3.10
314.94	0.81
318.95	0.98
320.97	5.03
321.97	0.79
322.98	0.68
323.94	1.36

Mass	% Base
329.95	0.80
330.94	6.62
331.95	1.36
332.95	28.26
333.95	2.39
334.96	1.57
335.95	0.55
341.93	0.97
342.93	1.41
348.98	2.51
349.96	7.66
350.97	1.37
354.96	0.59
360.97	5.53
361.95	2.66
362.96	1.18
368.97	0.68
373.94	1.42
374.95	4.23
375.96	0.50
380.93	4.30
385.94	0.69
388.96	1.84
389.99	0.62
392.95	1.82
404.98	1.82
411.96	1.06
416.98	1.36
418.96	1.70
423.95	1.11
430.95	2.08
434.98	0.74
435.95	0.66
442.95	1.95
445.10	1.42
446.09	0.85
447.01	0.60
449.04	2.03
450.03	0.55
454.96	0.94
461.95	0.72
473.95	0.94
480.94	1.30
492.97	1.29
504.94	0.91
516.96	0.42
523.95	0.59
530.95	0.71
535.95	0.66
542.95	0.91
554.95	0.90
573.95	0.78
592.97	0.57
604.96	0.99
611.96	0.47
617.01	0.42
623.99	1.04
635.95	0.93
654.96	0.90
657.24	0.69

Mass	% Base
658.86	0.88
661.12	1.02
664.96	0.65
679.04	0.60
685.79	0.57
690.54	0.59
708.73	0.47

8. Addition product of 1,4-dioxane to HFA (98) & (99)

EI+ Mass Spectrum

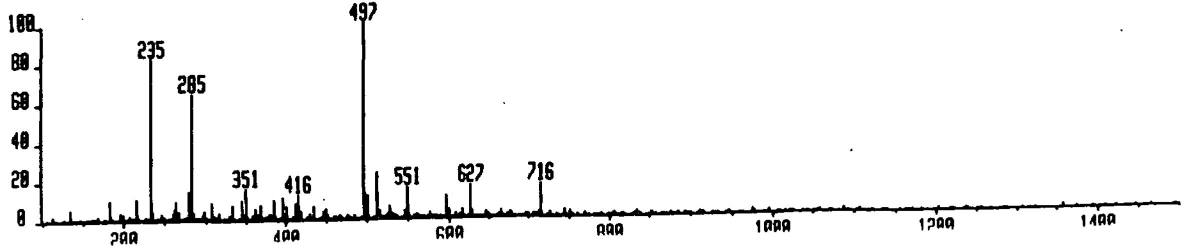


Mass	% Base
49.01	11.11
49.99	10.56
51.00	14.97
52.01	0.38
53.00	13.98
54.00	3.70
55.01	84.04
56.01	6.79
57.01	5.95
58.00	3.76
59.02	3.86
60.00	0.52
61.00	2.22
63.01	0.88
64.00	2.23
65.01	2.88
66.99	2.50
68.00	0.41
68.99	79.72
70.00	1.98
71.00	2.60
73.01	2.97
74.01	0.54
75.01	14.84
76.02	1.56
77.02	8.98
77.99	10.39
79.00	4.84
80.01	0.38
81.01	1.93
82.01	0.63
83.02	1.77
84.02	2.84
85.03	2.20
87.01	4.03
88.02	1.40
89.02	5.17
90.00	0.94
91.01	6.11
92.02	0.46
93.01	2.11
94.01	0.49
95.02	4.09
96.99	17.63
98.01	3.02
99.01	1.79
100.00	4.14
101.01	0.52
103.02	1.54
104.03	0.70
105.03	10.21
106.03	3.70
107.01	17.80
108.02	1.10
109.02	1.76
110.02	0.40
111.03	2.81
112.01	1.10
113.02	4.67
115.03	0.43
117.01	1.94
119.00	2.63
121.01	0.60
123.02	5.47
124.03	1.11
125.03	24.35
126.01	3.70
127.02	14.51
128.00	26.42
129.00	17.09
130.01	0.73
131.01	1.03
133.02	1.16
135.02	2.68
136.03	0.41
137.01	4.54
138.00	0.57
139.01	4.81
140.01	0.59
141.00	2.31
143.02	0.66
145.01	3.90
146.99	14.27
148.00	28.37
149.01	3.95
150.01	0.78
153.03	3.70
154.03	0.58
155.01	7.41
156.01	1.43
157.01	13.13
158.02	2.59
159.00	6.56
160.00	0.41
161.01	4.88
162.02	0.33
163.01	2.94
164.04	0.37
165.02	0.66
167.01	9.59
168.02	0.67
169.00	6.57
170.01	0.31
173.01	2.31
175.02	2.33
176.02	0.35
177.02	14.87
178.00	6.40
179.01	1.81
180.02	0.44
181.02	23.68
182.03	2.34
183.02	0.59
185.01	1.58
187.02	0.44
189.02	0.63
191.00	2.99
193.02	6.32
194.03	0.40
195.01	0.59
197.02	0.63
203.02	0.33
205.02	2.19
207.01	0.95
209.01	1.46
211.04	0.41
213.00	0.51
215.01	0.48
223.04	1.61
224.99	5.48
231.01	0.32
232.99	0.44
234.99	2.70
236.99	0.80
250.01	1.32
251.02	13.72
252.03	5.42
253.03	0.62
255.03	0.59
259.04	0.32
261.02	0.79
263.01	1.38
278.97	91.96
279.98	8.38
280.98	0.81
282.97	0.40
290.96	0.37
294.04	0.56
301.02	0.82
303.05	0.32
311.01	1.58
313.00	1.19
329.05	0.54
330.03	0.82
331.03	1.51
333.03	0.33
347.96	18.52 F
348.99	100.00 F
349.99	10.13
351.01	1.19
359.00	0.61
379.01	8.94
380.03	1.03
381.02	1.11
382.02	0.80
399.01	1.04
401.02	0.85
418.02	31.02
419.02	3.70
420.04	0.52

9. Perfluoro(polypropyl-18-crown-6) (**105**)

CI- Mass Spectrum

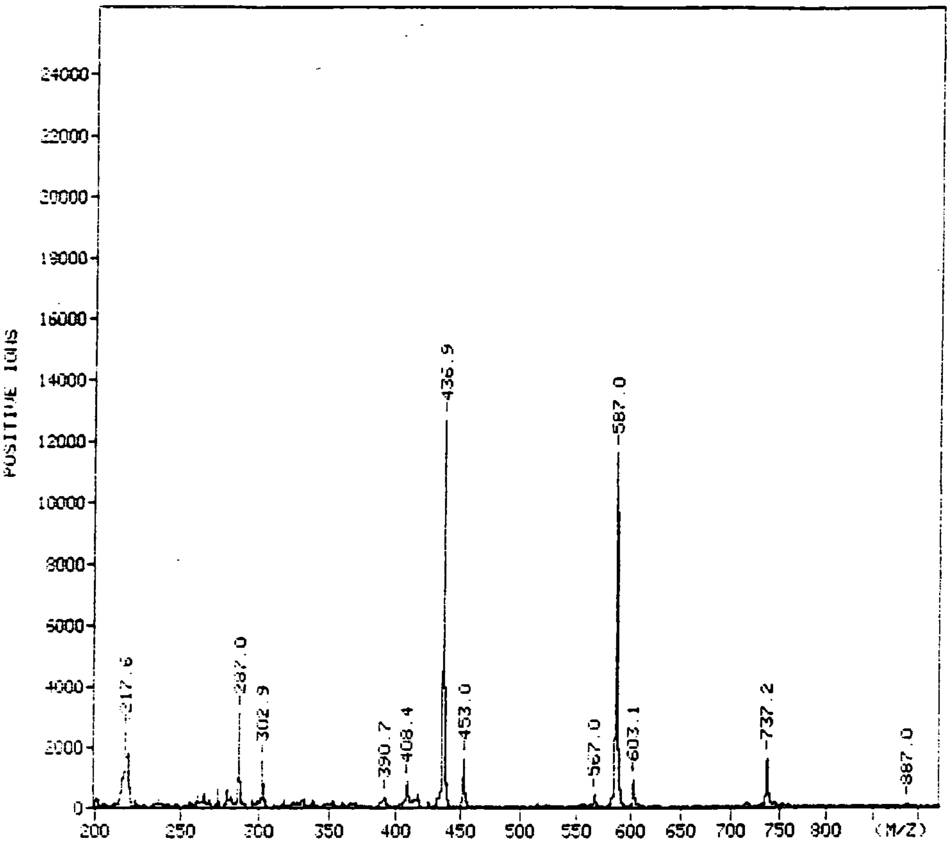
```
RKJ353814+      x1    Bgd=11    1-MAY-91  14:19+0:01:24  70E        CI-                        HMR:     65534000
BpM=0     I=10v    Hm=1731  TIC=557273984               Acnt:         Sys:HIGHACE              MASS:         497
A.JOEL                                                     PT= 0⁰     Cal:PFKMAY1
```



Mass	% Base
112.87	1.74
128.78	0.71
127.85	0.31
134.78	4.84
146.71	0.66
158.83	0.62
161.83	0.34
162.81	0.74
165.82	0.45
168.82	2.13
177.82	0.83
184.80	9.80
188.81	0.38
196.79	3.17
199.79	0.88
200.78	2.54
206.79	0.89
208.78	1.89
211.79	0.52
212.78	0.57
215.78	10.43
216.79	0.50
218.79	1.08
227.78	1.46
228.78	0.59
230.79	0.92
234.75	81.92 F
235.77	3.61 F
242.78	0.46
244.77	0.72
246.77	2.72
249.76	1.10
250.76	1.07
256.77	0.33
258.76	0.59
261.76	3.12
262.75	4.96
265.75	8.66
266.76	0.81
268.76	3.66
274.75	0.32
277.75	1.21
280.73	14.00 F
281.75	1.00 F
284.72	64.09 F
285.76	3.35 F
286.76	0.31
289.74	0.42
292.75	0.64
296.74	1.66
299.73	3.59
300.73	0.70
308.72	8.48
309.74	0.69
311.73	1.33
312.71	1.76
315.73	1.15
316.72	0.44
318.73	3.37
324.73	0.41
327.72	0.98
330.73	2.08
334.72	7.13
339.73	0.55
342.73	0.64
346.68	9.92 F
347.71	0.89 F
349.69	2.85 F
350.68	15.58 F
351.69	1.10 F
358.69	1.77
361.68	1.30 F
362.68	5.43 F
363.68	0.49
365.69	2.69
366.69	0.57
368.69	6.93
369.69	0.59
373.31	0.45 F
374.66	0.97 F
377.67	1.53 F
378.68	2.19 F
380.70	2.27
381.68	1.37
384.67	9.78
385.69	0.79
392.67	0.90
396.65	10.64 F
397.67	0.98 F
399.65	2.57 F
400.65	6.61 F
401.67	0.58 F
408.67	1.34
411.64	1.93 F
412.64	7.62 F
413.67	0.73 F
415.63	12.45 F
416.66	1.56 F
418.61	3.59
419.66	0.32
423.66	0.30
427.62	1.01
428.65	0.58
430.67	2.45
431.67	0.35
434.62	6.24 F
435.64	0.63 F
442.67	0.36
446.63	3.72 F
447.66	0.48 F
448.61	4.92 F
450.65	2.01 F
458.65	1.39
461.65	1.00
462.62	1.33
466.63	2.22
468.64	1.56
474.64	0.52
477.61	1.83
478.64	0.85
480.64	0.72
484.62	1.98
493.56	0.70 F
496.60	100.00 FO
497.61	12.59 F
498.62	1.18 F
499.60	2.52 F
500.60	11.38 F
501.75	1.16 F
508.63	0.74
511.48	0.78 F
512.59	23.13 F
513.59	2.52 F
515.50	3.94 F
516.62	1.60 F
518.60	0.93
524.45	1.66
527.57	5.51 F
528.72	2.82 F
530.60	0.59 F
531.61	2.21 F
532.61	0.46
534.61	1.20
539.63	0.32
542.62	0.30
546.55	3.67 F
547.59	0.60 F
549.52	2.77 F
550.58	15.68 F
551.70	1.82 F
558.59	1.15
561.54	1.79 F
562.60	1.12 F
565.60	0.37
566.59	0.60
568.59	0.52
574.61	0.41
577.59	2.58 F
578.62	0.83 F
582.63	0.33
584.63	0.50
589.61	0.44
596.51	11.11 F
597.56	1.60 F
599.50	4.05 F
600.70	1.71 F
608.59	1.66
609.60	0.31
612.80	1.21
615.58	0.71 F
616.57	3.74 F
617.60	0.48 F
618.58	0.38
624.56	0.54 F
627.49	16.05 F
628.66	3.10 F
644.60	0.74
646.50	2.64 F
647.56	2.11 F
648.53	0.42 F
649.87	0.87 F
650.61	1.31 F
662.52	1.08
665.58	1.24 F
666.58	3.15 F
667.60	0.39 F
674.56	1.27
677.56	2.86 F
678.74	1.00 F
696.51	1.49 F
697.60	0.45 F
700.54	1.44
705.55	0.31
706.14	0.50
706.59	1.28 F
706.78	0.79 F
707.97	0.41
708.42	1.55 F
708.58	0.66 F
709.03	0.43 F
709.21	0.87 F
710.28	0.55
711.30	0.81
711.72	0.30
711.87	0.42
713.05	0.49
713.60	0.56 F
713.77	1.03 F
714.04	1.42 F
714.23	2.33 F
715.36	0.56 F
715.79	16.96 F
715.96	3.58 F
716.36	0.58 F
716.57	0.75 F
724.18	0.86 F
725.28	0.62 F
726.94	0.58 F
728.08	1.87 F
735.45	0.82
742.09	0.31
744.38	0.91 F
745.37	3.10 F
746.47	0.53 F
752.71	2.58 F
755.19	0.58 F
759.57	0.56
770.59	1.12
791.57	0.40
805.52	0.69 F
806.64	1.18 F
817.16	0.32
831.54	0.61 F
832.69	0.43 F
835.24	2.13 F
837.42	0.43 F
848.74	0.31
853.08	1.32
874.75	0.54
882.02	0.30
884.90	0.40
892.61	0.73
910.18	1.31 F
911.40	0.48 F
914.70	0.42
943.93	0.56 F
946.76	0.74 F
975.88	1.70 F
977.81	0.43 F
994.59	1.16
1005.99	0.14
1009.41	0.12
1016.47	0.12
1020.94	0.15
1022.20	0.09
1024.11	0.19
1025.17	0.10
1036.59	0.07
1042.48	0.18
1043.39	0.06
1051.14	0.06
1054.38	0.15
1056.04	0.06
1057.88	0.40
1069.35	0.12
1070.34	0.06
1072.66	0.08
1087.66	1.11
1091.61	0.07
1103.21	0.10
1106.29	0.35
1117.78	0.13
1120.81	0.14
1121.89	0.09
1133.56	0.07
1136.66	0.12
1139.47	0.19
1140.50	0.07
1155.19	0.09
1162.37	0.16
1164.07	0.07
1167.19	0.09
1170.76	0.10
1183.17	0.09
1203.04	0.69
1217.37	0.08
1218.35	0.10
1220.63	0.09
1233.58	0.16
1236.76	0.89
1239.48	0.07
1252.73	0.17
1255.81	0.21
1257.27	0.06
1268.21	0.07
1284.26	0.07
1287.72	0.14
1306.98	0.07
1316.63	0.09
1324.01	0.08
1356.67	1.58
1373.25	0.08
1392.48	0.13
1409.66	0.21
1422.33	0.07
1446.30	0.10
1463.53	0.08
1494.55	0.08
1519.20	1.15
1550.54	0.09
1575.51	0.12
1576.98	0.07
1695.75	0.17
1731.59	0.11

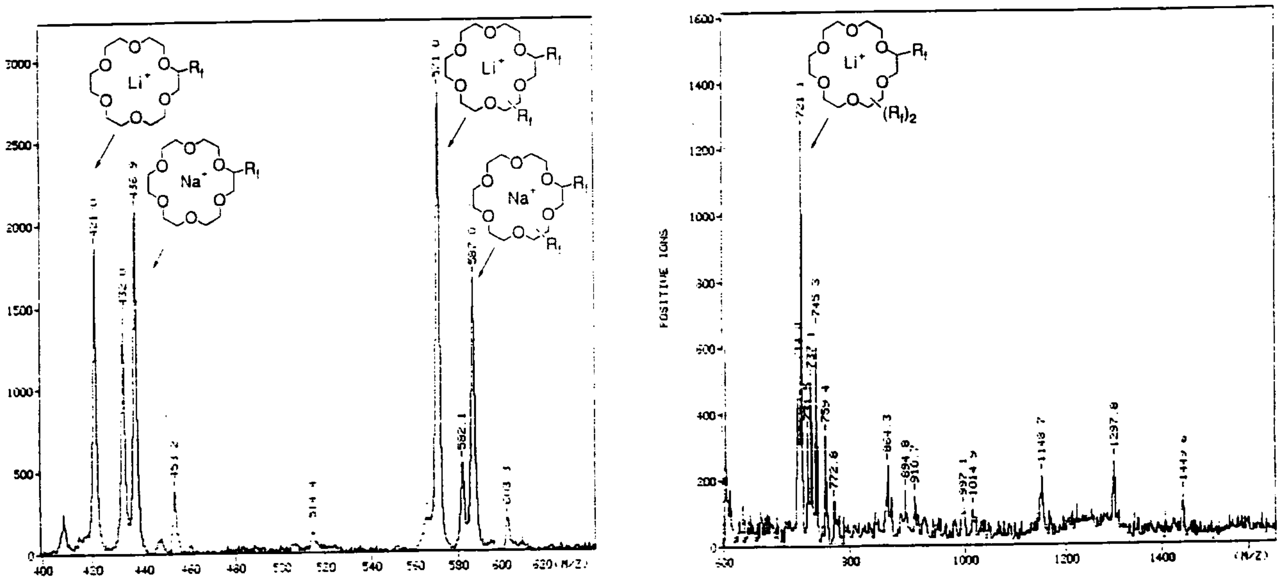
10. Poly(2*H*-hexafluoropropyl)-18-crown-6 (**65**)

Plasma Desorption Mass Spectrum

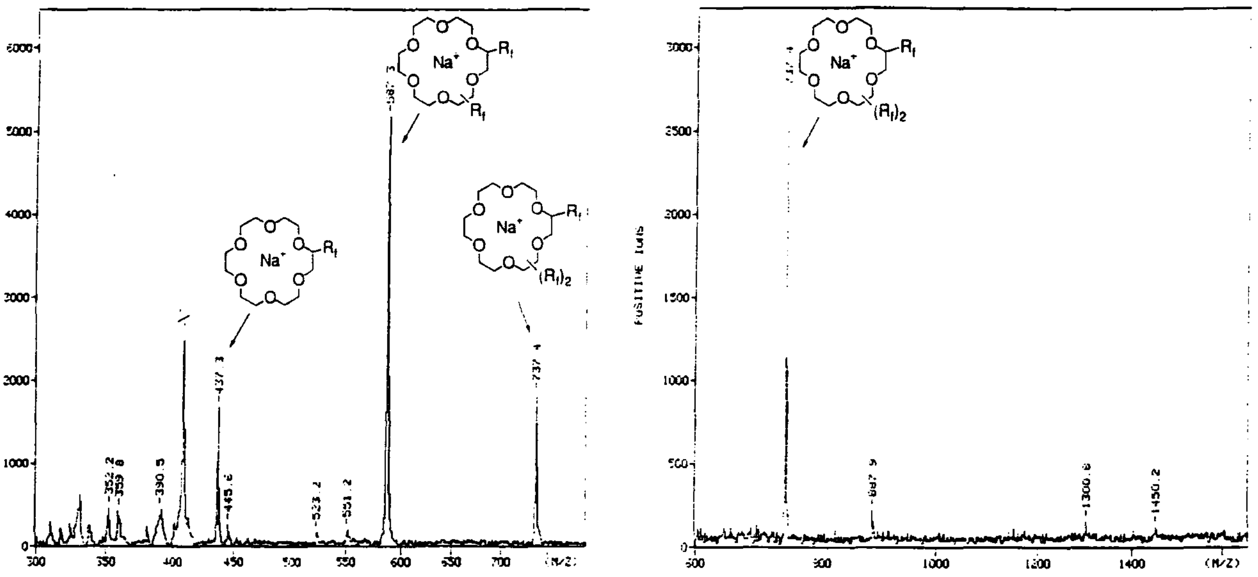


11. Poly(2*H*-hexafluoropropyl)-18-crown-6 washed with lithium chloride

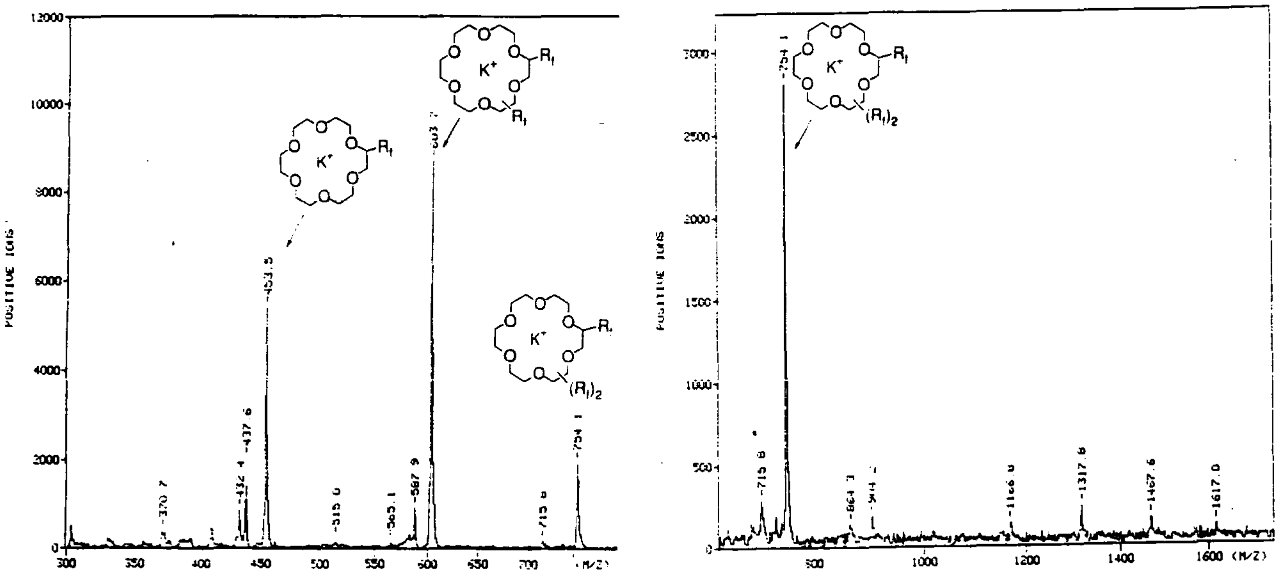
Plasma Desorption Mass Spectrum



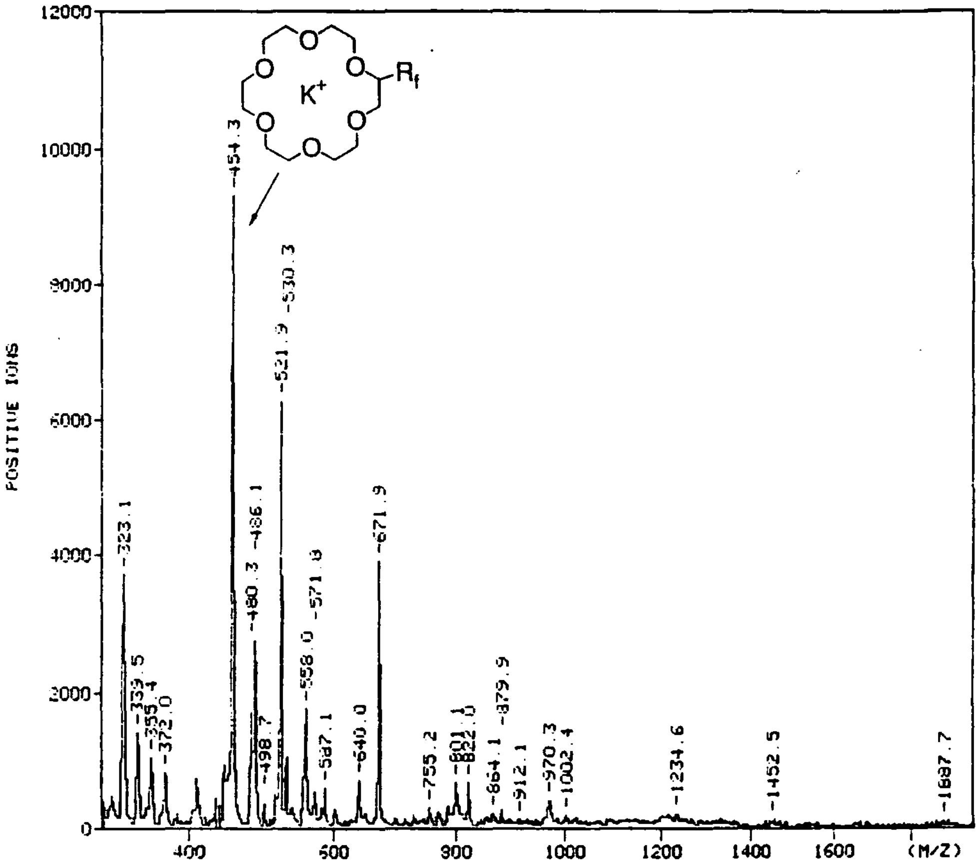
12. Poly(2*H*-hexafluoropropyl)-18-crown-6 washed with sodium acetate Plasma Desorption Mass Spectrum



13. Poly(2*H*-hexafluoropropyl)-18-crown-6 washed with potassium acetate Plasma Desorption Mass Spectrum

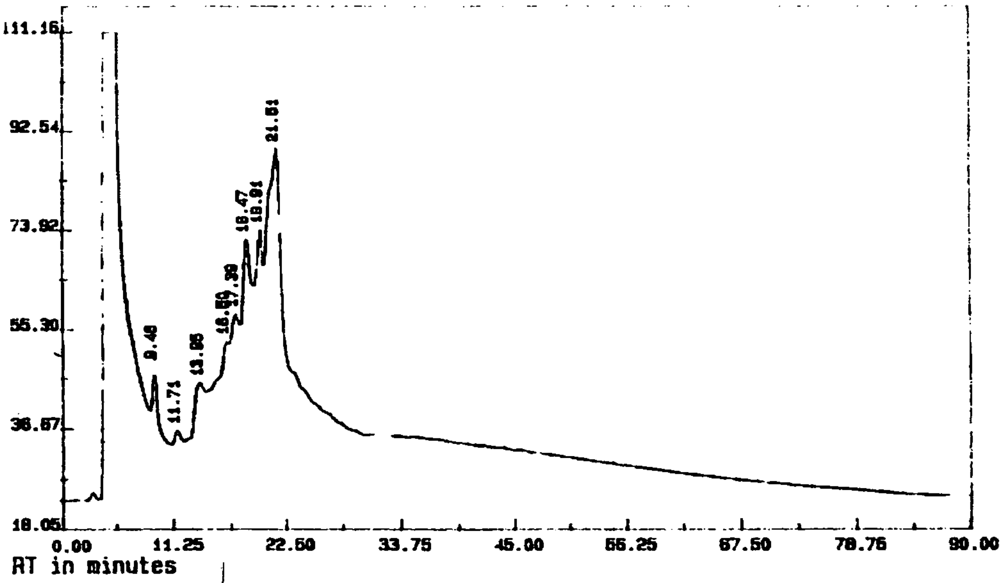


14. Poly(2*H*-hexafluoropropyl)-18-crown-6 washed with 1:1:1 lithium chloride, sodium acetate and potassium acetate



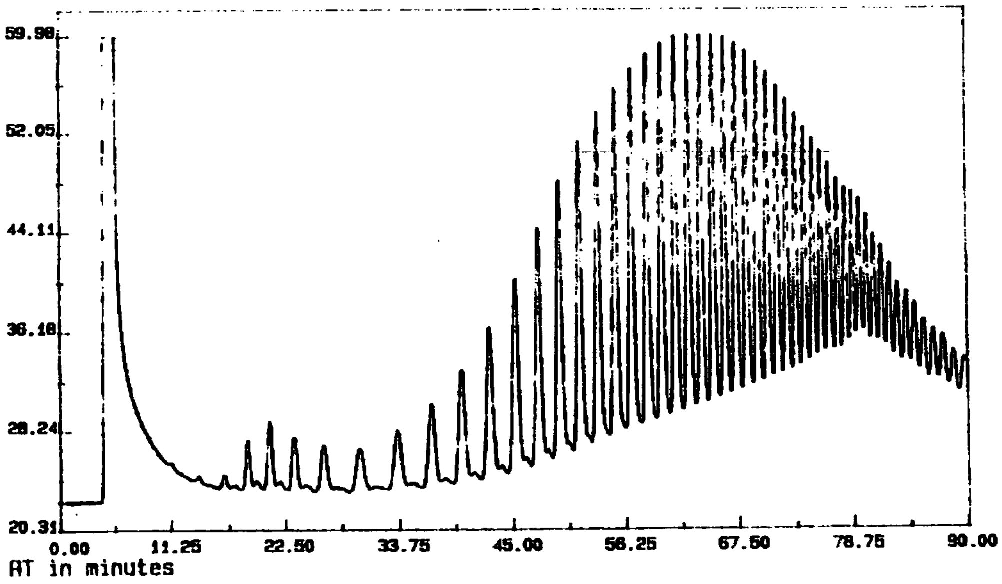
Appendix Five
Supercritical Fluid Chromatagrams

1. Perfluoro[polypropyl-α-ethyl-ω-ethoxy poly(ethylene oxide) 600] (**103**)



SAMPLE: MLO 91-104 INJECTED AT 11:22:32 ON MAR 13, 1992
Meth: KRY Raw: DB104A Proc: PP

2. Krytox AC



SAMPLE: MLO 71-6 INJECTED AT 13:40:01 ON FEB 3, 1992
Meth: KRY Raw: D716AQ Proc: *PRC01

Appendix Six

Colloquia, Conferences and Induction Courses

The Board of Studies in Chemistry requires that each postgraduate thesis contains an appendix listing;

a) all research colloquia, seminars and lectures arranged by the Department of Chemistry during the period of the author's residence as a postgraduate student.

b) all research conferences attended and papers presented by the author during the period in which the research for the thesis was carried out.

c) details of the postgraduate induction courses.

*a) Research Colloquia, Seminars and Lectures (those attended are marked *)*

6.10.88	Prof. R. Schmutzler (Technische Univerität, Braunschweig), *'Fluorophosphines Revisited - New Contributions to an Old Theme.'*
18.10.88	Dr. J. Dingwall (Ciba Geigy), *'Phosphorus-containing Amino Acids: Biologically Active Natural and Unnatural Products.'*
18.10.88	Dr. C.J. Ludman (Durham University), *'The Energetics of Explosives.'**
21.10.88	Prof. P. von Rague Schleyer (Universität Erlangen, Nurnberg), *'The Fruitful Interplay Between Calculational and Experimental Chemistry.'*
27.10.88	Prof. W.C. Rees (Imperial College, London), *'Some very Heterocyclic Compounds.'**
9.11.88	Dr. G. Singh (Teesside Polytechnic), *'Towards Third Generation Anti-Leukaemics.'*
10.11.88	Prof. J.I.G. Cadogan (British Petroleum), *'From Pure Science to Profit.'*
16.11.88	Dr. K.A. McLauchlan (Oxford University), *'The Effect of Magnetic Fields on Chemical Reactions.'*
24.11.88	Dr. R.R. Baldwin and Dr. R.W. Walker (Hull University), *'Combustion - Some Burning Problems.'*
1.12.88	Dr. R. Snaith (Cambridge University), *'Egyptian Mummies: What, Where, Why and How.'*
2.12.88	Dr. G. Hardgrove (St. Olaf College, USA), *'Polymers in the Physical Chemistry Laboratory.'*
9.12.88	Dr. C.D. Jaeger (Friedrich-Schiller University, GDR), *'NMR Investigations of Fast Ion Conductors of the NASICON Type.'*

25.1.89	Dr. L. Harwood (Oxford University), *'Synthetic Approaches to Phorbols* via *Intramolecular Furan Diels-Alder Reactions: Chemistry under Pressure.'*
26.1.89	Prof. K.R. Jennings (Warwick University), *'Chemistry of the Masses.'*
2.2.89	Prof. L.D. Hall (Addenbrooke's Hospital, Cambridge), *'N.M.R. - A Window to the Human Body.'**
9.2.89	Prof. J.E. Baldwin (Oxford University), *'Recent Advances in the Bioorganic Chemistry of Penicillin Biosynthesis.'*
13.2.89	Prof. R.R. Schrock (Massachusetts Institute of Technology), *'Recent Advances in Living Metathesis.'*
15.2.89	Dr. A.R. Butler (St. Andrews University), *'Cancer in Linxiam: The Chemical Dimension.'*
16.2.89	Prof. J.B. Aylett (Queen Mary College, London), *'Silicon-Based Chips:- The Chemist's Contribution.'*
22.2.89	Dr. G. MacDougall (Edinburgh University), *'Vibrational Spectroscopy of Model Catalytic Systems.'*
23.2.89	Dr. B.F.G. Johnson (Cambridge University), *'The Binary Carbonyls.'*
1.3.89	Dr. R.J. Errington (Newcastle University), *'Polymetalate Assembly in Organic Solvents.'*
9.3.89	Dr. I. Marko (Sheffield University), *'Catalytic Asymmetric Osmylation of Olefins.'*
15.3.89	Dr. R. Aveyard (Hull University), *'Surfactants at your Surface.'*
20.4.89	Dr. M. Casey (Salford University), *'Sulphoxides in Stereoselective Synthesis.'*
27.4.89	Dr. D. Crich (University College, London), *'Some Novel Uses of Free Radicals in Organic Synthesis.'**
3.5.89	Dr. P.C.B. Page (Liverpool University), *'Stereocontrol of Organic Reactions Using 1,3-dithiane-1-oxides.'*
10.5.89	Prof. P.B. Wells (Hull University), *'Catalyst Characterisation and Activity.'*
11.5.89	Dr. J. Frey (Southampton University), *'Spectroscopy of the Reaction Path: Photodissociation Raman Spectra of NOCl.'*
16.5.89	Dr. R. Stibr (Czechoslovak Academy ofSciences), *'Recent Developments in the Chemistry of Intermediate-Sited Carboranes.'*

17.5.89	Dr. C.J. Moody (Imperial College, London), *'Reactive Intermediates in Heterocyclic Synthesis.'**
23.5.89	Prof. P. Paetzold (Aachen), *'Iminoboranes XB≡NR: Inorganic Acetylenes?'*
15.6.89	Prof. J. Pola (Czechoslovak Academy of Sciences), *'Carbon Dioxide Laser Induced Chemical Reactions - New Pathways in Gas-Phase Chemistry.'*
17.10.89	Dr. F. Palmer (Nottingham University). *'Thunder and Lightning.'*
25.10.89	Prof. C. Floriani (Lausanne University, Switzerland), *'Molecular Aggregates - A Bridge between Homogeneous and Heterogeneous Systems.'*
1.11.89	Dr. J.P.S. Badyal (Durham University), *'Breakthroughs in Heterogeneous Catalysis.'*
9.11.89	Prof. N.N. Greenwood (Leeds University), *'Novel Cluster Geometries in Metalloborane Chemistry.'*
10.11.89	Prof. J.E. Bercaw (California Institute of Technology), *'Synthetic and Mechanistic Approaches to Ziegler-Natta Poymerisation Of Olefins.'*
13.11.89	Dr. J. Becher (Odense University, Denmark), *'Synthesis of New Macrocyclic Systems using Heterocyclic Building Blocks.'*
16.11.89	Dr. D. Parker (Durham University), *'Macrocycles, Drugs and Rock 'n' Roll.'**
29.11.89	Prof. D. J. Cole-Hamilton (St. Andrews University), *'New Polymers from Homogeneous Catalysis.'*
30.11.89	Dr. M.N. Hughes (King's College, London), *'A Bug's Eye View of the Periodic Table.'**
4.12.89	Dr. D. Graham (British Petroleum), *'How Proteins Absorb to Interfaces.'*
6.12.89	Dr. R.L. Powell (ICI, Chemicals and Polymers), *'The Development of C.F.C. Replacements.'**
7.12.89	Dr. A. Butler (St. Andrews University), *'The Discovery of Penicillin: Facts and Fancies.'**
13.12.89	Dr. J. Klinowski (Cambridge University), *'Solid State NMR Studies of Zeolite Catalysts.'*
15.12.89	Prof. R. Huisgen (Universität München), *'Recent Mechanistic Studies of [2+2] Additions.'**
24.1.90	Dr. R.N. Perutz (York University), *'Plotting the Course of C-H Activations with Organometallics.'*

31.1.90	Dr. U. Dyer (Glaxo), *'Synthesis and Conformation of C-Glycosides.'*
1.2.90	Prof. J.H. Holloway (Leicester University), *'Noble Gas Chemistry.'**
7.2.90	Dr. D.P. Thompson (Newcastle University), *'The Role of Nitrogen in Extending Silicate Crystal Chemistry.'*
8.2.90	Rev. R. Lancaster (Kimbolton Fireworks), *'Fireworks - Principles and Practice.'*
12.2.90	Prof. L. Lunazzi (University of Bologna, Italy), *'Application of Dynamic NMR to the Study of Conformational Enantiomerism.'*
14.2.90	Prof. D. Sutton (Simon Fraser University, Vancouver BC), *'Synthesis and Applications of Dinitrogen and Diazo Compounds of Rhenium and Iridium.'*
15.2.90	Prof. L. Crombie (Nottingham University), *'The Chemistry of Cannabis and Khat .'*
21.2.90	Dr. C. Bleasdale (Newcastle University), *'The Mode of Action of some Anti-tumour Agents.'*
22.2.90	Prof. D.T. Clark (ICI Wilton), *'Spatially Resolved Chemistry (using Nature's Paradigm in the Advanced Materials Area).'**
28.2.90	Dr. R.K. Thomas (Oxford University), *'Neutron Reflectometry from Surfaces.'*
1.3.90	Dr. J.F. Stoddart (Sheffield University), *'Molecular Lego.'**
8.3.90	Dr. A.K. Cheetham (Oxford University), *'Chemistry of Zeolite Cages.'*
21.3.90	Dr. I. Powis (Nottingham University), *'Spinning off in a huff: Photodissociation of Methyl Iodide.'*
23.3.90	Prof. J.M. Bowman (Emory University), *'Fitting Experiment with Theory In Ar-OH.'*
29.5.90	Prof. N. Bartlett (University of California, Berkeley), *'Silver trifluoride.'**
9.7.90	Prof. L.S. German (USSR Academy of Sciences, Moscow), *'New Syntheses in Fluoroaliphatic Chemistry. Recent Advances in the Chemistry of Fluorinated Oxiranes.'**
9.7.90	Prof. V.E. Platonov (USSR Academy of Sciences, Novosibirsk), *'Polyfluoroindanes. Synthesis and Transformation.'**
9.7.90	Prof. I.N. Rozhkov (USSR Academy of Sciences, Moscow), *'Reactivity of Perfluoroalkyl Bromides.'**

20.7.90 Prof. G.K.S. Prakash (Loker Hydrocarbon Institute, USA),
_'Novel Synthetic Methods.'_*

11.10.90 Dr. W.A. Macdonald (ICI Wilton),
_'Materials for the Space Age.'_*

24.10.90 Dr. M. Bochmann (University of East Anglia),
_'Synthesis, Reactions and Catalytic Activity of Cationic Titanium Alkyls.'_*

26.10.90 Prof. R. Soulen (South Western University, Texas),
_'Preparation and Reactions of Bicycloalkenes.'_*

31.10.90 Dr. R. Jackson (Newcastle University),
_'New Synthetic Methods: α-Amino Acids and Small Rings.'_*

1.11.90 Dr. N. Logan (Nottingham University),
'Rocket Propellants.'

6.11.90 Dr. P. Kocovsky (Uppsala, Denmark),
_'Stereo-controlled Reactions Mediated by Transition and Non-Transition Metals.'_*

7.11.90 Prof. W.R. Dolbier (University of Florida),
_'Thermal Rearrangements of Bis(trifluorovinyl) Aromatics as a New Route to 1,3,5-Hexatrienes.'_*

7.11.90 Dr. D. Gerrard (British Petroleum),
'Raman Spectroscopy for Industrial Analysis.'

8.11.90 Dr. S.K. Scott (Leeds University),
'Clocks, Oscillations and Chaos.'

14.11.90 Prof. T. Bell (SUNY, Stoney Brook, USA),
_'Functional Molecular Achitecture and Molecular Recognition.'_*

21.11.90 Prof. J. Pritchard (Queen Mary & Westfield College, London),
'Copper Surfaces and Catalysts.'

28.11.90 Dr. B.J. Whitaker (Leeds University),
'Two-Dimentional Velocity Imaging of State-Selected Reaction Products.'

29.11.90 Prof. D. Crout (Warwick University),
_'Enzymes in Organic Synthesis.'_*

5.12.90 Dr. P.G. Pringle (Bristol University),
_'Metal Complexes with Functionised Phosphines.'_*

13.12.90 Prof. A.H. Cowley (University of Texas),
'New Organometallic Routes to Electronic Materials.'

15.1.91 Dr. B.J. Alder (Lawrence Livermore Laboratories, California),
'Hydrogen in all its Glory.'

17.1.91 Dr. P. Sarre (Nottingham University),
'Comet Chemistry.'

24.1.91 Dr. P. J. Sadler (Birkbeck College, London),

	'Design of Inorganic Drugs: Precious Metals, Hypertension + HIV.'
30.1.91	Prof. E. Sinn (Hull University), *'New Results in High T_c Superconductivity.'*
31.1.91	Dr. D. Lacey (Hull University), *'Liquid Crystals.'**
6.2.91	Dr. R. Bushby (Leeds University), *'Biradicals and Organic Magnets.'**
14.2.91	Dr. M.C. Petty (Durham University), *'Molecular Electronics.'**
20.2.91	Prof. B.L. Shaw (Leeds University), *'Syntheses with Coordinated, Unsaturated Phosphine Ligands.'**
28.2.91	Dr. J. Brown (Oxford University), *'Can Chemistry Provide Catalysts Superior to Enzymes?'*
6.3.91	Dr. C.M. Dobson (Oxford University), *'NMR Studies of Dynamics in Molecular Crystals.'*
7.2.91	Dr. J. Markam (ICI Pharmaceuticals), *'DNA Fingerprinting.'*
24.4.91	Prof. R.R. Schrock (Massachusetts Institute of Technology), *'Metal-Ligand Multiple Bonds and Metathesis Initiators.'*
25.4.91	Prof. T. Hudlicky (Virginia Polytechnic Institute), *'Biocatalysis and Symmetry Based Approaches to the Efficient Synthesis of Complex Natural Products.'*
20.6.91	Prof. M.S. Brookhart (University of North Carolina), *'Olefin Polymerizations, Oligomerizations and Dimerizations using Electrophilic Late Transition Metal Catalysts.'*
29.7.91	Dr. M.A. Brimble (Massey University, New Zealand), *'Synthetic Studies Towards the Antibiotic Griseusin-A.'**
12.9.91	Prof. D.J. Burton (University of Iowa, USA), *'Fluorinated Organometallic Reagents.'**
12.9.91	Prof. J.L. Adcock (University of Tennessee, USA), *'Aerosol Direct Fluorination.'**
17.10.91	Dr. J.A. Salthouse (Manchester University), *'Son et Lumiere - a Demonstration Lecture.'*
03.10.91	Dr. R. Keeley (Metropolitan Police Forensic Science), *'Modern Forensic Science.'*
06.11.91	Dr. B.F.G. Johnson (Edinburgh University), *'Cluster-Surface Analogies.'*
07.11.91	Dr. A.R. Butler (St. Andrews University), *'Traditional Chinese Herbal Drugs: a Different Way of Treating Disease.'*
8.11.91	Prof. H. F. Koch (Ithaca College, USA),

*'Relative Leaving Abilities of fluoride Ion Versus Proton Transfer, in the Neutralisation of Carbanions, Generated in Alcohols.'**

13.11.91 Prof. D. Gani (St. Andrews University),
*'The Chemistry of PLP-Dependant Enzymes.'**

20.11.91 Dr. R. More O'Ferrall (University College, Dublin),
*'Some Acid-Catalysed Rearrangements in Organic Chemistry.'**

28.11.91 Prof. I.M. Ward (Leeds University),
*'The Science & Technology of Orientated Polymers.'**

04.12.91 Prof. R. Grigg (Leeds University),
'Palladium Catalysed Cyclisation and Ion Capture Processes.'

05.12.91 Prof. A.L. Smith (ex-Unilever),
'Soap, Detergents and Black Puddings.'

11.12.91 Dr. W.D. Cooper (Shell Research),
'Colloid Science, Theory, and Practice.'

09.01.92 Mr. C.E. Snyder (U.S. Air Force, Ohio),
'Perfluoropolyethers.'

16.01.92 Dr. N.J. Long (Exeter University),
'Metallocenophanes-Chemical Sugar-tongs.'

22.01.92 Dr. K.D.M. Harris (St Andrews University),
'Understanding the Properties of Solid Inclusion Compounds.'

29.01.92 Dr. A. Holmes (Cambridge University),
*'Cycloaddition Reactions in the Service of the Synthesis of Piperidine and Indolizidine Natural Products.'**

30.01.92 Dr. M. Anderson (Shell Research, Sittingbourne),
'Recent Advances in the Safe and Selective Chemical Control of Insect Pests.'

12.02.92 Dr. D.E. Fenton (Sheffield University),
'Polynuclear Complexes of Molecular Clefts as Models for Copper Biosites.'

13.02.92 Dr. J. Saunders (Glaxo Group Research Limited),
*'Molecular Modelling in Drug Discovery.'**

19.02.92 Prof. E.J. Thomas (Manchester University),
*'Application of Organo-Stannanes to Organic Synthesis.'**

20.02.92 Prof. E. Vogel (University of Cologne),
'Porphyrins: Molecules of Interdisciplinary Interest.'

25.02.92 Prof. J.F. Nixon (University of Sussex),
'Phosphaalkynes, New Building Blocks in Inorganic and Organometallic Chemistry.'

26.02.92 Prof. M.L. Hitchman (Strathclyde University),
'Chemical Vapour Deposition.'

05.03.92	Dr. N.C. Billingham (University of Sussex), *'Degradable Plastics - Myth or Magic?'*
10.03.92	Dr. H.C. Fielding (ICI, Chemicals & Polymers), *'Fluoropolymer Membranes'**
11.03.92	Dr. S.E. Thomas (Imperial College, London), *'Recent Advances in Organoiron Chemistry.'*
12.03.92	Dr. R.A. Hann (ICI Imagedata), *'Electronic Photography - An Image of the Future.'*
18.03.92	Dr. H. Maskill (Newcastle University), *'Mechanistic Studies of Organic Group Transfer Reactions.'**
07.04.92	Prof. D.M. Knight (Durham University), *'Interpreting Experiments: The Beginning of Electrochemistry.'*
30.04.92	Dr. A. Marhold (Bayer Co., Leverkusen), *'Fluorine Chemistry in the Bayer Company.'**
13.05.92	Dr. J-C. Gehert (Ciba Geigy, Basel), *'Some Aspects of Industrial Agrochemical Research.'**

b) Research Conferences attended

December 1988.
Royal Society of Chemistry Perkin Division,
One Day Meeting.
York University.

April 1989.
North-East Graduate Symposium.
Durham University.

December 1989.
Royal Society of Chemistry Perkin Division,
One Day Meeting.
Durham University.

March 1990.
SCI Fine Chemicals Group,
Graduate Symposium,
University of York

April 1990.
Polymer NMR Training Day.
Durham University.

April 1990.
North East Graduate Symposium.
Newcastle University.

September 1991.
XIIIth International Symposium on Fluorine Chemistry.
Ruhr Universität, Bochum,
Germany.

September 1992
Xth European Symposium on Fluorine Chemistry.
University of Padua CIS,
Italy.

c) Postgraduate Induction Course

This course consists of a series of one hour lectures on the services availlable in the department.

Department organisation - Dr. E. J. F. Ross.
Safety matters - Dr. M. R. Crampton.
Electrical appliances - Mr. B. T. Barker
Chromatography and microanalysis - Mr. T. F. Holmes.
Atomic absorptiometry and inorganic analysis - Mr. R. Coult.
Library facilities - Mrs. M. Hird.
Mass spectrometry - Dr. M. Jones.
NMR spectroscopy - Dr. R. S. Matthews.
Glassblowing techniques - Mr. R. Hart and Mr. G. Haswell.

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31. Krytox Grease technical handout, *Krytox, Fluorinated Greases,* E.I Du Pont de Nemours & Co. (inc.).

32. USP 3 650 928.

33. USP 4 451 646.

34. Galden technical handout, *Galden Electronic Fluids,* Montefluos.

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