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Use of telechelic fluorinated diiodides to obtain well-defined fluoropolymers

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Abstract

Different methods of synthesis involved in the preparation of fluorinated telechelics (or α,ω-difunctional compounds) from α,ω-diiodoperfluoroalkanes for obtaining well-defined fluoropolymers are described. This review focuses on molecules in which fluorinated chains are located on the backbone and not in a lateral position. First, a bibliographical approach develops the syntheses of α,ω-diiodoperfluoroalkanes (**1**) either by chemical transformations of telechelic derivatives or by telomerisation of fluoroolefins with molecular iodine or diiodoperfluoroalkanes. Then, fluorotelechelics are synthesised by means of four different processes: (a) by the chemical change in the presence of metalic salts; (b) from the bismonoaddition of **1** to ω-functional unsaturated derivatives; (c) from the bis(monoethylenation) of **1** followed by difunctionalisation (e.g., nucleophilic substitution); (d) from the coupling reactions between **1** and α-iodo-ω-functional reactants. Finally, this review describes how several well-defined fluoropolymers can be produced from these fluorinated telechelics. Their specific chemical, physical and thermal properties are discussed with regard to modern industrial requirements. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: α,ω-Diiodides; Telechelics; Fluorinated functional compounds; Radical; Fluoropolymers

1. Introduction

Fluorinated polymers exhibit a unique combination of high thermal stability, chemical inertness (to acids, bases, solvents and petroleum), low dielectric constants and dissipation factors, low water absorptivities, excellent weatherability and a good resistance to oxidation and ageing, low flammabilities and very interesting surface properties [1–3].

Therefore, such products are involved in many applications (aerospace, aeronautics, engineering, optics, textile finishing, microelectronics) in spite of their high price but are undergoing an increasing market.

Well-architectured polymers can be prepared either from controlled radical polymerisation [4,5] or from polycondensation or polyaddition. In these two last processes, telechelic or α,ω-difunctional (i.e., the functional groups are located at both extremities of the chain) precursors are required to obtain high molecular weight materials with satisfactory properties [6]. In the case of fluorinated telechelics, the literature describing their synthesis is abundant and it was reviewed several years ago [7,8].

Two kinds of fluorinated telechelics exhibiting different properties are suggested and hence the polymers prepared from them can be involved in different applications. On the one hand, those possessing the fluorinated group in a lateral position about the polymeric backbone are searched for their enhanced surface properties but can not be used as thermostable materials resistant to oxidation and to chemicals. On the other hand, those containing the fluorinated chain in the backbone exhibit much better thermal properties and are also resistant to aggressive media, to UV radiations and to ageing.

Various strategies have been proposed to prepare this second family of fluorinated telechelics. In 1969, Rice and Sandberg [9] used the dead end copolymerization of vinylidene fluoride and hexafluoropropene in the presence of telechelic peresters. More recently, such a process was successfully achieved from hydrogen peroxide [10].

Nowadays, among fluorinated telechelics prepared on an industrial scale only three commercially available polyethers have already been obtained as follows:

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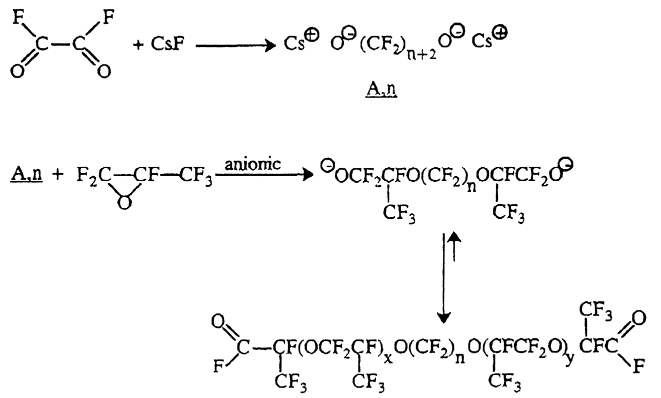
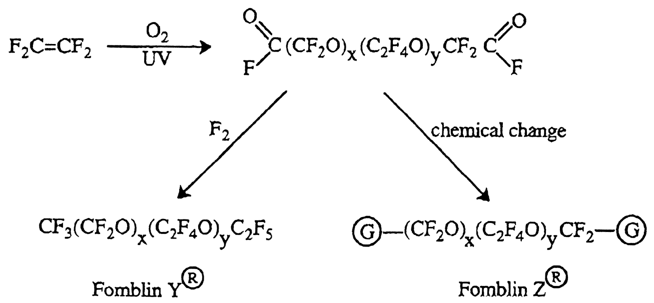
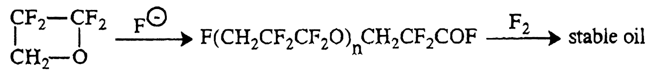
1. the anionic polymerisation of perfluoroepoxides (especially hexafluoropropylene oxide) led to Krytox® produced from Du Pont de Nemours Company [11,12] as follows;



2. the photooxidation of perfluoroolefins (e.g., tetrafluoroethylene [13], hexafluoropropene (HFP) [14] and perfluorobutadiene [15]) was performed by the Ausimont Company yielding functional or nonfunctional Fomblin® oligomers ranging from 1000 to 2000 in molecular weights [16] (where Ⓖ represents a function;



3. the Daikin Company commercialises Demnum® oligomers, which can be inert or functional, from the ring opening polymerisation of fluorinated oxetanes followed by a fluorination to obtain thermostable oils [17].



A part from fluorinated polyethers, original fluorotelechelic oligodiols as random copolymers containing vinylidene fluoride (VDF) and HFP base units, e.g. $HOCH_2CF_2(CH_2CF_2)_p[CF(CF_3)CF_2]_qCF_2CH_2OH$ have been synthesised by Chan et al. [18].

In addition, the synthesis of telechelic fluorinated diols from direct fluorination [19] of hydrogenated diols, produced in pilot plants, has successfully been achieved [20].

In spite of the lack of industrial fluorotelechelics (different from polyethers) about fluorinated nonfunctional homo and copolymers, the nowadays tendency shows that a growing interest is still required, as evidenced by numerous investigations [7,8]. It seems that many reactions involve α,ω-diiodoperfluoroalkanes as reactants, to prepare telechelic intermediates preserving the fluorinated chain in the backbone.

Hence, it was worth summarising the usefulness of these diiodides as precursors of well-defined fluoropolymers. The objective of that review is to reshuffle surveys in this field of research. It is composed of three parts, each of them being dependent of both others in the chain of the preparation of these special fluoropolymers. The first one describes the various routes leading to α,ω-diiodofluoroalkanes while the second one overviews the syntheses of fluorotelechelics from them. Then, how can one use these original telechelics to prepare well-defined polymers? This last part also details the properties and applications of these latters.

2. Synthesis of α,ω-diiodo(per)fluoroalkanes

Although perfluoroalkyl iodides are widely used as reactants for the synthesis of fluorinated derivatives [21,22], this is not the case for α,ω-diiodoperfluoroalkanes, because of the difficulty of synthesis, and their corresponding price.

However, a large variety of preparations of α,ω-diiodoperfluoroalkanes has been investigated and can be gathered in two different ways: from organic synthesis (mainly by chemical change of fluorotelechelics) and from telomerisation reactions of fluoroolefins with iodine or with α,ω-diiodoperfluoroalkanes.

2.1. From organic synthesis

The literature reports various methods of syntheses leading to different chain length-diiodides exhibiting specific groups or functions in the fluorinated chain (e.g., ether linkage or perfluorinated group).

2.1.1. Obtaining of ICF_2I

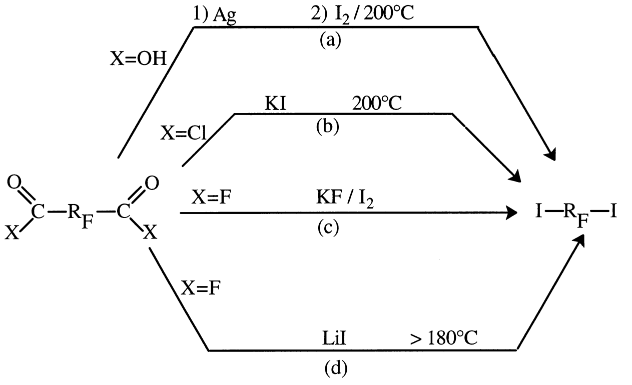
Difluorodiiodomethane is the shortest fluorinated diiodide, synthesised for the first time in 1963 by Mahler [23]. His low-yield procedure involved the addition of difluorocarbene to molecular iodine. Later, Mitsch [24] followed by Burton et al. [25] and then by Chen and Zhu [26] slightly improved the yield.

In 1984, Elsheimer et al. [27] reported the synthesis of such a reagent by fluorination of readily available tetraiodomethane [28,29] with mercury (II) fluoride as follows:

$$CI_4 + HgF_2 \rightarrow ICF_2I + HgI_2$$

Although the yield was still low (minimum of 27%), the authors mentioned that an attempt to carry out this transformation by using an initial $[KF]_0/[HgF]_0$ molar ratio of 9/1 led to unsatisfactory results [27].

But the preparation described by Su et al. [30] reasonably improved the yield of ICF_2I up to 60%. This Chinese team reacted chloro (or bromo) difluoromethylacetate with potassium iodide and molecular iodine in the presence of a catalytic amount of cuprous iodide with a quantitative conversion of the polyhalogeno acetate.



references : a [33,34] ; b [38a, 38b] ; c [39] ; d [40]

Scheme 1. Telechelic fluorinated diiodides from α,ω-dicarbonylated derivatives.

Interestingly, difluorodiiodomethane is a source of difluoroiodomethyl or, better, of difluorocarbene radicals [31] which however have not yet been able to initiate any polymerisations [32].

2.1.2. Iodination of carboxylic diacids or acid dihalides

2.1.2.1. Hunsdiecker reaction. This is one of the most used methods to prepare α,ω-diiodides from the pyrolytic reaction of silver salts of perfluorocarboxylic acids in the presence of iodine, in moderate yields [33] (Scheme 1). This rather old reaction has been often applied to monoadduct compounds and Rice [34] successfully used it from $O(C_2F_4CO_2H)_2$ diacid to prepare an original diiodide containing an ether linkage.

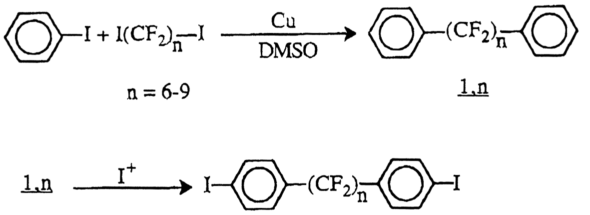
Although the synthesis of $HO_2C(CF_2CFCl)_nCF_2CO_2H$ was achieved in two steps [8,35] from the telomerisation of chlorotrifluoroethylene (CTFE) with carbon tetrachloride [8,36] or with bromotrichloromethane [8,37], no attempt to obtain $I(CF_2CFCl)_nCF_2I$ was performed so far.

2.1.2.2. Other methods. As above, fluorinated telechelic esters, acids, acid chlorides or acid fluorides are useful precursors of the corresponding diiodides (Scheme 1).

Obviously, an excess of iodinated reactant was required to achieve the synthesis of the telechelic compound, otherwise only one end-group is converted. For example, this is the case of the iodination involving lithium iodide [40]. The authors reported that an equimolar amount of LiI gave only the α-iodo-ω-acyl fluoride in 50% yield while an excess of LiI produced $I(CF_2)_nI$ ($n = 3$) in 72% yield.

As Rice [34], Riley et al. [39] obtained original telechelic diiodides containing ether bridges useful to preserve softness of the fluorosilicones generated from them.

On the other hand, Mc Loughlin prepared aliphatic perfluoroalkanes from preheated crystallised potassium iodide in anhydrous medium [38] as useful intermediates of telechelic aromatic diiodides according to an Ullman coupling, as follows [41]:



2.1.3. Halogen exchanges

Such a method was found also useful to obtain diiodinated derivatives. For example, telomers (see Section 2.2) of tetrafluoroethylene (TFE) with iodine monochloride [42,43] or iodine monobromide [43] afforded the corresponding diiodides by further reaction with molecular iodine.

2.2. Radical reactions involving iodine or α,ω-diiodofluoroalkanes

2.2.1. From iodine

2.2.1.1. Reaction with TFE. The addition of molecular iodine to fluorinated alkenes is one of the simplest methods to prepare telechelic diiodides since it does not require other reactants (e.g., catalyst or radical initiators). In 1949, 1,2-diiodotetrafluoroethane was synthesised for the first time by Coffman et al. [44]. After 15 h at 60°C in a silver-lined tube under pressure, the addition of iodine to TFE led to 74% of IC_2F_4I (based on I_2). 4 years later, Haszeldine and Leedham [45] reported a slightly higher yield when the reaction was carried out in a stainless steel autoclave. Then, Brace slightly improved the process while Knunyants et al. [46] reached 83% yield of 1,2-diiodotetrafluoroethane in steel ampoule. Although these reactions were initiated thermally, the photochemical induced addition of iodine to TFE by means of a halogen lamp (wavelength of 250–800 nm) successfully led to IC_2F_4I with very high yields (94%) [47].

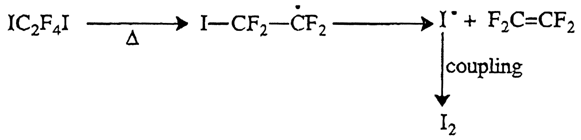
But, prior to this recent work, most additions to iodine to TFE were performed under pressure, at rather high temperatures. Moreover, as expected, an excess of TFE, under thermal telomerisation [48,49], led to higher $I(C_2F_4)_nI$ adducts ($n = 1$–5) showing the good propagation of TFE in such a radical process.

$$I_2 + nF_2C{=}CF_2 \xrightarrow[\Delta]{} I(C_2F_4)_nI$$

This procedure, called telomerisation (see Section 2.2.3), was pioneered by Bedford and Baum [50] while Tortelli and Tonelli [51] interestingly optimised that reaction: the best conditions were in autoclave at 180–200°C for 8 h with a 2–3 fold excess of TFE. Similarly, Kotov et al. [52] used that way, but with TFE being produced from PTFE wastes. Nowadays, the thermal process for obtaining these α,ω-diiodoperfluoroalkanes is industrialised by the Asahi [53] and Daikin companies.

Like perfluoroalkyl iodides, these diiodides exhibit weak carbon–iodine bonds [22,49] which allowed 1,2-diiodoperfluoroethane to produce higher telomers under heating.

This can be explained by the well-known β scission (or reversion) [54,55] of that reactant leading back to TFE and iodine as follows:



Furthermore, Knunyants et al. [46] noted that the higher the temperature, the more homologues are formed.

But, surprinsingly, when $As(C_2F_5)_2$ was used as the catalyst for the addition of molecular iodine to TFE, the diiodides were not produced [56].

2.2.1.2. Reaction with CTFE. In contrast to the section above, few works dealing with the addition of molecular iodide to CTFE have been described in the literature. The most interesting study was reported by Chambers et al. [57] who showed that iodine is slightly soluble in liquid CTFE under autogenous pressure at room temperature. The radical initiations were under sunlight, UV or gamma-radiations yielding a complete conversion of all solid iodine to ICF_2CFClI (**2**), which, in the presence of light or heat, led back to I_2 and CTFE.

$$I_2 + F_2C{=}CFCl \xrightarrow{h\nu} \underset{\underline{2}}{ICF_2CFClI} \xrightarrow{CTFE} I(CF_2CFCl)_nI$$

Such an observation was confirmed [58] and we showed that from 40°C, **2** decomposed. However, additional irradiation of **2** with an excess of liquid CTFE yielded irreversible formation of telomers $I(CF_2CFCl)_nI$, $n = 2$–10 [57], much more stable than **2**.

Moreover, even in the course of the addition of iodine monobromide to CTFE, traces of **2** were noted beside $I(C_2F_3Cl)Br$, majorly produced [59].

2.2.1.3. Reaction with hexafluoropropylene oxide. Yang [60] investigated the nickel catalysed addition of I_2 to hexafluoropropylene oxide (HFPO) at 185°C, producing $I(CF_2)_nI$, $n = 1$ (mainly), 2, 3, in 78–90% yield. Further, similar reaction starting from ICl or IBr led to ICF_2I, ICF_2X, CF_2X_2 (X = Cl or Br) and CF_3COF.

2.2.2. From iodobromodifluoromethane

Ashton et al. [61] noted that the UV pyrolysis of $BrCF_2I$ with TFE led to $I(CF_2)_nI$, with $n = 2$–5, after 45 min. at 100°C under telomerisation conditions.

2.2.3. Telomerisation of commercially available fluoroolefins with α,ω-diiodoperfluoroalkanes

Telomerisation reactions, introduced for the first time by Hanford in 1942 [62], in contrast to polymerisation, usually lead to low molecular weight polymers, called telomers, or even to monoadducts with well-defined end-groups. Such products (**3**) are obtained from the reaction between a telogen or a transfer agent (X–Y), and one or more (n) molecules of a polymerisable compound M (called monomer or taxogen) having ethylenic unsaturation, under radical polymerisation conditions, as follows:

$$X{-}Y + nM \xrightarrow{\text{free radical}} \underset{\underline{3}}{X{-}(M)_n{-}Y}$$

Various ways to initiate such a process (i.e., to generate free radicals) can be used: thermal, photochemical sources or the presence of redox catalysts or radical initiators.

We have reviewed such a reaction [48] in which the mechanisms and kinetics of radical and redox telomerisations are described and recently, the telomerisation of fluoroolefins has quasi exhaustively been reviewed [49].

Indeed, in this present case, X–Y telogens represent $I{-}R_F{-}I$ from which several works have been reported in the literature, in contrast to many investigations involving perfluoroalkyl iodides [49].

Below are described various telomerisations of fluoroalkenes (especially tetrafluoroethylene, vinylidene fluoride, and hexafluoropropene) with different diiodides of increasing fluorinated chain lengths.

Interestingly, IC_4F_8I or higher TFE adducts still preserve a good thermostability at least up to 260°C for 3 days [46,63] and for which such a property is enhanced for telomers containing an increasing TFE base unit number [64]. In contrast, IC_2F_4I starts to degrade from 180°C [46,63], whereas ICF_2I decomposes below 90°C [31] while ICF_2CFClI undergoes a reversion from 40°C [58] or at room temperature under sunlight [57].

2.2.3.1. From diiododifluoromethane. Li and Chen [31] reported original end-cappings of diiododifluoromethane by TFE, VDF and HFP in the presence of lead tetraacetate (LTA) as the catalyst. Such a redox initiation, surprisingly performed at mild temperature (70°C), was never achieved before in the presence of HFP, the only previous redox catalysis in the presence of Yttrium salts leading to by-products [65].

In addition, the use of LTA seemed to produce a regioselective reaction:

$$ICF_2I + F_2C{=}CFCF_3 \xrightarrow[70^\circ C,\ 30\,h]{LTA} \underset{85\%}{ICF_2CF_2CFICF_3}$$

This lead complex was very selective in monoaddition, since with a 3-fold excess of TFE which telomerises easily in the presence of metal salts or complexes [49], the authors only obtained traces of $ICF_2(C_2F_4)_2I$ or $I(C_2F_4)CF_2(C_2F_4)I$ diadduct. The yields of monoadduct where very high (85, 90 and 92 in the case of end-cappings with HFP, TFE and VDF, respectively). However, no stepwise monoaddition was described.

2.2.3.2. From α,ω-diiodoperfluoroalkanes containing TFE base units

2.2.3.2.1. Telomerisation of TFE. The telomerisation of TFE with $I(C_2F_4)_nI$ ($n = 1$ or 2) can be initiated thermally (at 230°C) [51], in the presence of dibenzoyl peroxide [66] or by gamma rays from a Co^{60} source [67] leading to molecular distributions of $I(C_2F_4)_pI$ with $p = 2$–4, 1–3 and 1–5, respectively.

2.2.3.2.2. Telomerisation of VDF. In contrast to the selective redox catalysis ($FeCl_3$/Ni at 160°C) [68], the thermal induced telomerisation of VDF led to a telomeric distribution (up to the first six adducts) [63]. The monoadduct contained the only $I(C_2F_4)_nCH_2CF_2I$ isomer while the diadduct was composed of two isomers: $ICF_2CH_2(C_2F_4)_nCH_2CF_2I$ (A) and $I(C_2F_4)_n(VDF)_2I$ (B), the ratio of which interestingly varied according to the number of TFEs: for $n = 1$, A and B were equimolar, whereas for $n = 2$, A/B molar ratio was 9 [63].

Moreover, these TFE/VDF cotelomers are also original transfer agents to be end-capped by HFP An elegant example demonstrates the regioselectivity of addition of the $IC_2F_4CH_2CF_2^{\bullet}$ radical toward the less hindered side of HFP [69] as follows:

$$\begin{aligned}&IC_2F_4CH_2CF_2I + F_2C{=}CFCF_3\\ &\xrightarrow{230^{\circ}C/65\,h} \underset{55\%}{IC_2F_4CH_2CF_2CF_2CFICF_3}\end{aligned}$$

2.2.3.2.3. Telomerisation of hexafluoropropene. HFP is known to homopolymerise in drastic conditions (at high temperatures ant at ca. 1000 bars [70]; consequently its telomerisation is also limited. However, under thermal conditions, we have found that the first three adducts were produced [71].

Tortelli and Tonnelli [51] followed by Baum and Malik [72], pioneered the thermal telomerization of HFP with 1,4-diiodoperfluorobutane, leading to the following adducts:

$$\begin{aligned}&IC_4F_8I + F_2C{=}CFCF_3\\ &\xrightarrow[\Delta]{} IC_4F_8(C_3F_6)I + I(C_3F_6)C_4F_8(C_3F_6)I\\ &+ I(C_3F_6)_2C_4F_8I + I(C_3F_6)C_4F_8(C_3F_6)_2I\end{aligned}$$

Recently, the optimisation of such a reaction toward the formation of the diadduct was achieved (after 48 h reaction at 260°C with an initial $[HFP]_0/[IC_4F_8I]_0$ molar ratio of 3.2, $I(HFP)C_4F_8(HFP)I$ was majorly produced and in good yields) [73].

As above, such highly fluorinated diiodides were successful candidates to allow the telomerisation of VDF [74].

$$\begin{aligned}&I(HFP)_xC_4F_8(HFP)_yI + p\,VDF\\ &\rightarrow \underset{x+y=1-4}{I(VDF)_a(HFP)_x}\,C_4F_8\,\underset{a+b=4-15}{(HFP)_y(VDF)_bI}\end{aligned}$$

Such original cotelomers are interesting models of fluoroelastomers as mentioned in Table 1 which lists such commercially available fluoropolymers based on most commercial fluoroolefins, and produced by various companies. Indeed, two 2 step-routes can be possible to achieve the synthesis of functionalisable diiodide cotelomers based on TFE, VDF and HFP base units (Scheme 2).

Indeed, as the ''telomerisation'' of HFP occurred at rather high temperatures (>200°C), it is required to perform this reaction as a first step prior that involving the telomerisation of VDF. Because this latter reaction cannot produce $ICF_2CH_2(C_2F_4)_nCH_2CF_2I$ selectively, two consecutive VDF units induce thermal weak points which make VDF telomers unstable at high temperatures.

In addition to the thermal properties, such fluorinated cotelomers exhibit glass transition temperatures below −40°C, obviously explained by their molecular weights lower than those of commercially available fluoroelastomers.

Interestingly, these highly fluorinated diiodides have been functionalised into original nonconjugated dienes as precursors of hybrid fluorosilicones (see Section 4.4).

2.2.3.3. From $I(CF_2CFCl)_nI$. Chambers et al. [57] reported the thermal addition of CTFE telomers to TFE leading to monoadduct **4** without any trace of higher TFE adducts, as follows:

$$I(C_2F_3Cl)_6I + F_2C{=}CF_2 \xrightarrow[\text{HFP (trace)}]{16\,h/165^{\circ}C} \underset{\underline{\mathbf{4}}}{I(C_2F_3Cl)_6CF_2CF_2I}$$

2.3. Coupling reactions of diiodo(per)fluoroalkanes

Ford et al. [75] recently studied the coupling reactions of α,ω-diiodoperfluoroalkanes in the presence of Cadmium at mild temperatures. ^{19}F NMR at 80°C revealed an increase of the molecular weights and the fluorodiiodides produced exhibited low polydispersity indexes (PDI):

$$I(CF_2)_nI \xrightarrow[80^{\circ}C]{Cd} I(CF_2)_{16n}I \quad PDI = 1.00$$

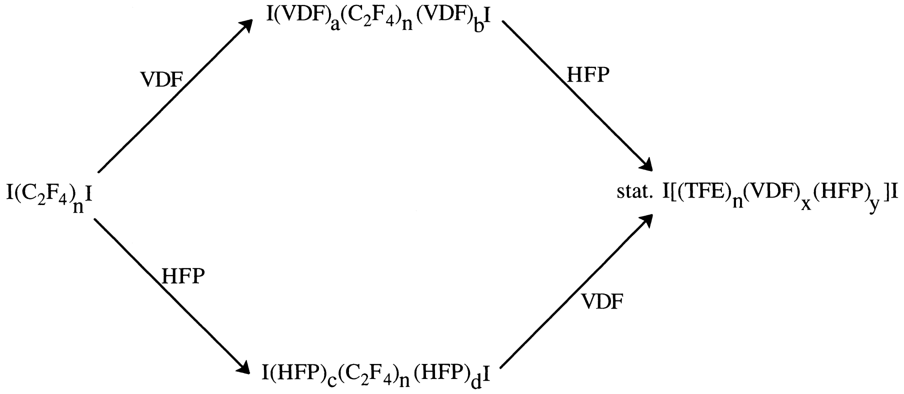
2.4. Use of IR_FI in iodine transfer polymerisation

Iodine transfer polymerisation (ITP) is one of the radical controlled or pseudo-living processes being developed in the late seventies by Tatemoto et al. [5,76–79]. The truly living character is usually demonstrated when molecular weight increase with conversion in a linear fashion. Polydispersity must be narrow and lower than that observed in classical processes (theoretical value, $\overline{M_w}/\overline{M_n} = 1.1-1.5$) which supposes in particular, a rapid initiation step. Obtaining high and strictly controlled molecular weights have thus been possible. Actually, the ITP process requires perfluoroalkyl iodides and also diiodides because their highly

Table 1
Main commercially available fluoroelastomers

	HFP[a]	PMVE[b]	CTFE[c]	*P*[d]	HPFP[e]
VDF	Daiel® 801 (Daikin)	–	Kel F® (Dyneon)	–	Tecnoflon SL (Ausimont)
	Fluorel® (3M/Dyneon)	–	SKF®-32 (Russia)	–	–
	Tecnoflon® (Ausimont)	–	Voltalef® (Elf Atochem)	–	–
	SKF®-26 (Russia)	–	–	–	–
	Viton® A (DuPont)	–	–	–	–
TFE[f]	–	Kalrez® (DuPont)	–	Aflas® (Asahi Glass)	–
VDF[g] + TFE	Daiel® 901 (Daikin)	Viton® GLT (DuPont)	–	–	Tecnoflon® T (Ausimont)
	Fluorel® (Dyneon)	–	–	–	–
	Tecnoflon® (Ausimont)	–	–	–	–
	Viton® B (DuPont)	–	–	–	–
	+ethylene: Tecnoflon® (Ausimont)	–	–	–	–
	+X: Viton® GH (DuPont)	–	–	–	–

[a] HFP: hexafluoropropene $F_2C=CFCF_3$.
[b] PMVE: perfluoromethyl vinyl ether $F_2C=CFOCF_3$.
[c] CTFE: chlorotrifluoroethylene $F_2C=CFCl$.
[d] *P*: propene $H_2C=CHCH_3$.
[e] HPFP: 1-hydro-pentafluoropropene $FHC=CF–CF_3$.
[f] TFE: tetrafluoroethylene $F_2C=CF_2$.
[g] VDF: vinylidene fluoride (or, 1,1-difluoroethylene) $F_2C=CH_2$.



Scheme 2. Synthesis of highly fluorinated α,ω-diiodoalkanes containing TFE, VDF and HFP base units as original models of fluoroelastomers.sc2

electron withdrawing perfluorinated group R_F allows the lowest level of the CF_2–I bond dissociation energy. Various fluorinated monomers (e.g., VDF) or nonfluorinated ones (styrene, acrylates or methacrylates) have been successfully used in ITP. Basic similarities in these living polymerisation systems are found in the stepwise growth of polymeric chains at each active species. The active living centre, generally located at the end-groups of the growing polymer, has the same reactivity at any time during polymerisation even when the reaction is stopped [76,77]. In the case of ITP of fluoroolefin, the terminal active bond is always the C–I bond originated from the initial iodine-containing chain transfer agent and monomer, as follows:

$$I-C_nF_{2n}-I + nH_2C=CF_2 \xrightarrow{R^\bullet \text{ or } \Delta} I-CF_2CH_2(VDF)_qC_nF_{2n}(VDF)_pCH_2CF_2-I$$

Usually molecular weights are not higher than 30 000 and yet polydispersity is narrow (1.2–1.3) [5,77,78]. Tatemoto et al. used peroxides as initiators of polymerisation. Improvement is also possible by using polyiodide compounds [5,76].

Several investigations have shown that iodine transfer polymerisation can occur by emulsion or radical initiation. When emulsion initiation is chosen, a perfluoroalkyl iodide or a diiodide is involved and limits the molecular weights [76–79].

The Daikin Company has thus been able to produce thermoplastic elastomers called Dai-El® [78,79] (Table 1). For example, a hard segment sequence can be composed of E/HFP/TFE in 43/8/49 molar ratio (E represents ethylene) whereas the soft part can consist of TFE/HFP/VDF in 20/30/50 molar ratio [5]. These commercially available Dai-El® Thermoplastics exhibit very interesting properties such as a high specific volume (1.90), a high melting point

(160–220°C), a high thermostability up to 380–400°C, a refractive index of 1.357 and good surface properties ($\gamma_c \sim 19.6$–20.5 dynes cm^{-1}). These characteristics offer excellent resistance against aggressive chemicals and strong acids, fuels, and oils. In addition, tensile modulus is close to that of cured fluoroelastomers.

More recently, the Du Pont [80] and Ausimont [81] Companies have also been attracted by this concept using IC_4F_8I or $IC_2H_4(TFE)_nC_2H_4I$, respectively, in the controlled radical polymerisations of VDF, TFE, trifluoroethylene and also in the VDF/HFP copolymerisation. In this last case, polydispersity indexes as low as 1.87 could be obtained [80].

2.5. Conclusion

Although less surveys have been performed compared to the preparation of perfluoroalkyl iodides, different ways of synthesis of α,ω-diiodoperfluoroalkanes have been investigated by various authors. Basically, two main groups of reactions have been developed: a rather wide range of organic syntheses have led to short diiodides while telomerisations of fluoroolefins with molecular iodine or with diiodoperfluoroalkanes have successfully supplied higher molecular weight-diiodides. Interestingly, this process has been scaled up and nowadays α,ω-diiodoperfluoroalkanes are commercially available. In contrast to TFE mainly and to CTFE, no addition of iodine to VDF, HFP or trifluoroethylene has already been reported in the literature.

Further, telomerisation of various fluoroolefins with I–R_F–I has offered a wide range of highly fluorinated original diiodides. Mostly thermal initiation and also photochemical, from Co^{60} gamma source or peroxidic initiations were attempted successfully.

For much higher molecular weight-diiodides, the Ullman coupling reaction of I–R_F–I and the iodine transfer polymerisation of fluoroolefins with I–R_F–I led to original polymeric diiodo materials with narrow polydispersities.

All these α,ω-diiodo(per)fluoroalkanes are very interesting precursors for obtaining telechelic derivatives, presented below.

3. Functionalisation of α,ω-diiodo(per)fluoroalkanes for the obtaining of fluorinated telechelics

Several ways are possible to enable the diiodides to be functionalized. Basically, these routes can be gathered into four families:

1. Direct transformation of both iodine atoms into functions, as follows (Met designates a metal):

$$I-R_F-I + 2Met-\textcircled{G} \rightarrow \textcircled{G}-R_F-\textcircled{G} + 2Met\ I$$

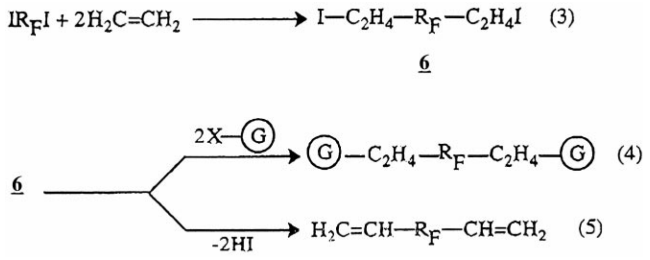
2. Functionalisation from the bis(monoaddition) of the diiodides to ω-functional-α-ethylenic derivatives ($\textcircled{G}$ and R designate a functional and a spacer groups, respectively):

$$I-R_F-I + 2H_2C{=}CH-R-\textcircled{G}$$
$$\rightarrow \textcircled{G}-R-CHICH_2-\underset{\underline{5}}{R_F}-CH_2CHI-R-\textcircled{G} \qquad (1)$$

$$\mathbf{5} + H_2 \text{ or } H^{\ominus} \rightarrow \textcircled{G}-R-C_2H_4-\underset{\underline{5}}{R_F}-C_2H_4-R-\textcircled{G} \qquad (2)$$

The first step can be possible thanks to easy cleavable CF_2–I bond as already mentioned above.

3. On the other hand, as a spacer is required between the function and the perfluorinated chain, the bis(ethylenation) of the diiodide (Eq. (3)) followed by a disubstitution (Eq. (4)) or a bis(dehydroiodination) (Eq. (5)) produce fluorotelechelics or α,ω-divinyl perfluorinated alkanes, respectively.



$$IR_FI + 2H_2C{=}CH_2 \longrightarrow I-C_2H_4-\underset{\underline{6}}{R_F}-C_2H_4I \qquad (3)$$

$$\underline{6} \xrightarrow{2X-\textcircled{G}} \textcircled{G}-C_2H_4-R_F-C_2H_4-\textcircled{G} \qquad (4)$$

$$\underline{6} \xrightarrow[-2HI]{} H_2C{=}CH-R_F-CH{=}CH_2 \qquad (5)$$

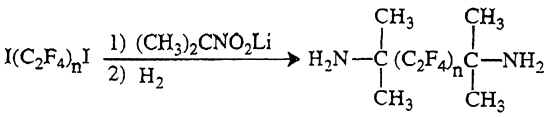
4. By coupling reactions between α,ω-diiodides and ω-functional-α-iodinated compounds:

$$I-R_F-I + 2I-\textcircled{G} \rightarrow \textcircled{G}-R_F-\textcircled{G} + 2I_2$$

These four classes of reactions are summarised in Scheme 3.

3.1. Direct chemical transformation

α,ω-diiodoperfluoroalkanes do not undergo normal S_N1 or S_N2 substitutions but react with selected nucleophiles by an $S_{RN}1$ process [98], as follows:



$$I(C_2F_4)_nI \xrightarrow[2)\ H_2]{1)\ (CH_3)_2CNO_2Li} H_2N-C(CH_3)_2(C_2F_4)_nC(CH_3)_2-NH_2$$

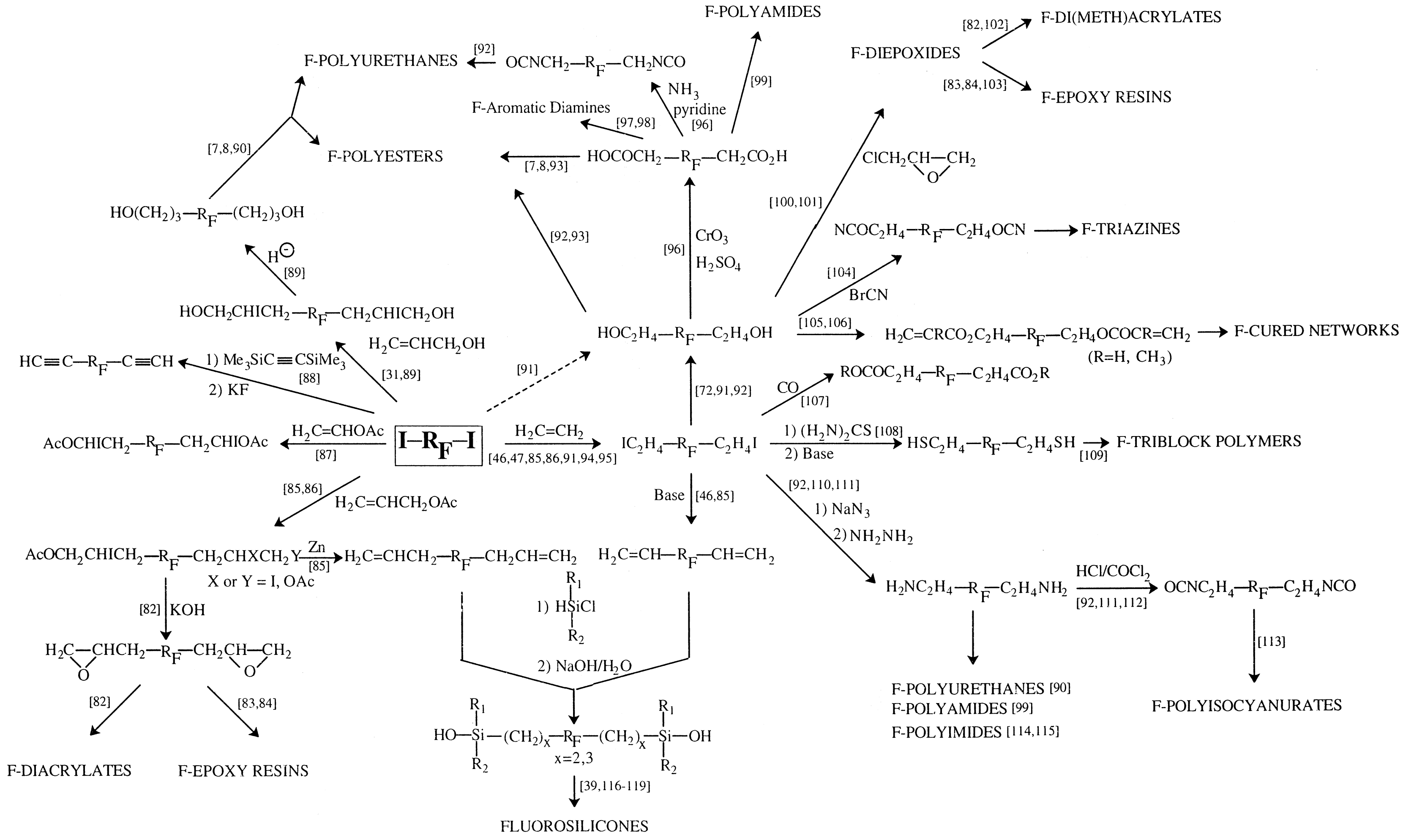
In this manner, a Chinese team [120] performed the sulfination of fluorinated diiodides with $Na_2S_2O_4$ in aqueous $NaHCO_3$ in moderate to high yields to produce NaO_2S–R_F–SO_2Na converted to sulfonyl chlorides.

3.2. Fluorinated telechelics from the bis(monoaddition) of diiodides to unsaturated ω-functional reactants

As in Eqs. (1) and (2), both steps are described hereafter.

3.2.1. Radical addition of diiodides to unsaturated functional reagents (Eq. (1))

Brace [121] has recently reviewed the addition of perfluoroalkyl iodides to unsaturated derivatives showing that



Scheme 3. α,ω-diiodofluoroalkanes as useful precursors of fluorinated telechelics and polymers. [83,84,87,93,97,103,106,110,115]

many investigations had been performed. Indeed, the use of these R_FI is a versatile means to enable the fluoroalkylation of compounds.

In the case of the diiodide series, less studies have been attempted and sometimes several authors did not pursue their investigations until the obtaining of fluoro telechelics.

As reported [122], the weak CF_2–I bond can easily be cleaved in the presence of various systems already described [121,123]: thermally, photochemically, biochemically, electrochemically, from various initiators or catalysts: organic peroxides and diazo compounds, hydrogen peroxide, sodium dithionite and related agents, triethyl borane, alkyl phosphines, various metals, metallic salts and metallic complexes.

Among the unsaturated ω-functional derivatives, allyl alcohol, vinyl and allyl acetate and acrylates have been mostly studied whereas Metzger's group [124] tried fatty ethylenic compounds successfully.

Usually the $ICF_2R_FCF_2^\bullet$ (or $^\bullet CF_2R_FCF_2^\bullet$) radical reacts towards the less hindered side of the unsaturated compound leading to expected $-CF_2R_FCF_2CH_2CHI-G$.

Interestingly, Khrlakyan et al. [125] compared the reactivity of allyl alcohol and allyl acetate toward $I(C_2F_4)_nI$ ($n = 1, 2$), in the presence of AIBN (at 80–90°C) or dicyclohexyl peroxidicarbonate at 58°C. They noted the higher reactivity of the unsaturated acetate with a quasi selective formation of telechelic (82%) in the presence of the dicarbonate. Slight exotherms occurred when these initiators were utilised with allyl acetate.

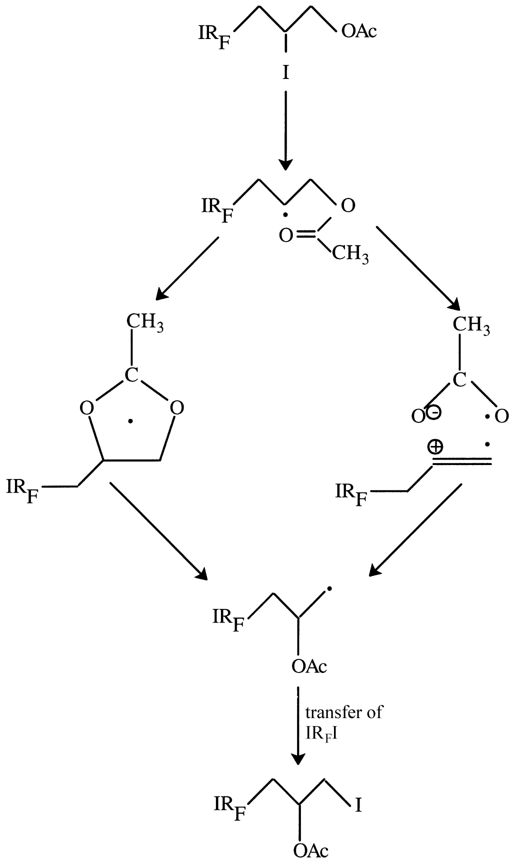
However, from the same monomer, initiated by dibenzoyl peroxide at 90°C, it was noted that the sharp exotherm occurred up to 170–180°C followed by a thermal rearrangement of the intermediate radical leading to unexpected $IR_FCH_2CH(OAc)CH_2I$ [86], as suggested by the mechanism depicted in Scheme 4 [123].

The produced fluorinated diiododiacetates were chemically changed into nonconjugated dienes [85] or diepoxides [82], whatever the amount of rearranged diacetates since they underwent the bis(deiodoacetalisation) or bis(cyclisation), respectively.

For bulkier unsaturated reactants, two examples are given below.

1. 1,4-diiodoperfluorobutane reacted cleanly with a five fold excess of norbornene leading to the 1:2 adduct in high yield, in the presence of sodium *p*-toluene sulfinate [126];
2. Huang et al. [127] reacted a two fold excess of ω-ethylenic sterol in the presence of sodium dithionite giving a fluorinated bisterol in 76% yield.

Another interesting study was achieved by Wilson and Griffin [128] who synthesised fluorinated copolymers containing fluorinated and hydrogenated microblocks, by radicals polyadditions of diiodoperfluoroalkanes to non-conjugated dienes as follows:



Scheme 4. Mechanism of the formation of rearranged diiodoacetate.sc4

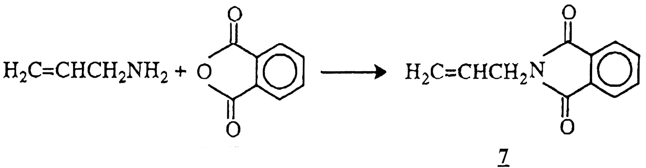
$$I(CF_2)_n I + H_2C{=}CH(CH_2)_pCH{=}CH_2 \xrightarrow[\text{2) SnBu}_3\text{H, AIBN, 90°C}]{\text{1) AIBN (85-145°C)}} \left[(CF_2)_n - (CH_2)_m \right]_q$$

$n = 4, 6$ $p = 2, 4, 6$ $m = p + 4$

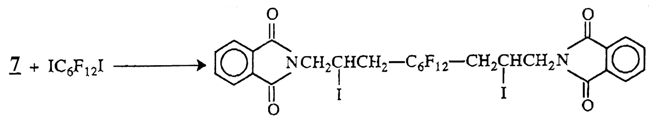
These polymers, having molecular weights of about 20 000, showed thermotropic mesophases on heating. These new class of liquid crystals was also investigated by Russell et al. [129].

Finally, although several authors focused on the addition of perfluoroalkyl iodides to acetylenic compounds, to our knowledge, the only work starting from diiodide was performed by Baum et al. [88] and led to $HC{\equiv}C{-}R_F{-}C{\equiv}CH$ in three steps from $HC{\equiv}C{-}Si(CH_3)_3$.

Allyl amine does not react with perfluoroalkyl iodides [130]; hence it is necessary to protect the amino group. Thus, the bismonoaddition of 1,6-diiodoperfluorohexane to allylphthalimide **7** enabled us to prepare telechelic diamines [131] as follows:



7



8

$$\mathbf{8} \xrightarrow[2)H_2N\text{-}NH_2,\ EtOH]{1)SnBu_3H} H_2NC_3H_6-C_6F_{12}-C_3H_6NH_2$$

3.2.2. Reduction of iodine atoms (Eq. (2))

Various ways to reduce selectively both iodine atoms into hydrogens have been successfully reported.

3.2.2.1. In the presence of tributylstannane (see Section 3.2.1). The simplest, but more expensive one, requires to use tributylstannane known as an efficient reducer [132]. Such a reactant has been employed frequently in the case of monoadduct R_FCH_2CHI–R–Ⓖ [95,121] but rather few papers described its use from telechelic diiodides.

Besides the example above, we have recently synthesised diol **9** according to the following scheme [89]:

$$IC_6F_{12}I + H_2C{=}CHCH_2OH$$
$$\overset{AIBN}{\rightarrow} HOCH_2CHICH_2C_6F_{12}CH_2CHICH_2OH$$
$$\overset{SnBu_3H}{\rightarrow} \underset{\underline{9}}{HOC_3H_6C_6F_{12}C_3H_6OH}$$

3.2.2.2. In the presence of hydrogen. Another alternative to perform the reduction deals with the use of hydrogen in the presence of the palladium/charcoal complex as carried out by Metzger et al. [124], Qui and Burton [133] or Gresham [134].

3.2.2.3. In the presence of zinc or zincic catalysts. Furthermore, a reduction realised in the presence of zinc/HCl [135] or in a $Zn/NiCl_2$ complex [136] was also successfull.

Interestingly, Qui and Burton [133] compared various conditions of reduction of fluorinated diiododiol and showed that the more efficient one which avoided the dehydroiodination was that in the presence of the following system: H_2/Pd–C (5%)/$NaHCO_3$/MeOH.

From the perfluoroalkyl iodide series, Brace [121] mentioned that several authors performed the synthesis of R_F–C_2H_4–R–Ⓖ in one step. To our knowledge, similar reference was not reported in the literature, from diiodides.

3.3. Functionalisation by substitution after ethylenation

This alternative is a two step-process as depicted by Eqs. (3) and (4) and in Scheme 3.

3.3.1. Ethylenation (Eq. (3))

Various authors have studied the ethylenation of perfluoroalkyl iodides or diiodides and different initiations were efficient. Four routes are given below.

3.3.1.1. Thermal initiation. This process was pioneered by Brace at 180–220°C [95] whereas Knunyants et al. [46] used it at 220°C to allow the bis(monoethylenation) of 1,2-diiodotetrafluoroethane with at least a 3.5 fold excess of ethylene, as follows, where E represents C_2H_4 unit:

$$\begin{array}{llll} IC_2F_4I & + H_2C{=}CH_2 & \rightarrow IC_2H_4C_2F_4C_2H_4I & + IC_2H_4C_4F_8C_2H_4I \\ 1 & 3.5 & 90\% & - \\ 1 & >10 & 90\% & 8\% \end{array}$$

The formation of the polyhalogenooctane was explained by the ethylenation of 1,4-diiodooctafluorobutane obtained from the addition of IC_2F_4I to TFE; this monomer being produced by reversion of IC_2F_4I at these high temperatures (see Section 2.2.1.1).

Attempts at higher temperatures (350°C) were performed by Bloechl [137].

More recently, Yang [138] proposed the ethylenation of ICF_2I at 120–240°C.

3.3.1.2. Photochemical initiation. Renn et al. [47] achieved the bis(monoethylenation) of 1,2-diiodotetrafluoroethane from a UV irradiation by means of a halogen lamp (250–800 nm wavelength).

3.3.1.3. From redox catalysis. Several teams used various metallic catalysts which were efficient in ethylenation of perfluoroalkyl iodides or diiodides. Interesting surveys were performed by Von Werner [94] who used different triphenyl phosphine complexes while Li and Chen [31] obtained the expected bis(ethylenated) derivative in good yield from diiododifluoromethane, in the presence of lead tetraacetate (LTA):

$$ICF_2I + H_2C{=}CH_2 \xrightarrow[\text{diglyme}]{\text{LTA } 70^\circ C} IC_2H_4CF_2C_2H_4I \quad 86\%$$

Researchers at the Ausimont Company [91] employed CuI as the catalyst and obtained the expected $IC_2H_4(C_2F_4)_nC_2H_4I$ ($n = 2, 3$).

In the presence of the same catalyst, we also noted satisfactory results (with minimum yield of 70%) from commercially available $I(C_2F_4)_nI$ ($n = 1, 2, 3$) ([85], part (a))or from cotelomers of VDF, TFE and HFP ([85], part (b)).

$$IR_FI + H_2C{=}CH_2 \xrightarrow[160^\circ C]{CuCl/H_2NC_2H_4OH} IC_2H_4R_FC_2H_4I$$

with R_F: $(VDF)_a(C_2F_4)_n(VDF)_b$ (with $n = 1, 2$ and $a = 0$, $b = 1$; $a = b = 1$ and $a = 0$, $b = 2$); $(HFP)_xC_4F_8(HFP)_y$ ($x = y = 1$; $x = 0$ and $y = 1$); C_2F_4(VDF)(HFP).

On the other hand, Urata et al. [107,139] used $Fe(CO)_{12}$, $Co_2(CO)_8$ or $Ru_3(CO)_{12}$ which catalysed effectively this reaction, leading to $IC_2H_4(CF_2)_nC_2H_4I$ ($n = 4, 6$) in 91% yield.

Finally, Chambers et al. [57] successfully achieved the ethylenation of CTFE telomers in the presence of platinum at 70°C in 32% yield:

$$I(CF_2CFCl)_6I + H_2C{=}CH_2 \xrightarrow[70^\circ C]{10\%\ Pt/C} IC_2H_4(CF_2CFCl)_6C_2H_4I$$

3.3.1.4. From radical initiation. Percarbonates have also been shown efficient in the bis(ethylenation) of α,ω-diiodo(per)fluoroalkanes containing VDF and/or HFP base units ([85], part (b)). Although it was required to fill the autoclave three times with the initiator and ethylene, the reactions have the advantage to be carried out at 60°C, only. The yields were ranging between 60% and 80%.

Peroxide initiators were also used: Baum et al. [88] performed the bis(monoethylenation) of $I(CF_2)_nI$ ($n = 4$, 6) in the presence of di*tert*-butyl peroxide at 130°C.

Hence, various kinds of initiations are possible to allow bis(ethylenation) reactions. Interestingly, these methods are very selective and also point out that two consecutive ethylene units were never observed.

3.3.2. Substitution of both iodine atoms by two functions Eq. (4)

These above α,ω-bis(monoethylenated) diiodides are versatile intermediates to obtain a large variety of fluorinated telechelics.

Scheme 3 shows non exhaustive possibilities to carried out the chemical transformation:

$$IC_2H_4{-}R_F{-}C_2H_4I \rightarrow \textcircled{G}{-}C_2H_4{-}R_F{-}C_2H_4{-}\textcircled{G}$$

Some of them are given as examples below.

3.3.2.1. Synthesis of telechelic diols. Diols are very interesting intermediates for the synthesis of various fluoropolymers [7,8,90,140] (see Section 4.1). Telechelic diols from the bis(monoethylenated) forerunners were prepared by the Daikin [141], Ausimont [91] or Fluorochem [92] Companies, starting from $NaNO_2$/betaine as surfactant, $CuSO_4{\cdot}5H_2O$ or AgOAc and H_2SO_4/SO_3, respectively, in yields higher than 92%. Such methods are more convenient than these requiring a water/DMF mixture which led to olefins or dienes.

These fluorodiols are particularly interesting precursors of a wide variety of fluorotelechelics as shown in Scheme 3.

3.3.2.2. Synthesis of fluorinated dienes (Eq. (5)). The bis(ethylenated) diiodides were easily changed into fluorinated nonconjugated dienes in alkali medium [46,85,88]. They are interesting precursors of hybrid fluorosilicones [39,116–119]. Interestingly, 3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene underwent hydrosilylation with trichlorosilane as precursors of fluorinated silsesquioxanes [142] as hybrid gels with a much better thermostability than the gels prepared from the corresponding hydrogenated dienes:

$$H_2C{=}CHC_4F_8CH{=}CH_2 + HSiCl_3 \xrightarrow[2)MeOH]{1)H_2PtCl_6} (CH_3O)_3SiC_2H_4C_4F_8C_2H_4Si(OCH_3)_3 \overset{F^{\ominus}}{\rightarrow} gel$$

3.3.2.3. Synthesis of telechelic dinitriles. Telechelic dinitriles, interesting precursors of diamines and diacids and then of fluoropolyamides, were prepared by Anton and MacKinney [143] by reacting HCN into divinyl dienes in the presence of tritolyl phosphite and a nickel complex.

3.3.2.4. Synthesis of fluorinated thiols. Although numerous studies report the synthesis of fluorinated mercaptans from $R_FC_2H_4I$, no fluorodithiol has been already described in the literature. However, in the presence of thiourea, Wathier [108] has recently succeeded in obtaining $HSC_2H_4C_6F_{12}C_2H_4SH$ from the corresponding 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,10-diiodide. Such a dithiol is a potential precursor of triblock copolymers as Fokina et al. [109] produced from α,ω-dimercapto polybutadienes.

On the other hand, original fluorinated mercaptan **10**, prepared from the dodecafluoro-1,10-diiodide acts as an efficient transfer agent for the telomerisation of tri(hydroxymethyl)acrylamido methane (THAM) as follows [144]:

$$IC_2H_4C_6F_{12}C_2H_4I \xrightarrow[2)(NH_2)_2CS/NH_4OH]{1)SnBu_3H} CH_3CH_2C_6F_{12}\underset{\underline{10}}{C_2H_4SH}$$

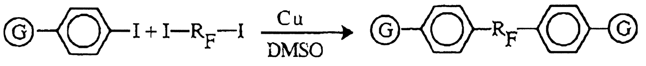
$$\mathbf{10} \overset{THAM}{\rightarrow} C_2H_5C_6F_{12}C_2H_4S\,(THAM)_n{-}H$$

These telomers were original precursors of nonionic surfactants to stabilise proteins in solution.

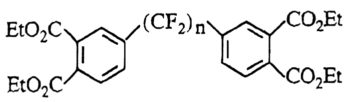
3.3.2.5. Miscellaneous. The literature reports also useful fluorinated α,ω-dinitro derivatives [145] and telechelic bis(quaternary ammonium salts) [99,111,146], especially dihydrobromide salts, which after neutralisation, underwent interfacial polymerisation with diacid chlorides to give polyamides [111].

3.4. Coupling reactions from α,ω-diiodo(per)fluoroalkanes

Mc Loughlin and Thrower [147], and several years later, Chen et al. [148] carried out an extensive research on the synthesis of diaromatic difunctional compounds linked to fluorinated chains according to the following Ullman coupling reaction:



where Ⓖ represents a functional group such as hydroxy (i.e., bisphenol), carboxylate, isocyanate [112], nitro (precursor of amine), in *para* or *meta* positions about the fluorinated chain. The first team also branched several functional groups onto each aromatic ring [149], in 85% yield, such as the following tetracarboxylates:



From these compounds, novel polymers were prepared such as polyesters [150], silicones [151] and polyimides [151].

3.5. Conclusion

Basically, among the four main reactions enabling the α,ω-diiodoperfluoroalkanes to produce fluorotelechelics, two of them have attracted much interest: (i) that involving the bismonoaddition of I–R_F–I to various α-functional unsaturated derivatives as a direct functionalisation and followed by selective reductions of both iodine atoms; (ii) that requiring first a bis(monoethylenation) of I–R_F–I (for which many investigations have been developed showing that most initiation processes were successful) followed by a substitution.

Less extensively studied was the Ullman reaction between I–R_F–I and α-functional-ω-iodo derivatives. More investigations should be expected.

Most fluorotelechelics are relevant monomers for polycondensations or polyadditions leading to fluoropolymers, as reported below.

4. Synthesis of well-architectured fluoropolymers from fluorinated telechelics

Telechelic diols, diacids, diisocyanates, diamines, dienes are among the most promising starting materials for the synthesis of well-architectured fluoropolymers via condensation polymerisations or polyaddition polymerisations.

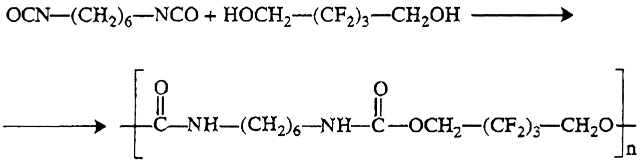
Several examples of preparation of such various fluoropolymers are presented in the following sections.

4.1. From fluorinated diols

Diols are interesting forerunners for the synthesis of various polymers (e.g., polyurethanes, polyesters, polyethers) and are also useful intermediates to be chemically changed into diepoxides, di(meth)acrylates or dicyanates (Scheme 3). Some of them are depicted hereafter.

4.1.1. Polyurethanes

The first fluorinated polyurethane (FPU) was patented in 1958 [152].12 years later, a relevant survey [153] detailed the comparison of the reactivity of fluorinated diols about that of nonhalogenated ones for the preparation of such polymers. An interesting work performed by a Russian team dealt with the reaction between 2,2,3,3,4,4-hexafluoro-1,5-pentanediol and hexamethylene diisocyanate [154], as follows:



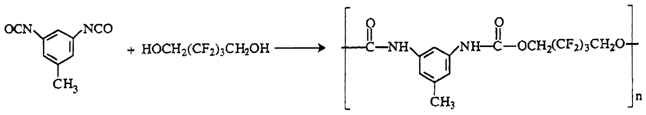
$$OCN{-}(CH_2)_6{-}NCO + HOCH_2{-}(CF_2)_3{-}CH_2OH \longrightarrow$$

$$\longrightarrow \left[\overset{O}{\overset{\|}{C}}{-}NH{-}(CH_2)_6{-}NH{-}\overset{O}{\overset{\|}{C}}{-}OCH_2{-}(CF_2)_3{-}CH_2O \right]_n$$

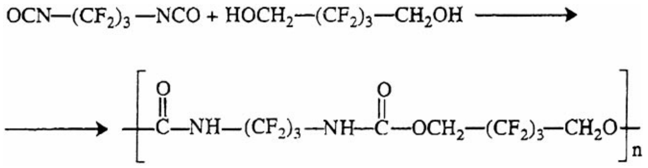
These authors have shown that such FPU exhibit a better thermostability than hydrogenated analogues, because of the fluorinated groups which prevent the urethane weak group from classical thermal decomposition.

Then, by polycondensation of various fluorodiols with hexamethylene diisocyanate, Keller [155] developed interesing polyurethanes which were amorphous, insoluble and transparent from brittle to tough as the reaction progressed, when they were prepared at temperatures above 75°C, whereas they became brittle and soluble in common organic solvents when the reaction was performed at a temperature below 75°C.

In addition, polyurethanes based on aromatic diisocyanates were prepared, the aromaticity enabling to increase the T_g values of the FPUs. The same fluorinated diol as above was involved in the synthesis of fluorinated polymers with 3,5-toluene diisocyanate and with a mixture of 2,4-toluene diisocyanate and 3,3′-bistolylene-4-4′-diisocyanate [156]:



Wall [157], Ho et al. [140] and more recently Brady [90] reported very interesting strategies of syntheses, properties and applications of fluorinated aromatic and aliphatic polyurethanes, even using a perfluorinated diisocyanate and a fluorinated diol, as follows:



$$OCN{-}(CF_2)_3{-}NCO + HOCH_2{-}(CF_2)_3{-}CH_2OH \longrightarrow$$

$$\longrightarrow \left[\overset{O}{\overset{\|}{C}}{-}NH{-}(CF_2)_3{-}NH{-}\overset{O}{\overset{\|}{C}}{-}OCH_2{-}(CF_2)_3{-}CH_2O \right]_n$$

However, such a polyurethane was shown to be hydrolytically unstable [158]. In addition, these authors reviewed the fluorinated polyurethanes prepared from polyesters of fluorinated diols, from fluorinated polyethers and detailed their properties.

Malichenko et al. [154] also used fluoroaromatic diisocyanates for better materials useful as containers of liquid oxygen and novel adhesives.

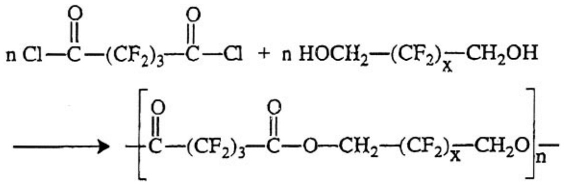
In addition, other FPU, prepared from fluorodiols containing HFP base units were also reported [72].

Takakura et al. [159] investigated on the structure and the mechanical properties of fluorinated segmented poly(urethaneurea)s, and showed that their structures were highly ordered and that such polymers behaved as elastomers. In addition, such FPU exhibited antithrombogenic properties [96] and durability for use in an artificial heart pump [159].

In addition, by X-ray photoelectron spectroscopy, Yoon and Ratner [160] studied the surface structure of segmented poly(ether urethane)s and poly(ether urethane urea)s with various perfluorinated chain extenders and noticed that the surface topography of such polymers depended strongly on the extent of the phase separation.

4.1.2. Polyesters

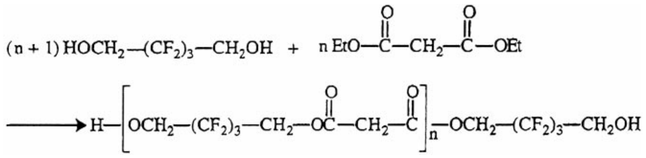
From 1952, Filler et al. [161] studied the polycondensation of fluorinated acid dichlorides and diols according to the following reaction:



$$n\,Cl-\overset{\overset{O}{\|}}{C}-(CF_2)_3-\overset{\overset{O}{\|}}{C}-Cl + n\,HOCH_2-(CF_2)_x-CH_2OH \longrightarrow -\!\left[\overset{\overset{O}{\|}}{C}-(CF_2)_3-\overset{\overset{O}{\|}}{C}-O-CH_2-(CF_2)_x-CH_2O\right]_n\!-$$

x = 3, 4

More recently, Gosnell and Hollander [162] carried out the synthesis:

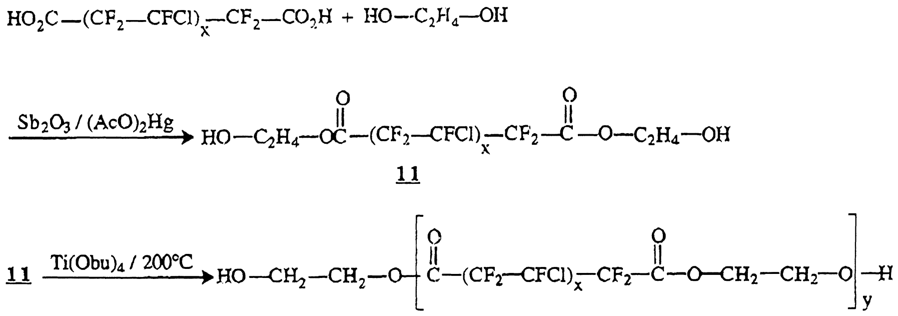


$$(n+1)\,HOCH_2-(CF_2)_3-CH_2OH + n\,EtO-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OEt \longrightarrow H-\left[OCH_2-(CF_2)_3-CH_2-O\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}\right]_n-OCH_2-(CF_2)_3-CH_2OH$$

leading to a polyester having a molecular weight of 1800.

These authors also used fluoroaromatic diesters to prepare original hydrophobic fluorinated polyesters which still preserve their properties at low temperatures ($T_g = -65°C$) and are resistant to oxidation, aggressive chemicals, petroleum and to fire, with good mechanical properties. They found applications as containers for liquid oxygen.

In our laboratory, the polytransesterification was used to obtain polyester diols **11** containing CTFE base units [163]:

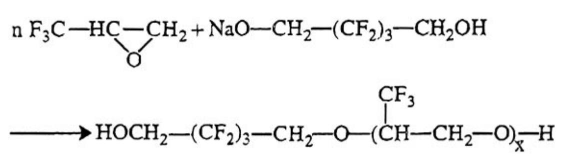


$$HO_2C-(CF_2-CFCl)_x-CF_2-CO_2H + HO-C_2H_4-OH$$

$$\xrightarrow{Sb_2O_3\,/\,(AcO)_2Hg} HO-C_2H_4-O\overset{\overset{O}{\|}}{C}-(CF_2-CFCl)_x-CF_2-\overset{\overset{O}{\|}}{C}-O-C_2H_4-OH \quad \underline{\mathbf{11}}$$

$$\underline{\mathbf{11}} \xrightarrow{Ti(OBu)_4\,/\,200°C} HO-CH_2-CH_2-O-\left[\overset{\overset{O}{\|}}{C}-(CF_2-CFCl)_x-CF_2-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_2-O\right]_y-H$$

In addition, the polymerisation of fluorinated epoxides was performed in Carius tubes [164], or by Gosnell and Hollander [162]:



$$n\,F_3C-\underset{\backslash O/}{HC-CH_2} + NaO-CH_2-(CF_2)_3-CH_2OH \longrightarrow HOCH_2-(CF_2)_3-CH_2-O-(\underset{}{\overset{\overset{CF_3}{|}}{CH}}-CH_2-O)_x-H$$

Pilati et al. [165], prepared polyesters from dimethylterephthalate, ethylene glycol and the diester $CH_3O_2C–R_F–O–R_F–CO_2CH_3$. The copolycondensation by transesterification was studied and the authors investigated the morphology, the thermal and surface properties of these obtained polyesters. It was noted that the PET/copolymer (PET–PFPE) blend thus obtained contained up to 35% in weight of PFPE but 7% only were linked to the prepared PET.

4.1.3. Polyethers

Besides Krytox® [11,12], Fomblin® [13–16] and Demnum® [17] commercialised by Du Pont, Ausimont and Daikin, respectively, the Du Pont Company [98] also suggested the synthesis of following fluoropolyether from the ionic polymerisation of hydroxy trifluorovinyl ethers with fluorodiol in the presence of CsF:

$$H-\left[(OCH_2C_3F_6CH_2O)_n-(CF_2CHFOCF_2CF(CF_3)OCF_2CF_2CH_2O)_m\right]-H$$

Fluoropolyethers can also be prepared from the reaction between a dialcoholate with a dihalogenide, as studied by Johncock [166]:

$$HOCH_2(CF_2)_nCH_2OH + X-R-X \xrightarrow[T<50°C]{NaH} -(R-O-CH_2-R_F-CH_2O)_n-$$

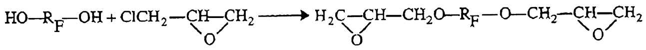
R : CH_2, CH_2OCH_2, $CH_2—C_6H_4—Z—C_6H_4—CH_2$ (with Z : O, S, CO, CH_2, $C(CH_3)_2$)

Fluoroelastomers, thermostable up to about 300°C were obtained (with T_g values ranging between −57°C and −5°C).

Similarly, Cook [167] synthesised original polyethers from the following highly fluorinated diene: $F_2C{=}CFCF_2CFClCF_2CF{=}CF_2$ in alkali medium.

4.1.4. Other fluoropolymers from diols

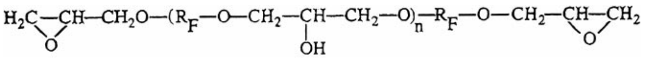
4.1.4.1. Fluorinated diglycidyl polyethers. This synthesis consists in the addition of a chlorohydrine in excess onto a diol [100,101,168,169]:



$$HO-R_F-OH + ClCH_2-\underset{\backslash O/}{CH-CH_2} \longrightarrow \underset{\backslash O/}{H_2C-CH}-CH_2O-R_F-O-CH_2-\underset{\backslash O/}{CH-CH_2}$$

$R_F = C_nF_{2n}$

According to the amount of chlorohydrine, diglycidic ethers with various chain-lengths were obtained:

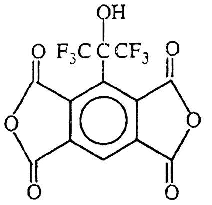


$$\underset{\backslash O/}{H_2C-CH}-CH_2O-(R_F-O-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-O)_n-R_F-O-CH_2-\underset{\backslash O/}{CH-CH_2}$$

Numerous authors have studied such as a reaction according to the nature of the R radical mainly fluoroaromatic, and found low T_g of these fluoropolyethers.

In the same way, O'Rear et al. [168] obtained prepolymers diols from a stoichiometric amount of diol and diglycidic ether. Such products also led to fluorinated polyurethanes.

Griffith's investigations on fluorinated epoxy resins are numerous and it is difficult to summarise them. An interesting patent [170] concerns a large variety of aliphatic and aromatic telechelic diepoxides, cured by various dianhydrides, even fluorinated as the following one:



Thanks to their good resistance to heat, light and to oxidation, such fluorinated epoxy resins have found interesting applications as hydrophobic and oleophobic coatings [168–170].

4.1.4.2. Fluorinated di(meth)acrylates. Fluorodiols are also interesting precursors for the obtaining of telechelic (meth)acrylates [82,102]. Guyman and Bowman [171] investigated the photopolymerisation of these latters which behaved as stabilised ferroelectrical liquid crystals. Such fluorotelechelics have also led to original fluorinated cured networks [105].

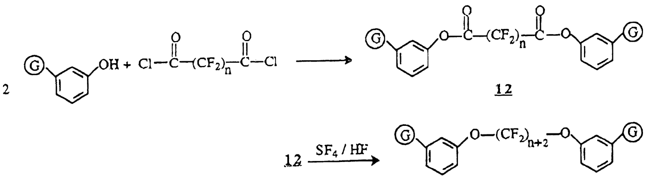
4.1.4.3. Fluorinated dicyanates. The condensation of an excess of cyanogen bromide to fluorodiols led to fluorinated α,ω-dicyanates (Scheme 3) that Snow and Buckley [104] extensively investigated. Such products, under heat, underwent a cyclotrimerisation reaction into triazine as thermostable derivatives exhibiting low electric field permitivity and hydrophobicity.

4.2. From fluorinated diacids

These telechelics are also precursor of a wide variety of compounds (polyesters, polyamides).

In aliphatic series, Anton and Mackinney [143] synthesised fluorinated telechelic diacids from the oxidation of α,ω-dinitriles prepared by addition of HCN to fluorinated nonconjugated dienes. These diacids polycondensed with 1,6-diaminohexane, were interesting precursor of fluorinated hydrophobic polyamides with a high melting point (268°C).

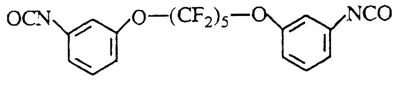
In aromatic series, from acid dichlorides, Webster et al. [172] obtained original telechelic molecules as follows (Ⓖ being a functional group):



Obviously this latter fluorotelechelic was more thermostable than **12** and a decreasing scale of thermostability was suggested:

$$ArCF_2 \sim ArOCF_2 >> ArCH_2OCF_2 \sim ArOCH_2CF_2$$

From this method, this team [113] performed the synthesis of diisocyanates to yield:



which produced polyisocyanurates. These polymers were compared to those prepared from diisocyanates which did not possess the ether bridges and they exhibited identical thermal properties. However, these authors showed that the stability to the hydrolysis of the polymers which had the C_6H_4–OCF_2 group was better than the other one.

4.3. From fluorinated diamines

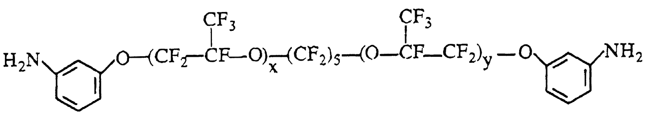
Telechelic diamines can be precursor of polyurethanes, polyamides, polyimides and polyureas.

4.3.1. Polyamides

They are prepared from the polycondensation between α,ω-diacids and α,ω-diamines.

Previously, fluorinated polyamides containing CTFE units were prepared in our Laboratory [173] from fluorotelechelic diesters.

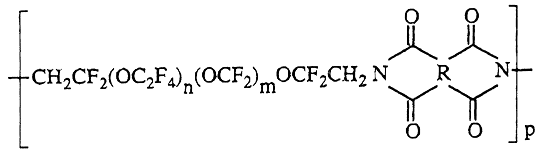
Other original fluorinated polyamides containing Krytox® units which supply high chemical resistance were synthesised by Webster et al. [113]:



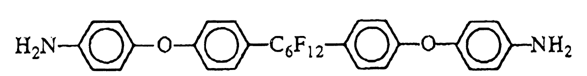
(where $x + y = 0, 1, 2$ and 3) also useful for the synthesis of novel fluoropolyamides and polyimides exhibiting high thermostabilities.

4.3.2. Polyimides

Telechelic diamines are also relevant intermediates for the synthesis of fluorinated polyimides (FPI). Such fluoropolymers exhibit very interesting properties such as high thermal, chemical and dimensional stability, low moisture uptake, dielectric constants, and coefficients of thermal expansion, good mechanical properties which are of special importance in electronic space and automotive applications. Many investigations have been performed on the preparation of FPI which possess hexafluoropropylidene groups. In contrast, few results have been obtained on FPI containing an aliphatic fluorinated group. Critchley et al. [174], followed by Webster [175] used phthalamide containing $(CF_2)_n$ with $n = 3$–8 or $O(CF_2)_5O$ groups, respectively, while Strepparola et al. [176] utilised perfluoropolyether (such as Fomblin®) which led to the following elastomeric FPI:

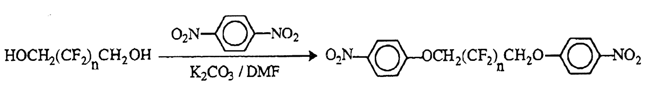


In addition, Labadie and Hedrick [114] synthesised original aromatic diamines:



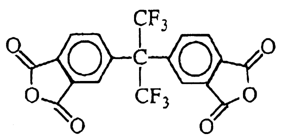
(from 1,6-diiodoperfluorohexane) which displayed good reactivity with pyromellitic dianhydride and yielded random FPI under conventional poly(amic acid) polycondensation conditions. These fluoropolymers exhibit low dielectric constants.

More recently, Eastmond and Paprotny [177] have developed an original method to prepare telechelic fluoroaromatic diamines in high yield (>95%), as follows:



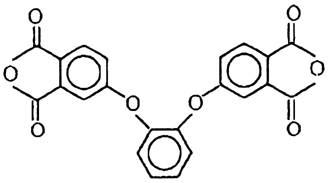
n = 3, 4, 8, 10

They condensed the corresponding diamines with 6 FDA and produced FPIs with high T_g and thermostability and low dielectric constants:



6 FDA

The same team also polycondensed these aromatic diamines with the following aromatic dianhydride to produce a wide range of FPIs, in which the fluorinated segments, distributed between the dianhydride and diamine moieties, led to wholly amorphous to highly crystalline polymers (T_m reaching 330°C) even exhibiting liquid crystallinity [177].



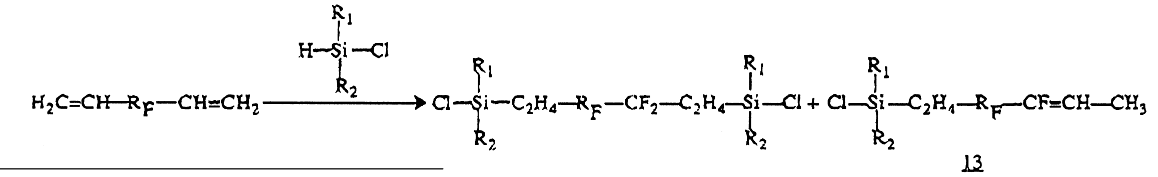
4.4. From fluorinated nonconjugated dienes

The synthesis of fluorinated dienes (Scheme 3) can be achieved:

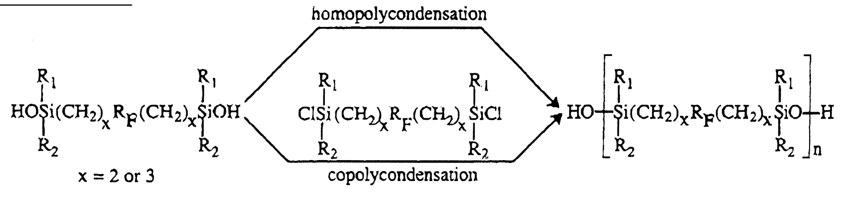
1. from the bis(dehydroiodination) of IC_2H_4–R_F–C_2H_4I [39,46,85,178,179],
2. from the bis(deiodoacetalisation) of $R_F(CH_2CHI$-$CH_2OAc)_2$ [85], or
3. from coupling of 1,3-diiodoperfluoropropane with an excess of 1-iodo-2-chloroethylene [180].

They can be precursor of original telechelic dinitriles [143], involved in cycloadditions with TFE or CTFE [179] or from the thermal addition of C_2F_5I [181], used in novel fluoroelastomers [81] or α,ω-disilanols, these latters being prepared by hydrosilylation reactions of hydrogenochlorosilanes with these dienes (Scheme 3).

Although the hydrosilylation be quite efficient from α,ω-diallyl compounds, even containing a bulky CF_3 side group from hexafluoropropene unit, adjacent to these allyl end-groups [119], similar reaction from α,ω-divinyl dienes led to lower yields. This was explained by the formation of side-product **13** coming from the unexpected $ClR_1R_2SiC_2H_4R_FCF_2CH(CH_3)SiR_1R_2Cl$ isomer:



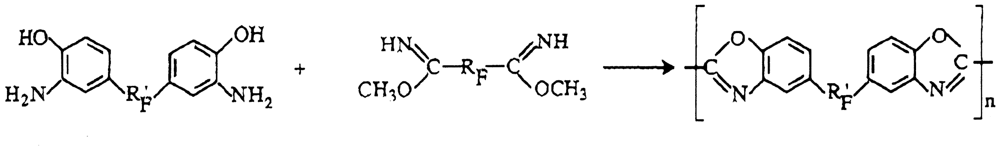
The hydrolysis of these dichlorosilanes yielded the α,ω-disilanols quantitatively. Interestingly, these disilanols can be either homopolycondensed or copolycondensed with α,ω-dichlorodisilanes to produce original hybrid silicones [116–119], as follows:



Such fluorosilicones exhibit very good properties at low and high temperatures. According to the nature of the fluorinated group and to their molecular weights, their T_g values ranged between −26°C and −52°C. They are also quite thermostable and start to decompose from 380°C which is 180°C better than the commercially available Silastic® (poly(methyltrifluoropropylsiloxane)) produced by the Dow Corning Company. They have been used as gaskets, O-rings in aerospace industry.

4.5. Miscellaneous

The monomers for bisbenzoxazoles can also be mentioned. Evers [182] had been investigating this topic for several years. The reaction is as follows:



where R'_F represents $(CF_2)_n$, with n = 3, 8 or $(CF_2)_2$-O-$(CF_2)_5$-O-$(CF_2)_2$.

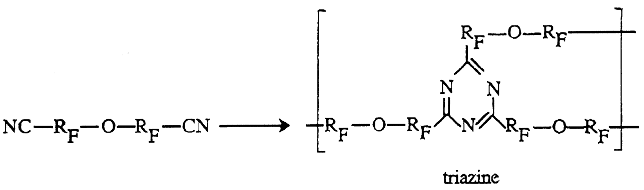
The dimethyl perfluorodiimidate was obtained by addition of methanol onto the corresponding dinitrile, under nitrogen, with a tertiary amine as catalyst.

Evers published numerous investigations on the outstanding thermal properties of these polybenzoxazoles, regarded as one of the most thermostable polymers.

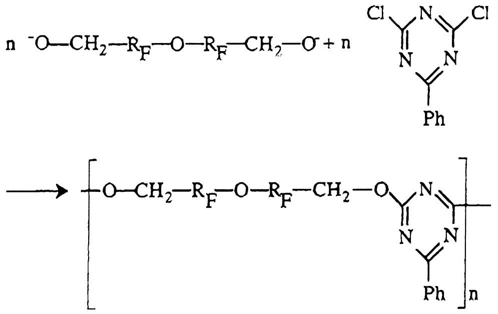
In contrast, in the cases of fluorinated polyurethanes or polyesters, the urethanes or esters links do not exhibit chemical or thermal resistances comparable to those of the fluorinated polyethers. Hence original researches started on the formation of novel stable bridges. Several examples are listed hereafter:

Chain-extension thanks to nitrile bonds:

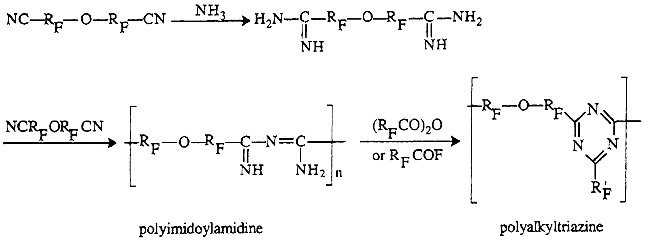
4.5.1. From dinitriles [183]



4.5.2. From dialcoholates [184]



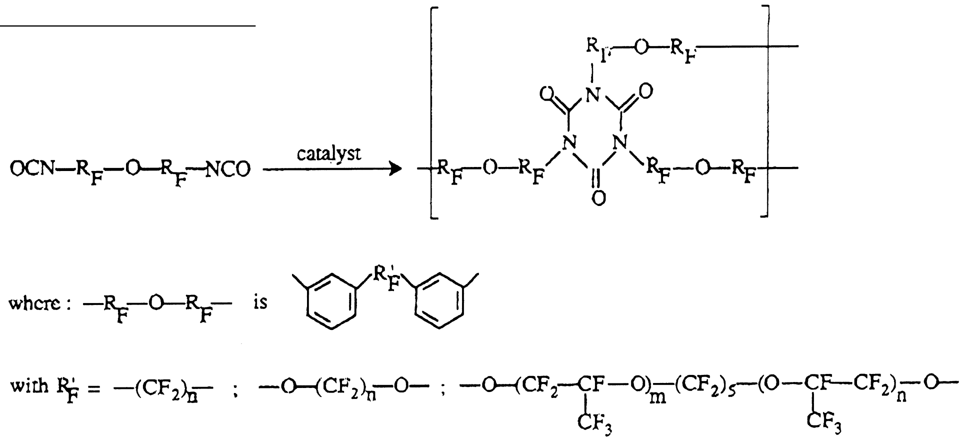
4.5.3. From a dinitrile/nitrile blend [185]



This latter method is interesting since a linear polymer was obtained, contrarily to the direct trimerization of dicyanated compounds.

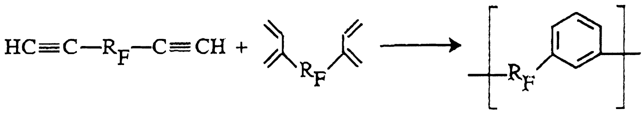
4.6. Chain-extension thanks to isocyanurate bonds

Webster et al. [113] prepared diisocyanated ethers with catalysts such as bis(*N*,*N*′-dimethyl)-1,4-diaminobutane leading to polyisocyanurates with the following structure:



4.7. Chain-extension with benzenic bonds

Such a reaction was carried out by De Pasquale [186] according to the following scheme:



The trimerisation of these α,ω-diacetylenic compounds at 300°C usually leads to thermostable polymers with high T_g [187], high dimensional stability and satisfactory adhesion to metals, low moisture uptake and an easy processability. Such polymers have found useful applications such as prepregs for composite matrix in electronics and space industry.

In addition, stable glassy resins have been produced by thermal polymerisation of fluorinated α,ω-diacetytenes $HC{\equiv}C(CF_2)_nC{\equiv}CH$($n = 6, 8, 10$) [188].

5. Conclusion and perspectives

Although perfluoroalkyl iodides are quite versatile compounds involved in many investigations to introduce a perfluorinated group on a molecule thanks to its low CF_2–I bond dissociation energy, α,ω-diiodofluoroalkanes have not got same fate since less researches have been performed from them. This is mainly due to their difficult synthesis and their price. However, it can be assumed that these drawbacks may be overcome by the improvement of the synthesis which should make them readily available. Such derivatives are quite interesting precursors of a wide variety of fluorinated telechelics, containing a (per)fluorinated chain on their backbone to enhance thermal properties, chemical inertness and resistance to oxidation and ageing.

Although three to four fluorotelechelics only are commercially available about the rather wide variety of fluorinated homopolymers and copolymers, they are still very useful intermediates and represent a window among the fluoropolymers regarded as speciality polymers. Hopefully, the market and the production are in good expansion; thermoplastic elastomers such as Dai-El® are real evidences since they are already produced on an industrial scale.

The synthesis of α,ω-diiodofluoroalkanes has been performed by various authors and obviously from companies producing TFE. From CTFE, the future is not optimistic because of environmental problems caused by this chloroalkene (ozone depletion). However, investigation has not yet been attempted to use VDF, or HFP or a mixture of both readily to molecular iodine.

However, stepwise cotelomerisation of different monomers with $I(C_2F_4)_nI$ appears as an attractive way.

More interesting is the preparation of model fluoroelastomers from these telechelic diiodides by means of the telomerisation. This reaction enables one to introduce key fluorinated base units in a controlled way, leading to well-architectured telomers able to be easily functionalised. So far, few works have been performed and it can be expected that more surveys should be focused on and especially the end-capping of HFP or the cotelomerisations of VDF, tetrafluoroethylene or trifluoroethylene to prepare new blocks able to introduce soft segments in thermostable polymers.

Attempts in functionalisation of these diiodides have been done via two-two step-processes. The first one requires a bis(monoethylenation) for which many efforts have been developed leading already to interesting results; however, still investigations deserve to be continued to allow the bis(ethylenated) diiodide to be chemically changed into a telechelic intermediate in higher yields. As for the second one, it can be expected that the direct functionalisation of IR_FI with ethylenic ω-functional derivatives should find the same success as that involving perfluoroalkyl iodides. However, if vinyl and allyl acetate, allyl alcohol have been mainly used, further choice of monomers could be expected.

Such intermediates allow the synthesis of well-defined polymers as high value added materials (fluorinated polyurethanes, polyesters, polyamides, polyimides, and so on). The fluorinated block in the backbone enables them to achieve good thermal properties. For example, recent investigations have shown that thermostable telechelic dicyanates, fluorosilicones or fluorinated polyamides and polyimides have found interesting application in aerospace, microelectronics or other high tech fields. Although their price is the main drawback, the properties and applications of these materials are still promising, and several industrial applications are already relevant: optical fibers prepared from a primary and, more recently, from a secondary cladding that contains a fluorinated group which allows to monitor the refractive index and also provides good hydrophobicity.

Another example deals with fluoropolyurethanes for which the fluorinated chain seems to reduce the thermodegradation of urethane bridges.

As for fluoropolyimides, if many investigations concern the use of gem-difluoromethyl groups, useful to improve the solubility of the polymers, only few involve reactants containing a linear perfluorinated group. One could expect more surveys in this area. In the same way, recent investigations on hybrid silicones have shown that those having a fluorinated chain in the backbone have got a higher thermostability even above 200°C than that of commercially available fluorosilicones.

Few fluoroaromatic telechelics have been described in this review. However, one interesting approach was pioneered by Mc Loughlin and deeply studied by Eapen in the coupling of *para*-iodo functionalised benzene with fluorodiiodides. It was noted that the nature of the function (electron-withdrawing) is a problem and more efforts should be required to go further.

Even if a couple of companies have overcome the fright to produce these diiodides, it can be expected that a further step be realised for industrial production of new fluorinated telechelic products which would open up new areas.

Such new targets are real challenges and should draw the interest of many academic and industrial researchers in this fascinating area.

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