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Fluorinated oligomers, telomers and (co)polymers: synthesis and applications

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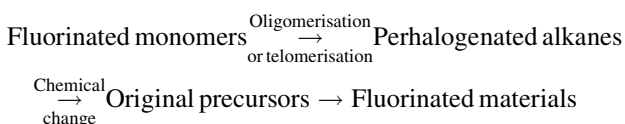8 Rue Ecole Normale, F-34296 Montpellier Cedex 5, France*

Abstract

An overview of the activities in fluorine chemistry at the Laboratory of Macromolecular Chemistry of the Ecole Nationale Supérieure de Chimie de Montpellier is presented, ranging from the synthesis of fluorinated monomers and initiators to the properties and applications of the corresponding (co)polymers. Concerning the monomers, acrylic, vinyl, allyl, styrenic, epoxides or silicon-containing monomers have been prepared. Then, original telomers of fluoroolefins from various chain transfer agents, and their functionalizations have been described. Further, fluorinated (co)polymers have been obtained and characterized: they can be produced either from radical (co)polymerization of commercially available or synthesized fluoromonomers (e.g. acrylic, trifluorovinyl monomers), or from polycondensation (e.g. fluorinated silicones or polyimides) or from polyaddition (e.g. fluorinated polyurethanes). Finally, several properties and applications are given. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The activities in fluorine chemistry have represented about 50% of the research since the creation of our laboratory. The originality of our work comes from the fact that we are able to synthesize fluorinated precursors directly from main fluorinated alkenes: vinylidene fluoride (VDF), chlorotrifluoroethylene (CTFE), trifluoroethylene (TrFE), hexafluoropropylene (HFP), and to a less extent, tetrafluoroethylene (TFE).

Our strategy is based on the following concept:

$$\text{Fluorinated monomers} \xrightarrow[\text{or telomerisation}]{\text{Oligomerisation}} \text{Perhalogenated alkanes}$$

$$\xrightarrow[\text{change}]{\text{Chemical}} \text{Original precursors} \rightarrow \text{Fluorinated materials}$$

From these forerunners, novel polymers bearing fluorinated groups, either in the backbone or as a side-group, have been prepared by radical polymerisation and also by polycondensation. This survey first describes several studies on the (co)telomerisation, and then (co)polymerisation from monomers. Finally, the syntheses of new fluoromonomers which can be used in polyaddition or polycondensation are mentioned, just like the preparation of optical materials, coatings, thermostables and thermoplastic elastomer materials.

It is difficult to summarize our activity on fluoropolymers which has led to one book [1], nine reviews or chapters in books [2–9], 25 patents and more than 180 publications. This topic ranges a wide area from the synthesis of fluorinated initiators and monomers to fluoromaterials.

The first experiments in fluorine chemistry performed in our laboratory in 1971 were dealing with the telomerisation of chlorotrifluoroethylene [10]. Telomerisation reactions are going to be detailed in Section 3 and have extensively been studied in our laboratory (so far, more than 200 papers have been published).

The CTFE telomers thus produced were functionalized and used in further reactions to prepare well-defined polymers, e.g. fluorinated polyurethanes, polyesters. Hence, the activities in fluorine chemistry have been spreading in a wide range of areas: organic synthesis, oligomerisation and telomerisation, and macromolecular chemistry.

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These three main topics have been investigated in both basic and applied points of view and the text is just an overview of our activities illustrated with various examples.

2. Organic chemistry

This field obviously brings up the synthesis of various key reactants such as initiators, transfer agents or monomers.

2.1. Fluorinated initiators

Our interest has been focussed on the synthesis of fluorinated azo or perester initiators although they are known for years [11].

The obtaining of azo compounds was achieved by esterification of commercially available azo initiators (**1**) [12], or condensation of fluorinated acid chloride to α,ω-diol azo as follows [13].
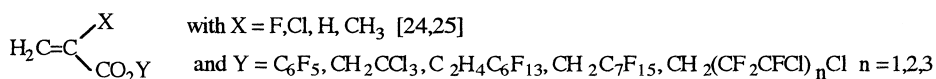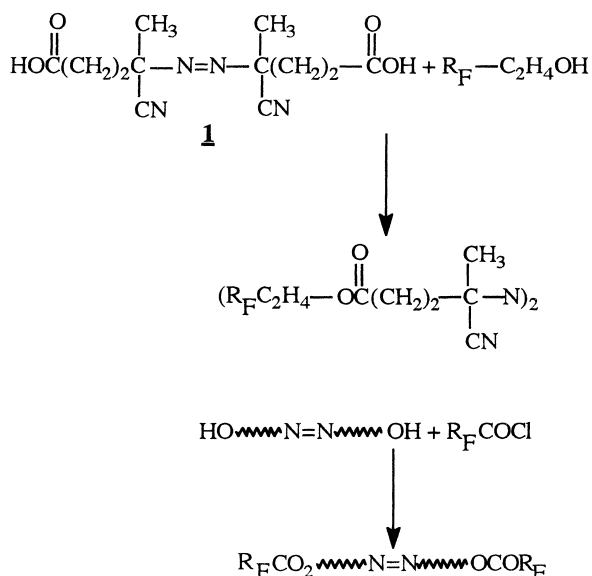
Fluorinated peresters have been synthesised by oxidation of highly fluorinated acid chlorides in the presence of hydrogen peroxide [14,15], leading to $R_FC_2H_4CO_2$–$OCOC_2H_4R_F$.

2.2. Fluorinated transfer agents

Telogens or transfer agents have been obtained from the addition of diatomic molecules to fluorinated alkenes [16], as follows:

1. $Br_2 + F_2C=CFCl \rightarrow BrCF_2CFClBr$ [17]
2. $I-Cl + F_2C=CFCl \rightarrow ClCF_2CFClI$ (major) $+$ Cl_2CFCF_2I (minor) [18]
3. $I_2 + IF_5 \rightarrow [IF]^{F_2C=CFCl} CF_3CFClI$ (major) $+$ $ClCF_2CF_2I$ (minor) [19]
4. $I-Cl + F_2C=CFH \rightarrow ClCF_2CFHI$ (major) $+$ $ClCFHCF_2I$ (minor) [20]
5. $I-Cl + F_2C=CH_2 \rightarrow ICH_2CF_2Cl$ selectively [21]

Semi empirical calculations are under progress in order to confirm the structure of the monoadducts [20–22].

In addition, 1,1,1-trichloro-2,2,2-trifluoroethane was obtained by isomerisation of F-113 [23] in the presence of $AlCl_3$.
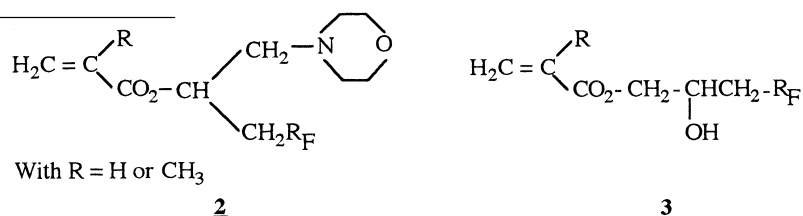
2.3. Synthesis of fluorinated monomers

A rather wide variety of fluoromonomers has been prepared and can fall in two families: acrylates and others.

2.3.1. Acrylates

They can be either acrylates or methacrylates or α-functionalized acrylates. For examples

with X = F, Cl, H, CH$_3$ [24,25]

and Y = C$_6$F$_5$, CH$_2$CCl$_3$, C$_2$H$_4$C$_6$F$_{13}$, CH$_2$C$_7$F$_{15}$, CH$_2$(CF$_2$CFCl)$_n$Cl n = 1,2,3

A recent investigation describes the synthesis of fluorinated (meth)acrylates **2**, and hydroxyl methacrylate **3** useful for textile finishing [26] and optical fibers [27,28], respectively. Interestingly, monomer **2** containing a morpholino group is new.

With R = H or CH$_3$

2   **3**

The following α-functionalized acrylates have been synthesized:

$$H_2C=C \begin{smallmatrix} OCH_2R_F \\ CO_2Et \end{smallmatrix} [29]; \quad H_2C=C \begin{smallmatrix} OCOC_2H_4C_8F_{17} \\ CO_2Et \end{smallmatrix} [30];$$

$$H_2C=C \begin{smallmatrix} OCOC_nH_{2n+1} \\ CO_2C_2H_4C_pF_{2p+1} \end{smallmatrix} [31]$$
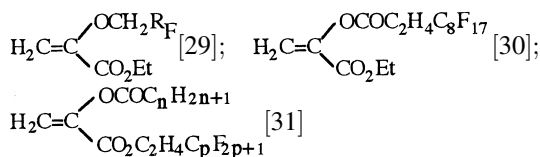
The k_p^2/k_{Te} (where k_p and k_{Te} designate the propagation rate of the monomer and the termination rate, respectively) ratios, which represent the intrinsic reactivity of the monomer, have been determined and compared to these of acrylates and methacrylates [31]. Logically, it is shown the following order for increasing k_p^2/k_{Te}

α-functionalized acrylates < methacrylates < acrylates

In addition, we have shown that the longer the methylene spacer between the ester group and the perfluorinated chain, the higher the reactivity of the monomer [32].

Recently, amphiphilic acrylates have been synthesized from the ring opening addition of fluorinated epoxides [33].
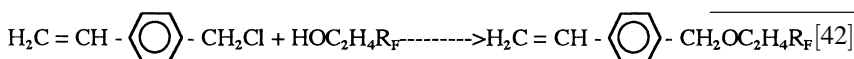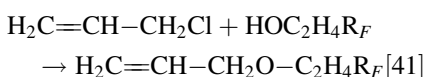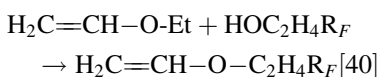
2.3.2. Other fluoromonomers

2.3.2.1. Fluorinated epoxides and allyl type monomers. The synthesis of the fluorinated oxiranes was optimized [34] from fluorinated iodoacetates $R_FCH_2CHICH_2$-$OCOCH_3$ prepared from the radical induced addition of perfluoroalkyl iodides to allyl acetate [35]. Interestingly, we have shown that such an intermediate may undergo a thermal rearrangement into $R_FCH_2CH(OCOCH_3)CH_2I$ [36], which also occurs from $IR_FCH_2CHICH_2OCOCH_3$ [37]. But, such a phenomenon was not observed from the corresponding fluorinated iodohydrins produced similarly from allyl alcohol [38].
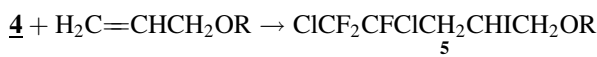
These fluorinated iodoacetates have been also used as precursors of allyl type olefins $R_FCH_2CH=CH_2$ [39]. As for synthesis of fluorinated epoxydes, the rearranged isomers are chemically changed into the unsaturated product.

2.3.2.2. Vinyl type monomers. The more simple fluorinated unsaturated compound $R_FCH=CH_2$ could be prepared by ethylenation of perfluoroalkyl iodides, followed by a dehydroiodination [39].
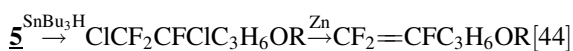
Fluorinated vinyl ether or allyl ether or styrenic derivatives have been synthesized from a fluorinated alcohol by transetherification or Williamson reaction, respectively, according to the following scheme:

$$H_2C=CH-O-Et + HOC_2H_4R_F$$
$$\rightarrow H_2C=CH-O-C_2H_4R_F [40]$$

$$H_2C=CH-CH_2Cl + HOC_2H_4R_F$$
$$\rightarrow H_2C=CH-CH_2O-C_2H_4R_F [41]$$

$$H_2C=CH-\langle\bigcirc\rangle-CH_2Cl + HOC_2H_4R_F \cdots\cdots\rightarrow H_2C=CH-\langle\bigcirc\rangle-CH_2OC_2H_4R_F [42]$$

2.3.2.3. Functional trifluorovinyl monomers. Their synthesis requires the use of an efficient transfer agent containing chlorotrifluoroethylene [18] as follows:

$$ICl + CF_2=CFCl \rightarrow ClCF_2CFClI$$
$$\underline{4}$$

$$\underline{4} + H_2C=CHCH_2OR \rightarrow ClCF_2CFClCH_2CHICH_2OR$$
$$\underline{5}$$

$$(R = H \text{ or } COCH_3)$$

$$\underline{5} \xrightarrow{Zn} CF_2=CFCH_2CH=CH_2 [43]$$

$$\underline{5} \xrightarrow{SnBu_3H} ClCF_2CFClC_3H_6OR \xrightarrow{Zn} CF_2=CFC_3H_6OR [44]$$

On a similar strategy, various trifluorovinyl functional monomers $F_2C=CF–R–G$ were prepared with

R: (CH_2) and G: $\begin{smallmatrix} CH-CH_2 \\ \diagdown O \diagup \end{smallmatrix}$, $CH(OH)CH_2OH$ [45];

R: $(CH_2)_3$ and G: $OCOCH_3$ [44];

R: $(CH_2)_3S$ and G: CH_2CO_2H [46] and C_2H_4OH [46].

The obtaining of $F_2C=CFC_3H_6OH$ was also achieved from $BrCF_2CFClI$ produced from the radical addition of IBr to CTFE [47].

Such monomers can be easily copolymerised with VDF or TFE, leading to functionalised PVDF, PTFE or fluoroelastomers in order to make them crosslinkable (see Section 4.1.2).

In addition, original deuterated monomers such as $F_2C=CFCO_2CD_3$ were also prepared [25].

Hence, a wide range of original initiators, transfer agents and especially monomers have been synthesised, this last family finding much interest in homopolymerisation and copolymerisation as presented in Section 4.

3. Telomerisation

3.1. Introduction

The telomerisation is a model of the synthesis of fluoropolymers in order to predict their degree of polymerisation, their structure, and the mechanism of the reaction.

The telomerisation, introduced for the first time by Hanford and Joyce in 1942 [48], in contrast to polymerisation, usually leads to low molecular weight polymers, called telomers, or even to monoadducts with well-defined endgroups. Such products $\underline{6}$ 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 taxogen or monomer) having ethylenic unsaturation, under radical polymerisation conditions, as follows:

$$X-Y + nM \xrightarrow{free\ radicals} X-(M)_n-Y$$
$$\underline{6}$$
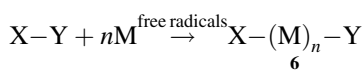
The cleavable bonds of the transfer agents can be C–H, S–H, P–H, Si–H or C–X where X = Cl, Br, I.

Telogen X–Y can be easily cleavable by free radicals (formed according to the conditions of initiation) leading to an X· radical which will be able to react further with monomer.

Telomers **6** are intermediate products between organic compounds (e.g. $n = 1$) and macromolecular species ($n = 100$). Hence, in certain cases, end-groups exhibit a chemical importance which can provide useful opportunities for further functionalisations.

The telomerisation was more investigated by Friedlina et al. [49] in 1966, then improved upon by Starks in 1974 [50], and further developed by Gordon and Loftus [51]. In 1989 and 1994, we reviewed such a reaction [52,53] in which mechanisms and kinetics of radical and redox telomerisations have been described, and we have been invited by Professor Chambers to write a review dealing with the telomerisation of fluoroalkenes [6].

All monomers involved in radical polymerisation can be utilized in telomerisation. Chlorotrifluoroethylene (CTFE) was the first fluoroalkene studied in Boutevin's Ph.D.

Basically, two ways of telomerisation are possible. The first one, called "redox" telomerisation usually leads to low molecular weight telomers in contrast to the "radical" telomerisation [7,49–53]. Few examples are given below.

3.2. Redox and radical telomerisations

3.2.1. Redox telomerisation

This reaction requires a transition metal salt (e.g. CuCl, CuCl$_2$, FeCl$_3$ or even triphenylphosphine complexes) which undergoes an efficient transfer in the last step of telomerisation. The transfer constant to the metal is higher (sometimes 100 times) than that of the telogen.

Deeper investigations have been done in the redox telomerisation of CTFE with CCl$_4$ [10], CCl$_3$Br [54] or also for that of tetrafluoroethylene (TFE) with CCl$_4$ [55] or with perfluoroalkyl iodides [56]. Some works were also performed on that of vinylidene fluoride (VDF) with CCl$_3$R (R = Cl, CO$_2$CH$_3$) [57] or with perfluoroalkyl iodides [58].

3.2.2. Radical telomerisation

Instead of using a metallic catalyst as in the case above, this process can be initiated either thermally, photochemically or in the presence of a radical initiator. This compound can be an azoic, peroxide, perester or peracid which usually allows the radicals formed to react with the telogen to produce the telogenic radical. Then this last species is added to the fluoromonomer.
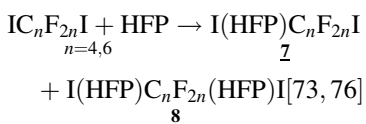
Many investigations were conducted on the telomerisation of CTFE with CCl$_4$ [10,59,60] or Cl$_3$CBr [54].

Later, attempts were performed with HP(O)(OEt)$_2$ [61], mercaptan [62] or chlorofluoroalkyl iodides [63].

Then, the following generations of fluoroolefins were investigated:

1. TFE with perfluoroalkyl iodides initiated thermally [56] or in the presence of radical initiators [64];
2. VDF with either RCCl$_3$ (R = H, Cl, Br [65]), mercaptan [66], methanol [67], fluorinated alcohols [68], dialkyl phosphonate [69], BrCF$_2$CFClBr, Br$_2$CF$_2$ [68], α,ω-diiodoperfluoroalkanes [70] or perfluoroalkyl iodides [58]. In this last case, the nature of the initiation is crucial since the thermal initiation produces the first five telomers, whereas that initiated from peroxides or from iron salts led to high molecular weight-telomers, or to the monoadduct, respectively [58];
3. Trifluoroethylene (TrFE) with either ICl [20] or R$_F$I [71];
4. Hexafluoropropene (HFP) with either methanol [68], R$_F$I [72], α,ω-diiodoperfluoroalkanes [73] or α,ω-diiodofluoroalkanes containing VDF and TFE base-units [74].

In the same way, well-architectured fluorinated cotelomers were produced either from perfluoroalkyl iodides (Scheme 1) [75] or α,ω-diiodo(per)fluoroalkanes by stepwise cotelomerisations as follows:

$$IC_nF_{2n}I + HFP \rightarrow \underset{\textbf{7}}{I(HFP)C_nF_{2n}I}$$
$$n=4,6$$

$$+ \underset{\textbf{8}}{I(HFP)C_nF_{2n}(HFP)I} [73,76]$$

$$\underline{\textbf{8}} + VDF \rightarrow I(VDF)_p(HFP)C_nF_{2n}(HFP)(VDF)_mI$$
$$m+p=4-20$$

It is also noted that direct cotelomerisation in one pot led to either random cotelomers (case of HOC$_2$H$_4$SH/VDF/CTFE [66,77]), or alternated cotelomers (case of C$_6$F$_{13}$C$_2$H$_4$SH/CTFE/vinyl ethers (VE) [62,78], and RSH/CF$_2$=CCl$_2$/VE [79]).

Kinetic laws [80–82] (i.e. control of the degree of polymerisation or telomerisation, control of the reactants and products concentrations versus time and determination of the polydispersity and of various kinetical rate-constants) have been used and successfully adapted onto CTFE/CCl$_4$ and CTFE/CCl$_3$Br systems.

In addition, deeper investigations were performed in order to:

1. Understand and to compare the reactivity of the telogens for fluoroolefins. For instance, the following decreasing reactivity series of fluoroalkenes about the same perfluoroalkyl iodides [83]:

   $$TFE = VDF > TrFE > HFP > CTFE \gg ClCF_2CF=CF_2$$
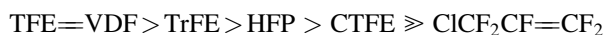
   The last one leads to unexpected perfluoroolefins R$_F$CF=CF$_2$ [84].
2. Establish a relationship dealing with the structure of the telogen and the reinitiated thermally chain transfer [56,64];

$R_F(VDF)_n(TrFE)_mI \xrightarrow{E} R_F(VDF)_n(TrFE)_mC_2H_4I$

$R_F(VDF)_nI$

$R_F(VDF)_n(HFP)I \xrightarrow{E} R_F(VDF)_n(HFP)C_2H_4I$

$R_F(TrFE)_x(VDF)_yI \xrightarrow{E} R_F(TrFE)_x(VDF)_yC_2H_4I$

R_F—I $\xrightarrow{TrFE} R_F(TrFE)_xI$

$R_F(TrFE)_x(HFP)I \xrightarrow{E} R_F(TrFE)_x(HFP)C_2H_4I$

$R_F(HFP)(VDF)_nI \xrightarrow{E} R_F(HFP)(VDF)_nC_2H_4I$

$R_F(HFP)I$

$R_F(HFP)(TrFE)_mI \xrightarrow{E} R_F(HFP)(TrFE)_mC_2H_4I$
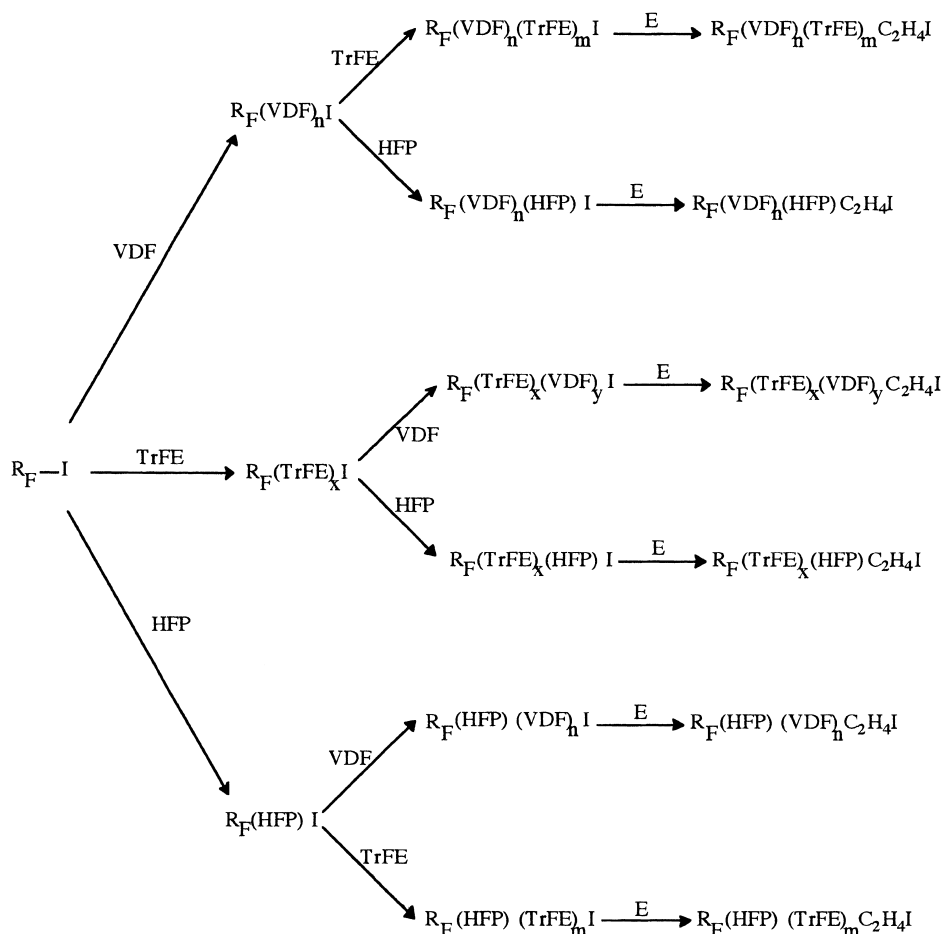
Scheme 1. Basic strategy of well-architectured cotelomers of vinylidene fluoride (VDF), trifluoroethylene (TrFE), chlorotrifluoroethylene (CTFE), hexafluoropropene (HFP) and ethylene (E) [75].

3. Study the defects of chaining (e.g. $IC_2F_4(VDF)I$ monoadduct contains $IC_2F_4CH_2CF_2I$ isomer only, whereas the diadduct is composed of 50% of $I(CF_2CH_2)C_2F_4(CH_2CF_2)I$, 47% of $IC_2F_4(CH_2CF_2)$-$(CH_2CF_2)I$ and 3% of $IC_2F_4(CH_2CF_2)(CF_2CH_2)I$ [70].

But starting from IC_4F_8I, the diadduct contains 90% of $ICF_2CH_2C_4F_8CH_2CF_2I$, 8% of $IC_4F_8CH_2CF_2CH_2CF_2I$ and 2% of $IC_4F_8CH_2CF_2CF_2CH_2I$ [70]. Similarly $R_F(HFP)I$ is composed of reverse R_FCFCF_2I over CF_3 adduct (1–10%) [72].

An explanation was proposed by the balance: electrophilicity of the telogenic radical and the "nucleophilicity" of the olefin [58,71,72] and some explanations are proposed from semi-empirical calculations [22].

3.3. Use of fluorinated transfer agents in telomerisation

The telomerisation of acrylamide with perfluoroalkyl iodides (R_FI) was successfully achieved leading to $R_F(CH_2CH-)_nI$ with $O=CNH_2$ telomers used as novel surfactants [85], presently commercially available from Elf Atochem. More recently, the telomerisation of 1,3-butadiene with R_FI was

achieved and the transfer constants of R_FI were assessed. The high values ($C_r = 2.5$) thus led to a mixture of fluorinated polybutadienes and oligobutadienes [86].

A similar behaviour was noted in the telomerisations of styrene [87] or diethyl allyl phosphonates [88] with $C_6F_{13}C_2H_4SH$ which were more selective contrary to that of methacrylic monomers [89] or even acrylic acid that could be performed in emulsion in water, even in the presence of this fluorinated mercaptan [90].

3.4. Chemical modification of fluorinated telomers

Chemical change of these produced telomers could be achieved in various ways to synthesise novel monomers.

3.4.1. Vinyl or allyl monomers

Fluoroalkyl iodide telomers are interesting precursors of unsaturated products as follows [39,83] (although the ethylenation of trifluoroiodomethane or the dehydrohalogenation of $R_FC_2H_4I$ were already reported by Haszeldine in 1949 [91] or reviewed by Hudlicky in 1976 [16], respectively)

$$R'_F I + H_2C=CH_2 \longrightarrow R'_F C_2H_4I \xrightarrow{\text{KOH}} R'_F CH=CH_2 \ [39, 83]$$

$$R'_F I + H_2C=CHCH_2OCOCH_3 \longrightarrow R'_F CH_2CHICH_2OCOCH_3 \rightleftharpoons R'_F CH_2CH(OCOCH_3)CH_2I$$

KOH ↙　　↓ Zn

$$R_F CH_2-\underset{\underset{O}{\diagdown\diagup}}{CH}-CH_2 \qquad R'_F CH_2CH=CH_2 \ [39,83]$$

A similar approach was also possible from α,ω-diiodoperfluoroalkanes [92] or α,ω-diiodoperfluoroalkanes containing VDF/HFP base units [93], leading to fluorinated non-conjugated dienes.

These vinyl or allyl fluorotelomers are interesting precursors of fluorosilanes [39,94–98] or fluorinated trialkoxysilanes precursors of original fluorosilsesquioxanes obtained by a sol–gel process [99].

3.4.2. Hydroxyl, carboxy or acetate functional telomers

Such functional telomers have been mainly formed from CTFE telomers. Indeed, $Cl_3C(C_2F_3Cl)_xX$ (where X represents Cl or Br) can be chemically changed into $HO_2C(C_2F_3Cl)_xX$ [100,101], $HOCH_2(C_2F_3Cl)_xX$ [102], $CH_3CO_2CH_2CHClCH_2CCl_2(C_2F_3Cl)_xX$ [103], alcohols [101–103] or epoxides [104] or require an ethylene spacer to generate $ClC_2H_4CCl_2(C_2F_3Cl)_xX$ [105], $CH_3CO_2C_2H_4$-$CCl_2(C_2F_3Cl)_xX$ [106].

In addition, fluorinated phosphonates or phosphonic acids have also been prepared by addition of fluorinated thiols to diethyl allyl phosphonate [88].

Such a concept was successfully applied to α,ω-bis(trichloromethyl) telomers, $Cl_3C(C_2F_3Cl)CF_2CCl_3$ to generate telechelic chlorofluoroacids, diols [107–109] and diacetates [109]. Further telechelic fluorodiols can be achieved from the bis(monoaddition) of α,ω-diiodoperfluoroalkanes (prepared via various ways [110]) to allyl alcohol [111], as follows:

$$HOCH_2CH=CH_2 + I-R_F-I \xrightarrow[2) \text{SnBu}_3\text{H}]{1) \text{AIBN}} HOC_3H_6-R_F-C_3H_6OH$$

Interestingly, fluorinated telechelic diols have been reviewed to be excellent candidates for fluorinated well-defined polymers [4,5].

4. Macromolecular chemistry

The synthesis and the characterisation of fluoropolymers and chemical change of polymers have been investigated in our laboratory. Our fluoropolymers can be prepared either by direct radical homopolymerisation, copolymerisation or by polycondensation.

4.1. Radical polymerisation

4.1.1. Homopolymerisation

As mentioned in Section 2.3.1, homopolymerisation of acrylic monomer allowed the determination of k_p^2/k_{Te} representing the reactivity of the monomer. Obviously, acrylates react better than methacrylates, these latter having a reactivity rather similar to that of α-functionalized acrylates.

These polyfluoro acrylates are quite interesting materials either for textile finishings (case of α-functionalized acrylate or morpholino containing polyfluoroacrylate with a good hydrophobic–hydrophilic balance) or optic materials [6,112–114] (thanks to the low-absorption in visible and near IR of C–F and C–Cl bonds) and Table 1 shows the refractive indexes and the glass transition temperatures of the obtained polymers [25].

We found it interesting to determine the molecular weights of fluoropolymers by an original technique. Indeed, the use of "labelled" radical initiators (either chlorinated or aromatic diazo) in the radical polymerization of fluorinated (meth)acrylates allowed us to achieve such a goal from the chlorine content (via elemental analysis) or the aromatic groups well-identified by ^{1}H NMR of the end-groups coming from the initiator [115].

We have also investigated the kinetics of homopolymerisation of VDF in methanol as solvent, allowing us to determine the k_p^2/k_{Te} [116].

We have also been interested by the photopolymerisation of new fluoroacrylates $H_2C=CH-CO_2-R-C_nF_{2n+1}$ with R: $(CH_2)_x$; $x = 2, 3$ and $n = 6, 8$ [117] and R: $C_2H_4SC_3H_6$ and $n = 6, 8$ [118] and also cotelomers of trifluoroethyl methacrylate (TFEMA) and acrylic acid [119]. These telomers reacted with glycidyl methacrylate which brought the photocuring group as follows:

$$HOC_2H_4SH + H_2C=C\overset{\diagup CH_3}{\underset{\diagdown CO_2CH_2CF_3}{}} + H_2C=CH\overset{}{\underset{\diagdown CO_2H}{}} \xrightarrow{\text{AIBN}} HOC_2H_4S\,(\text{TFEMA})_x(\text{AA})_y H$$

　　　　TFEMA　　　　　　AA　　　　　　　　**9**

$$\mathbf{9} + H_2C=C\overset{\diagup CH_3}{\underset{\diagdown CO_2CH_2CH-CH_2}{}} \longrightarrow HOC_2H_4S\,(\text{TFEMA})_x(\text{AA})_{y1}(CH_2-CH)_{y2}H$$

10

$$\mathbf{10} \xrightarrow{h\upsilon} \text{Crosslinked Network}$$

Table 1
Physical and optical characteristics of halogenated polymers[a]

Homopolymer	n^{20}	T_g (°C)	N_{CH} (10^{-3})
Acrylic			
$-(CH_2-CCl)-$ $\|$ $CO_2C_6F_5$	1.5000	120	12
$-(CH_2-CF)-$ $\|$ $CO_2C_6F_5$	1.4650	160	14
$-(CH_2-C(CH_3))-$ $\|$ $CO_2CH_2(CF_2CFCl)_3Cl$	1.4438	31	26
$-(CH_2-CCl)-$ $\|$ $CO_2CH_2CCl_3$	1.5342	140	28
$-(CH_2-CF)-$ $\|$ $CO_2CH_2CCl_3$	1.4995	124	30
$-(CH_2-C(CH_3))-$ $\|$ $CO_2C_6F_5$	1.4873	125	32
$-(CH_2-C(CH_3))-$ $\|$ $CO_2CH_2(CF_2CFCl)_2Cl$	1.4551	47	34
$-(CH_2-C(CH_3))-$ $\|$ $CO_2C_2H_4C_6F_{13}$	1.3800	49	37
$-(CH_2-C(CH_3))-$ $\|$ $CO_2CHClCCl_3$	1.5179	165	37
$-(CH_2-CF)-$ $\|$ $CO_2CH_2CF_3$	1.3850	123	39
$-(CH_2-CF)-$ $\|$ $CO_2CH_2CF_2CF_2H$	1.3980	95	42
$-(CH_2-C(CH_3))-$ $\|$ $CO_2CH_2CF_2CFCl_2$	1.4639	67	45
$-(CH_2-C(CH_3))-$ $\|$ $CO_2CH_2CCl_3$	1.5251	134	49
$-(CH_2-CF)-$ $\|$ $CO_2C_6H_5$	1.5600	180	56
$-(CH_2-C(CH_3))-$ $\|$ $CO_2CH_2CF_3$	1.4146	80	60
$-(CH_2-C(CH_3))-$ $\|$ $CO_2CH_2CF_2CF_2H$	1.4220	71	61

Table 1 (*Continued*)

Homopolymer	n^{20}	T_g (°C)	N_{CH} (10^{-3})
$-(CH_2-CF)-$ $\|$ CO_2CH_3	1.4600	140	68
$-(CH_2-C(CH_3))-$ $\|$ CO_2CH_3	1.4890	105	92
Vinyl carbonate			
$-(CH_2-CH)-$ $\|$ $OCO_2C_2H_4C_6F_{13}$	1.3342	37	26
$-(CH_2-CH)-$ $\|$ $OCO_2CH_2CCl_3$	1.4965	74	36
$-(CH_2-CH)-$ $\|$ OCO_2CD_3	1.4619	55	37
$-(CH_2-CH)-$ $\|$ $OCO_2CH_2CF_3$	1.4045	57	47
$-(CH_2-CH)-$ $\|$ $OCO_2C_6F_5$	–	65	–

[a] n^{20} is the refractive index at 20°C, T_g is the glass transition temperature, N_{CH} is the number of C–H bonds per cm^3.

4.1.2. Copolymerisation

The copolymerisation of two monomers both or only one being fluorinated, has drawn more interest. Fluorinated alkenes are known to be electron withdrawing and have a tendency to react with electrodonating monomers to lead to alternating copolymers. The reactivity of both comonomers and the mechanism of such a copolymerisation was reviewed [120–122].

This was easily illustrated by key couples such as CTFE/vinyl ethers [62]; VDF/vinyl ethers [62,77]; CF$_2$=CCl$_2$/vinyl ethers [79]; VDF/vinyl acetate [77]. The applications searched are devoted to paints and coatings. In addition, fluorinated maleimides have been synthesized and react easily with vinyl ethers yielding alternated copolymers [123,124]. In the same way, non-fluorinated maleimide (acceptor) reacts successfully with fluorinated alkyl allyl ether (donor) [125].
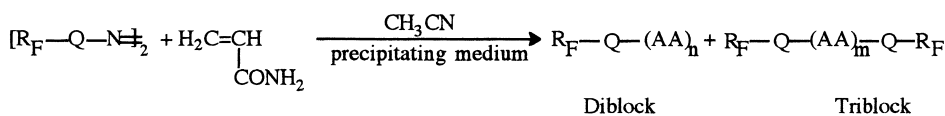
On the other hand, numerous copolymerisations have not been alternated. For example, this is the case of the couple morpholinoethyl methacrylate/fluorinated (meth)acrylate or α-acetoxy methacrylate for which the reactivity ratio [126] and the Alfrey and Price parameters (*Q* and *e*) [127] of each comonomer have been determined. In this case too, the application concerns textile materials.

Recently, we have studied the copolymerisation of tri-fluorovinyl monomers (specified in Section 2.3.2.3) with

TFE and VDF [128]. The reactivity ratios were determined and showed that random copolymers were produced. TFE was noted to be more reactive than hydroxy comonomer [129,130] whereas acetoxy [131] and thioacetoxy [132] ones demonstrated a higher tendency to react, compared to VDF.

4.1.3. Obtaining of well architectured polymers

Beside fluorinated telechelics (described in Sections 3.4.2, 4.2 and 4.4.1) or graft copolymers (mentioned in Section 4.4.2), interesting block copolymers have been prepared. For example, the radical polymerization of acrylamide with an azoïc initiator containing two perfluorinated end-groups led to a mixture of di- or triblock amphiphilic copolymers [12] according to the following reaction (where R_F and Q designate C_8F_{17} and $C_2H_4OCOC_2H_4C(CH_3,CN)$, respectively:

a monomer M (such as styrene, methyl methacrylate and ethyl acrylate) with fluorinated telomers of VDF exhibiting a CCl_3 end-group [65], as follows:

$$Cl_3C(VDF)_nH + M \underset{bulk}{\overset{CuCl/bipyridine}{\longrightarrow}} P(VDF-b-M)$$
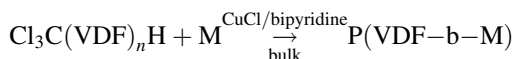
Interestingly, these copolymers were synthesized in a living behaviour up to molecular weights of 60,000 and showed a narrow polydispersity ($I_p < 1.20$), whatever the molecular weight of the starting fluorinated telomer (n ranging from 1 to about 100) [135].

4.2. Polycondensation

This way of polymerisation is quite useful for the synth-

It was noted that the amount of triblock copolymer ranged from 50 to 85% when the initial [initiator]$_0$/[acrylamide]$_0$

esis of fluorosilicones, prepared according to the following scheme [8,136–140]:
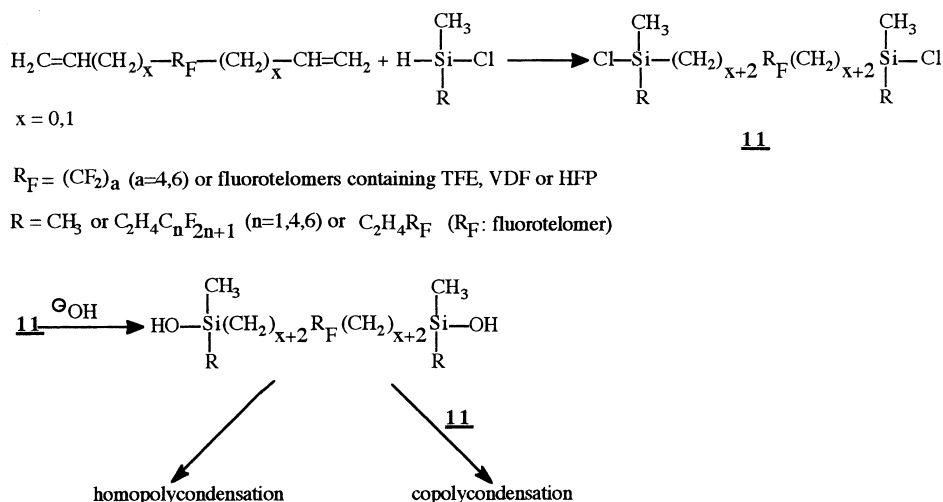
molar ratio varied from 1 to 7%.

These block copolymers showed interesting associative properties [12] and triblock poly(acrylamide) were used as additives in fire-fighting aqueous formulations [133] or as associative thickener in painting formulations [134].

Another example of block copolymers was observed from the atom transfer radical polymerization (ATRP) of

Similarly, random or alternated copolymers **12** have been synthesized, their thermal properties (T_g and decomposition temperatures) have been determined and they depend on the structures of R_F, R, R′ groups and x [8,138]. By comparison with those of commercially available fluorosilicones, our polymers show much better properties (improvement of the thermostability of 150°C and
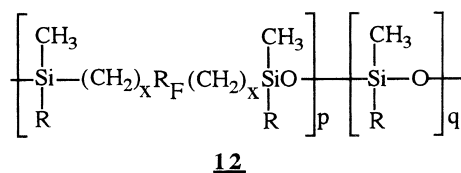
Table 2
Molecular weights and thermal properties of fluorinated hybrid homopolymers HO$\left[\begin{array}{c} CH_3 \\ | \\ SiC_2H_4(CH_2)_x-R'-(CH_2)_xC_2H_4SiO \\ | \\ R \end{array}\begin{array}{c} CH_3 \\ | \\ \\ | \\ R \end{array}\right]_n$

R	R'	x	SEC (M_n)	DSC (10°C/min)			TGA (5°C/min)		State
				T_g	T_m	T_c	$T_{50\%}$ (N$_2$)	$T_{50\%}$ (Air)	
CH$_3$	C$_6$F$_{12}$	0	10000	−53	26	−11	470	380	Solid
		1	10000	−40	25	−27	465	330	Solid
CF$_3$C$_2$H$_4$	C$_6$F$_{12}$	0	40000	−28			480	410	Oil
		1	14000	−18			465	360	Oil
C$_4$F$_9$C$_2$H$_4$	C$_6$F$_{12}$	0	30000	−42			490	360	Oil
		1	12000	−29			470	310	Oil
CH$_3$	HFP/C$_4$F$_8$/HFP	1	10000	−49			425	300	Oil
CF$_3$C$_2$H$_4$	HFP/C$_4$F$_8$/HFP	1	30000	−34			445	310	Oil
C$_4$F$_9$C$_2$H$_4$	HFP/C$_4$F$_8$/HFP	1	50000	−38			450	320	Oil
	C$_2$F$_4$/VF$_2$/HFP	1	9000	−47			420	315	Oil

good properties at low temperatures: −40°C) [8,138–140] (Tables 2–4).

$$\left[\begin{array}{c} CH_3 \\ | \\ -Si-(CH_2)_xR_F(CH_2)_x SiO- \\ | \\ R \end{array}\begin{array}{c} CH_3 \\ | \\ \\ | \\ R \end{array}\right]_p \left[\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ R \end{array}\right]_q$$

12

These fluorosilicone elastomers are interesting candidates for connectics, lubricants and hydraulic fluids.

In addition, new photocrosslinkable fluorinated polysiloxanes were also prepared by copolycondensation of commercially available α,ω-dihydroxypolydimethyl siloxanes with a fluorinated grafted triethoxysilane [141,142].

In addition, homopolymerisation of quinazolones bearing chlorofluorinated side chains led to thermostable polymers ($T_g > 220$°C, begining of degradation from 320°C) [143].

Table 3
Molecular weights (from ^{1}H NMR) and thermal properties of fluorinated hybrid silicones random copolymers

	R$_1$	R$_2$	^{1}H NMR					SEC		DSC (10°C/min)	TGA (5°C/min)
			x	y	p	DP$_n$	M_n	M_n	(M_w/M_n)	T_g	$T_{50\%}$ (N$_2$)
	CH$_3$	C$_2$H$_4$C$_6$F$_{13}$	1	0.68	10.5	17.8	10000	10800	1.17	−40	475
	C$_2$H$_4$CF$_3$	C$_2$H$_4$C$_6$F$_{13}$	1	0.65	8.8	14.5	8900	5300	1.56	−42	460
	CH$_3$	C$_2$H$_4$CF(CF$_3$)C$_5$F$_{11}$	1	0.63	9.4	15.3	9200	7200	1.34	−44	470
	CH$_3$	C$_2$H$_4$CF(CF$_3$)CF$_2$CFCl$_3$	1	0.60	10.3	16.5	9300	9700	1.94	−46	460

$$C_6H_5-SiO\left[\begin{array}{c} CH_3\ CH_3 \\ | \quad | \\ SiC_2H_4C_6F_{12}C_2H_4SiO)_x \\ | \quad | \\ CH_3\ C_2H_4CF_3 \end{array}\right]\begin{array}{c} CH_3 \\ | \\ (SiO)_y \\ | \\ C_2H_4CF_3 \end{array}\begin{array}{c} R_1 \\ | \\ {}_p \\ | \\ R_2 \end{array}\begin{array}{c} CH_3 \\ | \\ SiC_6H_5 \\ | \\ CH_3 \end{array}$$

Table 4
Molecular weights (from SEC) and thermal properties of fluorinated hybrid silicones alternated copolymers

			SEC			DSC (10°C/min)	TGA (5°C/min)
			M_n	DP$_n$	M_w/M_n	T_g	$T_{50\%}$ (N$_2$)
$\left(\begin{array}{c} CH_3 \\ | \\ Si-C_2H_4C_6F_{12}C_2H_4-SiO \\ | \\ R_1 \end{array}\begin{array}{c} CH_3 \\ | \\ \\ | \\ R_1 \end{array}\right)$ **A**	R$_1$ = C$_2$H$_4$CF$_3$	(AB)$_n$	22000	21	1.8	−35	475
$\begin{array}{c} R_1 \\ | \\ (SiO) \\ | \\ R_2 \end{array}$ **B**	R$_2$ = C$_2$H$_4$C$_6$F$_{13}$	(ABA)$_n$	28000	16	1.6	−31	475
	R$_1$ = R$_2$ = C$_2$H$_4$C$_4$F$_9$	(BAB)$_n$	11000	7	1.35	−59	330

4.3. Ring opening polymerization of fluorinated oxetanes

New fluorooxetanes **13** have been synthesized and cationically polymerized producing telechelic diols with perfluorinated pendant groups ($M_n \sim 3000-5000$) according to the following scheme [144]:

4.4. Chemical modification of polymers

4.4.1. Telechelic diols containing fluorinated side groups

The radical addition of fluorinated mercaptans [145,146] or the hydrosilylation of fluorinated hydrogenosilanes [147] onto the double bonds of hydroxytelechelic polybutadiene have led to novel long chain diols bearing fluorinated side groups as follows:

Scheme 2. Various fluorinated products obtained from R_FI or VDF/TrFE/HFP/CTFE (co)telomers.

4.4.2. Graft copolymers

Original graft copolymers have been prepared from macroperoxides produced by ozonization of PVDF, as follows:
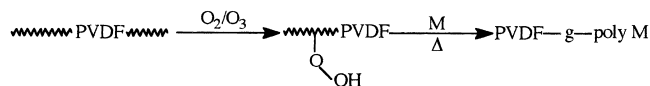
where M represents glycidyl methacrylate, acrylic acid [148] or $H_2C=CHCO_2C_2H_4P(O)(OH)_2$ [149,150].

The application concerns the preparation of new ion exchange membranes, whereas in the case of the polymer containing phosphorated grafts, anticorrosion properties are observed [149,150].

In addition, polyethylenes bearing fluorinated grafts were obtained by grafting a fluorinated maleimide onto HDPE [151].

5. Conclusion

In our laboratory, fluorine chemistry is touching a wide range of areas, from the organic to macromolecular chemistries. Our interest relies on the synthesis of novel molecules and materials which exhibit outstanding properties such as thermal, chemical and UV stabilities, low surface energy, optical properties, etc.

Traditional or step-wise or direct (co)telomerisations have produced a large amount of telomers, functionalized into unsaturated derivatives or hydroxy, carboxy, ester, mercaptan, epoxide (Scheme 2) which are precursors of high value added polymers: fluorosilicones, poly(fluoroacrylates) or well-controlled polymers such as original polycondensates (polyimides) or block and graft copolymers.

Acknowledgements

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