Supporting Information

"First MALDI-TOF Mass Spectrometry of Vinylidene fluoride Telomers Endowed with Low Defect-Chaining".

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Small overview on the telomerisation of vinylindene fluoride.

Vinylidene fluoride (or 1,1-difluoroethylene, VDF or VF_2) exhibits many advantages. It is a non-toxic, non-hazardous, non-explosive (in contrast to tetrafluoroethylene or trifluoroethylene) gas and environmental friendly (it does not contain any chlorine or bromine atoms). Moreover, it can easily polymerise under radical initiation [137] but also under ionic conditions [138]. In addition, it is a non-symmetrical alkene and its propagation may lead to a certain content of defect (i.e., tail to tail or head to head) of VDF chaining. PVDF [137,139] is an attractive polymer endowed with remarkable properties. It is piezo and pyroelectric, resistant to acids, solvents (except DMF, dimethyl acetamide, DMSO and trifluorotoluene), to nuclear radiation, and is a gas barrier polymer. Hence, it has been used in many applications such as loudspeakers, microphones, pianokeys, pyroelectric sensors, IR detectors, paints and coating and it has been involved in various fields of mines, engineering, biomedical, and food industries. However, the high chemical inertness linked to a high crystallinity rate, its difficult crosslinking, and its base sensitivity are limitations. That is why many copolymers of VDF have been synthesised and have been commercialised by most international companies producing VDF [2a,5,137,140].

The telomerisation of vinylidene fluoride has been investigated by many authors. Almost all kinds of transfer agents have been used, requiring various means of initiation: thermal, photochemical or from systems involving redox catalysts or radical initiators (Tables 3 [141-172] and in Table 4 [173-183]), and also hypofluorites.

1 Thermal initiation

In contrast to many telogens used in the telomerisation of VDF initiated photochemically or in the presence of radical initiators, few transfer agents have been used in the thermal telomerisation (Table 3). Only two series have to be considered: those which exhibit C-Br or a C-I cleavable bonds (no work involving a telogen with a C-Cl bond is described in the literature) and hypofluorites.

Table 1

Hauptschein *et al.* [141] have shown that VDF reacts with CF_2Br_2 and $CF_3CFBrCF_2Br$ at 190 °C and 220 °C, respectively, yielding telomeric distributions $R_F(CH_2CF_2)_nBr$ n = 1-8 (the $CF(CF_3)Br$ group being more reactive than CF_2Br in the case of the second telogen).

Concerning iodinated transfer agents, almost all perfluoroalkyl iodides and α,ω-diiodoperfluoroalkanes were successfully utilised in thermal telomerisation of VDF. One of the pioneers of such work was Hauptschein *et al.* [141,148] who used CF_3I, C_2F_5I, n-C_3F_7I, i-C_3F_7I, $ClCF_2CFClI$ and $ClCF_2CFICF_3$ at 185-220 °C leading to high telogen-conversions. Later, Apsey *et al.* [38] and Balagué *et al.* [39,40] used i-C_3F_7I and linear $C_nF_{2n+1}I$ (n=4,6,8) telogens, leading to telomeric distributions, with a better reactivity of the former branched

transfer agent. We have shown that, while the monoadduct exhibits only the structure $R_FCH_2CF_2I$, the diadduct is composed of two isomers [39,40], while the triadduct had a rather complex structure [139].

An original telogen $(CF_3)_3CI$ was successfully used by a Chinese team [151] as follows :

$$(CF_3)_3CI + nH_2C{=}CF_2 \longrightarrow (F_3C)_3C(CH_2CF_2)_nI \ (n=1,2).$$

Another example regarding the thermal initiation of VDF was investigated three years ago in the presence of octafluoro[2.2]paracyclophane (bearing trifluoromethyl groups) [171] although this fluorinated derivative can be regarded as initiator. Indeed, from 160 °C such an aromatic fluorinated reactant generates a trifluoromethyl radical able to initiate the telomerisation of VDF. However, the formation of the stable paracyclophane was left inert in the medium while recombination of primary oligo(VDF) radicals occurred.

In conclusion, two main series of transfer agents have been used having specific cleavable bonds (C-X with X=Br and I). They lead to telomeric distributions, in good yields, with more or less high $\overline{DP_n}$ according to the nature of the telogen (and especially the electrophilicity of the radical generated), the experimental conditions (initial pressures, [VDF]/[Telogen] molar ratios, and temperatures). However, our investigations have shown that the monoadduct is composed of $R_FCH_2CF_2X$ as the sole isomer, while the diadduct already consists of two isomers.

2 Radical initiation

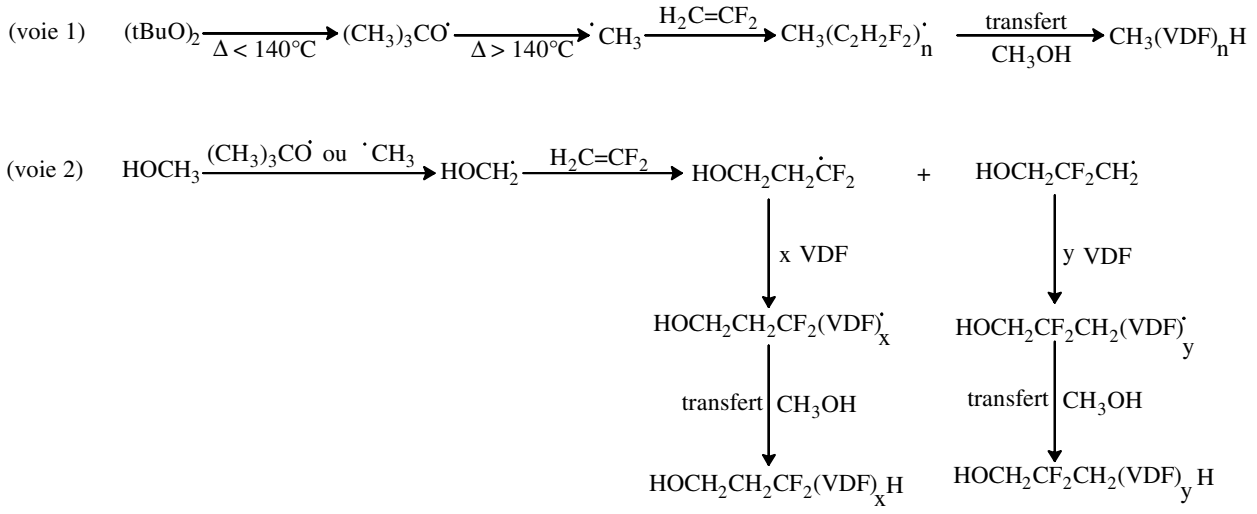
Various transfer agents easily cleavable by radical initiation have been used successfully (Table 1). In contrast to numerous works involving telogens which exhibit a weak C-H bond, and

especially for those which have a cleavable Carbon-Halogen bond, no investigations have been performed on transfer agents with a C-F bond. Two main telogens having a cleavable C-H group have been utilised in the radical telomerisation of VDF: chloroform and methanol. The former, already mentioned by Toyoda *et al.* in 1967 [153] requires di t-butyl peroxide as the best initiator [25]. Beside the formation of several by-products, the $Cl_3C(VDF)_n$-H telomers obtained were used as surfactants after a chemical change of the trichloromethyl into carboxyl end-group. We carried out similar telomerisations [25], even with a large excess of chloroform, and rather high molecular weight-telomers were produced yet with poor yields. This was linked to the low transfer constant to chloroform (c_T= 0.06 at 140 °C).

The radical telomerisation of VDF with methanol was investigated by Oku *et al.* [155] in 1986 who synthesised novel $H_2C=CHCO_2CH_2(VDF)_nH$ macromonomers (yield=40%).

A more extensive approach of this telomerisation was investigated in our Laboratory a few years ago [156], and high molecular weight-telomers were obtained in medium yields whatever the nature of the initiator (azo, peroxides, peresters, percarbonates), or even the way of initiation (photochemical, thermal or in the presence of redox catalysts, all of these three systems being unsuccessful). Starting from a five fold excess of methanol, telomers of $DP_{10\text{-}12}$ were obtained.

Indeed there were concommitant reactions of both expected telomerisation (way 2, *ca*. 80 %) and unexpected direct addition of the radical initiator onto VDF (way 1, *ca*. 20 %), clearly seen by ^{13}C and ^{1}H NMR spectroscopy [156] leading to both telomers and oligomers, as follows:



Interestingly, recent results on the homopolymerisation of VDF initiated by di *tert*-butyl peroxide, t-butyl peroxypivalate, and azo di-*tert*-butyl [139] have confirmed the presence of the same methyl end-group in the oligomers series. The presence of these radicals was shown by the rearrangement of *tert*-butoxy radicals generated by the di *tert*-butyl peroxide after homolytic scission [66,139]. The surprising formation of non-hydroxylated oligomers could be explained by the very low transfer constant to methanol: c_{MeOH}= 0.008 at 140 °C [184].

Such a case is rather unusual and demonstrates how the assessment of the transfer constant of the telogen is crucial to be sure that real telomers have been obtained.

We also attemped reacting fluorinated alcohols with VDF in the same conditions as above [166]; Indeed, CF_3CH_2OH was poorly reactive while hexafluoroisopropanol did not react at all. These *quasi* unsuccessful results were rather surprising since it was expected that the electron-withdrawing groups bearing the fluorine atoms enabled the fluorinated transfer agents to be more reactive.

Whereas only CCl_4, $Cl_3CCO_2CH_3$, and Cl_3CCH_2OH [34] have been used as telogens involving cleavage of the C-Cl bond [25,34,153], all kinds of brominated telogens were successfully used in the presence of peroxides : CCl_3Br [25], $ClCF_2Br$ [157], $BrCF_2Br$ [25,142,158], CF_3CF_2Br

[159], CF_3CFBr_2 [159], $BrCF_2CF_2Br$ [143-145], $BrCF_2CFClBr$ [66] for which CFClBr is quite reactive unlike the $BrCF_2$ end group, $CHBr_3$ [160], CBr_4 [160] or ω-bromoperfluoropolyethers $CF_3(OC_2F_4)_n(OCF_2)_pBr$ yielding original fluorinated block telomers [146].

Recently, the transfer constant to $BrCF_2CFClBr$ was assessed when the telomerisation of VDF with that transfer agent was investigated at 75°C, and initiated by t-butyl peroxypivalate. It was shown C_T = 1.3 (at 75 °C) that indicates the high efficiency of that telogen [66].

Various iodinated telogens have been used in radical initiation reaction: $ClCH_2I$, CH_2I_2 [162], CH_3I [163], CF_3I [147], $ClCF_2CFClI$ [141], C_4F_9I [127], and $I(C_2F_4)_nI$ (with n=1, 2, and 3, Table 5). C_4F_9I was used in the telomerisation of VDF in the presence of AIBN in supercritical carbon dioxide as the solvent [127].

More recently, VDF telomers were characterised by electron spray ionisation [186].

A few sulfurated transfer agents have been studied. In our Laboratory, 2-hydroxyethyl mercaptan reacted with VDF leading mainly to the first two telomers in the presence of dibenzoyl peroxide or to the six first telomers with di-*tert*-butyl peroxide, used with an excess of VDF [44,165]. More recently, we revisited this reaction and investigated the kinetics of telomerisation of VDF with the same transfer agent , leading to high values of the first two order transfer constants: C^T_1= 19.9 and C^T_2 = 25.3 at 140 °C, showing a high selectivity of the telomerisation and a high efficency of this thiol. However, it was observed that if the fluoroalkene was introduced in large excess about the mercaptan [45,166], this latter was consumed much quicker than the olefin (because of its high reactivity) and, consequently, a polymerisation of VDF was noted after total consumption of the thiol.

Grigor'ev *et al.* [49] or Tiers [167] used FSO_2Cl producing $FSO_2(CH_2CF_2)_nCl$ (n=1-3). Zhu *et al.* [168] tried Cl_3CSO_2Br initiated by dibenzoyl peroxide and obtained the first two

adducts in low yields. Neither disulfides nor thiocarbamates were tested in the radical telomerisation of VDF.

Among the phosphorated telogens, diethyl hydrogeno phosphonate (DEHP) behaves effectively for the telomerisation of VDF initiated by di t-butyl peroxide [169,170], perester [170] or azo [45,170]. As an exemple, the gas chromatogram of the total product mixture of the telomerisation of VDF with DEHP exhibits the first ninth telomers. The first four telomeric adducts were isolated and characterised by ^{1}H, ^{19}F, ^{13}C and ^{31}P NMR, and the infinite transfer constant to DEPH was assessed to be 0.34 at 140°C [170].

3 Photochemical initiation

The photoinduced telomerisation of VDF has been investigated by many authors (Table 2). The first work started in 1954 by Haszeldine [176] who used CF_3I as the transfer agent leading to the monoadduct after 28 days of irradiation (using a wave length λ>300nm) at room temperature. Cape *et al.* [177] studied the same reaction at 140°C for 12 h and determined the Arrhenius parameters for the addition of $CF_3^{\bullet}$ radicals to both sites of VDF. That of the isomer $CF_3CH_2CF_2I$ was about 3 times higher than that of $CF_3CF_2CH_2I$.

Tedder and Walton also used brominated methane derivated-telogens: $CFBr_3$ [35], even in excess, led to the expected normal and reverse monoadducts, five fluorobrominated by-products, (mainly formed by recombination of radicals) and to a diadduct. As described above, the kinetics of the reaction were investigated, as for CCl_3Br [173] and CF_2Br_2 [174].

In addition, various chain length-telomers were produced by γ-ray-induced telomerisation of VDF with CF_2Br_2, CF_3CFBr_2 or CF_3CBr_3 [175] by careful control of the molar ratio of the initial reactants.

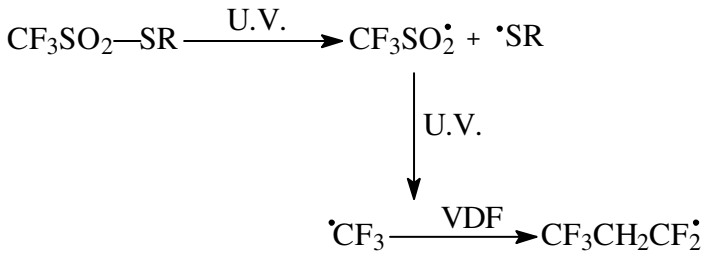
Telogens containing sulfur atom(s) were also utilised and, as for the above halogenated transfer agents, led mainly to monoadducts. For instance, Harris and Stacey [43] chose a large excess of H_2S leading to $HSCH_2CF_2H$ in 69% yield whereas in the presence of a lower amount of H_2S, the monoadduct and diadduct were produced in 62 and 19% yield, respectively. The former product is a fluorinated mercaptan, able to further react with other fluoromonomers [43]. The same authors [178] also used CF_3SH as the telogen with X ray-initiation yielding the monoadduct selectively.

UV initiation of reaction using CH_3SSCH_3 [46] and CF_3SSCF_3 [47] was also investigated. The hydrogenated transfer agent led to the monoadduct, but by-products were also formed, whereas the fluorinated one allowed a total conversion of VDF and yielded a telomeric distribution $CF_3S(C_2H_2F_2)_nSCF_3$ n=1-6 with reverse and normal adducts [46-48]. Interestingly, the diadduct has the structure $CF_3SCH_2CF_2CF_2CH_2SCF_3$ and shows that the telomers are formed by recombination of primary radicals.

In addition, PH_3 has successfully reacted with VDF under photochemical initiation leading to mono and diadduct from an equimolar starting materials ratio [50].

VDF and I-Cl were photolysed producing ICH_2CF_2Cl as the sole product in fair yield [180]. This monoadduct was characterised from ^1H and ^{19}F NMR spectra of CH_3CF_2Cl, obtained after addition of $SnBu_3H$.

More recently, alkyl or aryl trifluoromethanethiosulfonates were successfully involved in the telomerisation of VDF under photochemical initiation [179]. Indeed, in that photochemically induced condition, this transfer agent underwent a sulfur sulfur cleavage that generates a $CF_3SO_2^{\bullet}$ radical. That radical losses SO_2 to produce a trifluoromethyl radical able to initiate the telomerisation of VDF as follows :



Interestingly, $^{\bullet}SR$ radicals regarded as a soft radicals act as counter radicals and enable the formation of $CF_3(VDF)_nSR$ telomers. Telomers of structure $CF_3(VDF)_nSR$ were obtained with average n VDF units up to 86 [179].

In conclusion, photochemical telomerisation of VDF with iodoalkanes involving the cleavage of the C-I bond mainly produces the monoadduct, and reaction kinetics have been investigated. Addition onto the CH_2 side of VDF was favoured but non-negligible formation of various by-products was also observed. From brominated telogens, the presence of several by-products, besides the expected telomers, was also noted. The literature does not mention any work involving a telogen with a C-Cl cleavable bond probably due to its high bond dissociation energy. Sulfurated and phosphorated telogens were successfully utilised, with a special mention to CF_3SO_2SR which tends to control the telomerisation.

Table 2.

4 Redox telomerisation

Few investigations have been performed on the redox telomerisation of VDF (Table 2) showing a good selectivity in terms of low VDF content in the telomers. Several studies carried out in our Laboratory [34] have used CCl_4 in the presence of $FeCl_3$/Ni, $FeCl_3$/benzoin mixtures

or $CuCl_2$ as catalysts, with a two-fold excess of VDF over CCl_4. The first four telomers were produced and the diadduct was composed of two isomers: $Cl_3C(C_2H_2F_2)_2Cl$ and $ClCF_2CH_2CCl_2CH_2CF_2Cl$. In similar conditions, $CCl_3CO_2CH_3$ led to the first three adducts (monoadduct 60%, diadduct 32%, and triadduct 8%) whereas Cl_3CCH_2OH, catalysed by $FeCl_3$/benzoin in the same conditions, yielded 81% of monoadduct and 19% of diadduct. Usually, the yield of these reactions were poor to medium.

From C_4F_9I and $FeCl_3$/Ni, only $C_4F_9CH_2CF_2I$ was obtained in a 55% yield [39,40]. The structure of this monoadduct is the same as that produced by thermal initiation. Such a selectivity was confirmed by Chen and Li [181] who obtained $ICF_2CH_2CF_2I$ from ICF_2I in the presence of lead tetraacetate.

5 Other ways of initiation

Belfield *et al.* [142] have recently showed that boranes behaved efficiently as catalysts / initiators in the telomerisation of VDF with $BrCF_2Br$. These authors obtained telomers in good yields with average degrees of telomerisation ranging between 10 and 20.

Hypohalites and silanes also enable the telomerisation of VDF. DesMarteau *et al.* have performed the most interesting research using fluorinated hypohalites . Johri and DesMarteau [85] achieved the addition of trifluoromethylhypofluorite to $CH_2=CF_2$ leading to $CF_3OCH_2CF_3$, $CF_3OCF_2CH_2F$ and CF_3CH_2F in proportion 97.5, 2.0 and 0.5%, respectively. A similar investigation conducted by Sekiya and Ueda [86] selectively produced the first isomer.

Linear CF_3CFZCF_2OX (Z=Cl, Br and X=F,Cl) and branched $R_{F,Cl}R'_{F,Cl}CFOX$ ($R_{F,Cl}=R'_{F,Cl}=CF_2Y$ with Y=H,Cl or $R_{F,Cl}=CF_2Y$; $R'_{F,Cl}=CF_3$ polyhalogenoalkyl hypochlorite and hypofluorite were reacted with VDF in equimolar ratio from -145°C to room temperature for 18-24 h giving the monoadduct in 20-70% yield with a major amount of normal

$R_{F,Cl}OCH_2CF_3$ isomer [88]. The authors noted that for the same $R_{F,Cl}$ group, $R_{F,Cl}OF$ led to better yields than those obtained from $R_{F,Cl}OCl$, that $CF_3CFBrCF_2OF$ was more reactive than $CF_3CFClCF_2OF$, and that branched hypohalites reacted more easily than linear ones.

The same group [96] also synthesised novel branched perfluorohypobromites which reacted with VDF from -93°C to room temperature for 8-12 h as follows :

$$R_FOBr + H_2C{=}CF_2 \longrightarrow \underset{(20\text{-}31\%)}{R_F OCF_2CH_2Br} + \text{by products } (R_FOH)$$

$R_F = (CF_3)_3C$ or $C_2F_5C(CF_3)_2$

Surprisingly, both hypobromites produced monoadducts composed exclusively of the reverse $R_FCF_2CH_2Br$ isomer.

Hydrosilylation mainly led to monoadducts [55].

Table 3.

6 Conclusion

Many investigations have been performed on the telomerisation of VDF with a wide range of transfer agents using various means of initiation : thermal, photochemical (mainly UV and few studies with γ rays or X rays), redox catalysts or radical initiators.

Thermal initiation has the advantage of leading to the formation of well-defined telomers with either selective production of the monoadduct or with higher $\overline{DP_n}$ than those obtained from photochemical initiation. It appears easy and attractive since, except for an autoclave, no special

equipement or solvent or expensive reagents (e.g., initiators) are required. In addition, this route provides "clean" reactions with no formation of by-products.

Work on photoinduced telomerisation has led to most impressive results, with interesting kinetics studies being performed by Tedder and Walton [35,173,174,177]. VDF was used to obtain lower telomeric distributions mainly for monoadducts except from $CF3SO_2SR$ (from which DP_n up to 86 were achieved [179]), but also yielded several by-products from brominated telogens.

Radical initiation is an “intermediate” means involving many kinds of telogens but formation of by-products from the initiator end-group sometimes occurred (case of the telomerisation with methanol [156]).

Few surveys have been developed in redox type telomerisation. Most involve CCl_3R, others C_4F_9I, or ICF_2I and produced mainly the monoadduct [34,39,40,181] in the presence of ferric or lead catalysts.

Many investigations were realised from (per)fluorinated iodides or diiodides in different conditions of initiations and solvents, summarised in Table 3. Highly fluorinated telomers of various molecular weights were thus obtained.

Concerning the structure of the telomers, chaining defects have been observed, since already a head to head addition occurred in the diadduct. New processes or the use of several ligands should be worth investigating and might afford regioselective telomers.

Most industrial production of VDF is generated from F141b (Cl_2CFCH_3) or F142b ($ClCF_2CH_3$) and since this process is unlikely to be stopped, it can be imagined that (co)telomerisation and (co)polymerisation of such olefins still have a prosperous future.

Table 4.

7 Iodine transfer polymerisation

Iodine transfer polymerisation is one of the radical living process being developed in the late seventies by Tatemoto at the Daikin Company [377,409]. Actually, it is required to use (per)fluoroalkyl iodides because their highly electron withdrawing (per)fluorinated group R_F allows the lowest level of the CF_2-I bond dissociation energy. Such a C-I cleavage is also possible in $R_FCH_2CH_2I$ [379a]. Various fluorinated monomers have been successfully used in ITP [376-379,409]. Basic similarities in these living polymerisation systems are found in the stepwise growth of polymeric chains at each active species[408]. The active living center, 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. In the case of ITP of fluoroolefins, the terminal active bond is always the C-I bond originated from the initial iodine-containing chain transfer agent and monomer, as follows :

$$C_nF_{2\,n+1}-I + (p+1)\,H_2C{=}CF_2 \xrightarrow{R^{\cdot}\ \text{or}\ \Delta} C_nF_{2\,n+1}-(C_2H_2F_2)_p-CH_2CF_2-I$$

Nowadays, this concept is still applied at Dai-Act company (for preparing Dai-el® thermoplastic elastomers) and has also been used by the Solvay Solexis (formerly Ausimont S.p.A.) and DuPont Companies for the production of Tecnoflon® [376] and Viton®[379], respectively (see chapter IV, section II-1-2-4-1).

Similarly, by stepwise cotelomerisations of VDF, HFP and TrFE, a wide variety of highly fluorinated telomers of various structures were obtained (Figure 4). Interestingly, the position of a branched CF_3 group arising from a HFP unit affects drastically the crystallinity of the telomers

(e.g., a telomer that exhibits a C_7F_{15} chain is crystalline while a $C_5F_{11}CF(CF_3)$ is totally amorphous[40]).

Characterization of the VDF Telomers

Gas chromatography (GC) analyses were performed using a Delsi apparatus. The nitrogen pressure at the entrance to the column was maintained in a range of 3-5 bars and the temperatures of the injector and detector were 250 and 260°C respectively. The temperature programme started from 30°C and reached 240°C at a heating rate of 10°C/min.

The products were characterized by ^{1}H- NMR and ^{19}F -NMR, all undertaken at room temperature. ^{1}H- NMR spectra were recorded on Bruker AC 200 while ^{19}F -NMR spectra on a Bruker AC 250 with deuterated chloroform as the solvent and TMS as the internal reference. The letters s and m stand for singlet and multiplet, respectively. The experimental conditions for recording ^{1}H (^{19}F) NMR spectra were as follows: flip angle=90° (30°), acquisition time=4.5s (0.7 s), pulse delay= 2 s (5 s), number of scans= 16 (64) and pulse width= 5 □s for ^{19}F-NMR.

The FTIR spectra were recorded by means of a Genesis ATI Mattson spectrometer.

Telomerization of VDF with $C_6F_{13}I$ and obtaining of the monoadduct

The synthesis of the VDF telomers from $C_6F_{13}I$ was carried out by thermal telomerization of VDF followed by the distillation of $C_6F_{13}CH_2CF_2I$ monoadduct.

Telomerization of VDF with CF_3I

In a 160-mL Hastelloy (HC-276) autoclave equipped with inlet and outlet valves, a manometer and a rupture disc, were placed the initiator (t-amyl or t-butyl peroxypivalate) and acetonitrile. Then, the autoclave was cooled, degassed and pressurized with 20 bars of nitrogen to check

eventual leaks. CF_3I was first introduced in the autoclave, followed by VDF, the amount of both reactants being assessed by double weighing. Several trials were carried out to have different molar ratios between both reagents and to obtain various lengths of the VDF chains, as reported in Table 5.

Table 5.

After distillation in the conditions reported in Table 2, the products were characterized by ^{1}H- and ^{19}F-NMR and by GC, and distinguished for a different average number of VDF units.

$CF_3(VDF)_nI$:

^{1}H-NMR($CDCl_3$): δ: 3.8 - 3.6 (m, 2H, -CF_2**CH_2**I), 3.2 (m, 2H, CF_3**CH_2**-), 2.9 (m ,-CF_2**CH_2**CF_2-);

^{19}F-NMR ($CDCl_3$) : δ : -38 (m , 2F , -**CF_2**I), -58 (m , 3F , **CF_3**CH_2-), -91 (m, -CH_2**CF_2**CH_2-), -108 (m ,-CF_2**CF_2**CH_2I), -113 (m ,- CF_2CH_2**CF_2**CF_2-); -116 (m, - CH_2**CF_2**$CF_2CH_2CH_2$ CF_2-).

The molecular weights of the different products and the yields of the reactions are collected in Table 6.

Table 6.

TABLE CAPTIONS

Table 1. Thermal and radical telomerisations of vinylidene fluoride (DTBP, DBP and sc mean ditertiary peroxide, dibenzoyl peroxide and supercritical, respectively).

Table 2. Photochemical, redox and special telomerisations of vinylidene fluoride.

Table 3. Telomerisation of vinylidene fluoride with iodinated transfer agents (d, RT, sc, DTBP, LTA and PFPE mean day, room temperature, super critical, Di*tert*-butyl peroxide, lead tetraacetate and perfluoropolyether group, respectively).

Table 4. Photochemical telomerisation of tetrafluoroethylene (RT stands for room temperature).

Table 5. Reagents used in the telomerization reaction (TBPPI and TAPPI stand for t-butyl and t-amyl- peroxypivalate, respectively)**Table 6.** VDF-containing telomers: yield and characteristics

Table 1. Thermal and radical telomerisations of vinylidene fluoride (DTBP, DBP, PFPE and sc mean di-*tert*-butyl peroxide, dibenzoyl peroxide, perfluoropolyether and supercritical, respectively).

Telogen	Way of initiation	Structure of telomers	References
CF_2Br_2	190°C	$R_F(C_2H_2F_2)_nBr$, n=1-8	141
CF_2Br_2	DTBP	$R_F(C_2H_2F_2)_nBr$, n=5-25	142
$CF_3CFBrCF_2Br$	220°C	$R_F(C_2H_2F_2)_nBr$, n=1-5	141
$BrCF_2CF_2Br$	peroxides	$BrCF_2CF_2(VDF)_nBr$	143-145
PFPE-Br	peroxides	PFPE-b-PVDF	146
$ClCF_2CFClI$	181°C/26h	$ClCF_2CFCl(VDF)_nI$ n=1-6	141
CF_3I	peroxide	$CF_3(VDF)_nI$, n=5-20	147
$C_nF_{2n+1}I$, n=1-8	180-220°C	$R_F(C_2H_2F_2)_nI$, n = 1-7	39,141,147,148
C_4F_9I	250°C	$C_4F_9(VDF)_nI$	149
iC_3F_7I	185-220°C	$iC_3F_7(VDF)_nI$, n=1-5	38-40,150
$(CF_3)_3CI$	Thermal	$(CF_3)_3C(VDF)_nI$, n=1,2	151
$IC_nF_{2n}I$ n=2,4,6	180-200°C	$I(VDF)_pC_nF_{2n}(VDF)_qI$ p,q=1,2,3	152
Cl_3C-H	DTBP, 140°C	$Cl_3C(C_2H_2F_2)_nH$ n>3	25,153
CCl_4	acyl peroxide	$CCl_3(VDF)_nCl$	154
$RCCl_3$	peroxide	$RCCl_2(C_2H_2F_2)_nCl$	25,34
$HOCH_3$	DTBP, DBP or AIBN	$HOCH_2(C_2H_2F2)_nH$ n>10	155,156
RBr	peroxide	variable n	25,157-160
$BrCF_2CFClBr$	DTBP	$BrCF_2CFCl(C_2H_2F_2)_nBr$	66
RI	peroxide	variable n	161-163
C_4F_9I	AIBN, $scCO_2$	n=1-9	127
PFPE-I	DTBP	n=5-50	164
HOC_2H_4SH	AIBN, DBP (or DTBP)	n=1,2 (or 1-6)	44,45,165,166
FSO_2Cl	DBP	$FSO_2(C_2H_2F_2)_nCl$ (n=1-3)	49,167
Cl_3CSO_2Br	DBP	$Cl_3C(C_2H_2F_2)_nBr$ (n=1,2)	168
$(EtO)_2P(O)H$	DTBP or perester	$(EtO)_2P(O)(VDF)_nH$ (n=1-5)	169,170
CF_3-paracyclophane	T > 160°C	CF_3-PVDF	171
cyclopentane or cyclohexane	DTBP	c-$C_pH_{2p-1}(VDF)_nH$ (n>1)	172
ICH_2I	DTBP / 130°C	$ICH_2CH_2CF_2I$ (91%)	162
THF	DTBP	monoadduct	27

Table 2. Photochemical, redox and special telomerisation of vinylidene fluoride.

Telogen	Way of initiation	Structure of telomers	References
$CFBr_3$	UV	$Br_2CF(C_2H_2F_2)_nBr$ (n=1,2)	35
Cl_3CBr, CF_2Br_2	UV	low n	173,174
$BrCF_2Br$	Borane / RT	$BrCF_2(VDF)_nBr$	142
CF_2Br_2,CF_3CFBr_2,CF_3CBr_3	γ ray	$R_F(C_2H_2F_2)Br$ variable n	175
CF_3I	UV/28d/RT	n=1	176
CF_3I	UV/140°C	$CF_3CH_2CF_2I$ (major) $CF_3CF_2CH_2I$ (minor)	177
CF_2HI	UV	$HCF_2CH_2CF_2I$	161
H_2S	X ray	$H_{2-x}S(CH_2CF_2H)_x$ x=1,2	43
CF_3SH	X ray	$CF_3SCH_2CF_2H$	178
RSSR(R=CH_3 or CF_3)	UV	$RS(C_2H_2F_2)_nSR$, n=1-6	46,48,49
CF_3SO_2SR	UV	$CF_3(VDF)_nSR$, n = 1-86	179
PH_3	UV	$H_{3-x}P(CH_2CF_2H)_x$ x=1,2	50
ICl	UV or CuCl	ICH_2CF_2Cl	180
$RCCl_3$ R=Cl,CO_2CH_3,CH_2OH	$FeCl_3$/Ni (or benzoin) or $CuCl_2$	$RCCl_2(VDF)_nCl$ n=1-4	34
C_4F_9I	$FeCl_3$/Ni	$C_4F_9CH_2CF_2I$	39
ICF_2I	Lead tetraacetate	$ICF_2CH_2CF_2I$	181
R_FOX (X=F or Br)	-145 to RT	$R_FOCH_2CF_3$ mainly	85,86,88,96
HI (gas)	-	CH_3CF_2I	182
R_3SiH	H_2PtCl_6 or UV	$R_3SiCH_2CF_2H$	55
H_2O_2	UV	$HO(VDF)_nG$	183

Table 3. Telomerisation of vinylidene fluoride with iodinated transfer agents (d, RT, sc, DTBP, LTA and PFPE mean day, room temperature, super critical, Di*tert*-butyl peroxide, lead tetraacetate and perfluoropolyether group, respectively).

Telogen	Method of initiation	Structure of telomers	Ref.
ICl	Various initiations	$ClCF_2CH_2I$	180
HI	thermal	CH_3CF_2I	182
CF_3I	UV, 28 d/RT	$CF_3(VDF)_1I$	176
CF_3I	UV/0-100 °C	$CF_3(C_2F_2H_2)I$	188
CF_3I	UV/ 140 °C	$CF_3CH_2CF_2I$ (major) $CF_3CF_2CH_2I$ (minor)	177
CF_3I	TBPPI	CF3(VDF)nI (n=10-30)	147
CF_2HI	UV	$HCF_2CH_2CF_2I$	161
iC_3F_7I	185-220°C	$iC_3F_7(VDF)_nI$; n=1-5	38-40
nC_3F_7I	20hrs/UV/140-210°C	$nC_3F_7(C_2F_2H_2)I$	177
$(CF_3)_3CI$	Thermal	$(CF_3)_3C(VDF)_n$ I, n=1,2	151
C_4F_9I	230°C/15h	$C_4F_9(VDF)_nI$	149
C_4F_9I	AIBN, scCO2	$C_4F_9(VDF)_nI$; n=1-9	127
C_4F_9I	$FeCl_3$/Ni	$C_4F_9CH_2CF_2I$	39,40
$C_pF_{2p+1}I$ (p=1-8)	180-220 °C	$C_nF_{2p+1}(VDF)_nI$; low n	38-40
$C_5F_{11}CFICF_3$	180-190 °C	$C_5F_{11}CF(CF_3)(CH_2CF_2)_nI$	40
$ClCF_2CFClI$	181°C/26h	$ClCF_2CFCl(VDF)_nI$	141
ICH_2I	DTBP/130°C	ICH_2-CH_2CF_2I (91%)	162
ICF_2I	LTA/70°C	$ICF_2CH_2CF_2I$	181
$I(C_2F_4)_nI$, n=1, 2, 3	180°C or Rad.	$I(VDF)_p(C_2F_4)_n(VDF)_qI$; variable p+q	152,189
PFPE-I	DTBP, 140°C	diblock PFPE$(VDF)_nI$ $\bar{n}$=5-50	164

Table 4. Photochemical telomerisation of tetrafluoroethylene (RT stands for room temperature).

Telogen	Initiation way	n	Ref.
$R_1R_2C(OH)$-H (MeOH, EtOH, iPrOH)	UV (RT)	1,2	29
X_3CS-SCX_3 X=H,F	UV (RT)	1-5	47,48
Cl_3Si-H	UV (RT)	1	132
$(CH_3)_3Si$-H	UV (RT)	1	134
CF_3I	UV (RT)	1-10	193,194
R_FI	UV (185-220°C)	1.3	150
$BrCF_2CF_2Br$	UV (RT)	variable	119,120,196

Table 5. Reagents used in the telomerization reaction (TBPPI and TAPPI stand for t-butyl and t-amyl- peroxypivalate, respectively)

Initiator (g)	**Type of initiator**	**Acetonitrile (g)**	**VDF (g)**	**CF_3I (g)**	**Obtained R_fI**
2.21	TBPPI	59	15	75	**$CF_3(VDF)_{2.3}I$**
3.20	TAPPI	60	33	37	**$CF_3(VDF)_{3.1}I$**
0.68	TBPPI	57	14	41	**$CF_3(VDF)_{4.8}I$**

Table 6. VDF-containing telomers: yield and characteristics

R_FI	Yield (%)	b.p (°C)	Pressure (mmHg)
$CF_3(VDF)_{2.3}I$	11	50	20
$CF_3(VDF)_{3.1}I$	41	52	20
$CF_3(VDF)_{4.8}I$	8	55	20