# Iodine Transfer Polymerization (ITP) of Vinylidene Fluoride (VDF). Influence of the Defect of VDF Chaining on the Control of ITP

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ABSTRACT: Iodine transfer polymerization (ITP) of vinylidene fluoride (VDF) in the presence of two chain transfer agents (CTA, such as $C_6F_{13}I$ and $HC_2F_4CH_2I$) is presented. Various experimental conditions in terms of the nature of the radical initiators, time, temperature and initial $[initiator]_0/[VDF]_0$ and $[CTA]_0/[VDF]_0$ molar ratios influenced the yield of the reaction, the obtained average degree of polymerization in number, $\overline{DP}_n$, of PVDF−I, the defect of VDF-chaining, and the $CX_2I$ functionality (where X = H or F). The microstructures of these produced PVDF−I oligomers were characterized by $^1H$ and $^{19}F$ NMR spectroscopy which enabled one to assess the $\overline{DP}_n$ values and to quantify the head-to-head or tail-to-tail defects of VDF-chainings. A low amount of defect of chaining in PVDF−I when $C_6F_{13}I$ was used in contrast to a higher content from $HC_2F_4CH_2I$. These PVDF−Is exhibited a favored $-CH_2CF_2I$ functionality from the former CTA which was not observed in the latter one. A good agreement between the targeted and the obtained $\overline{DP}_n$ values was noted for ITP of VDF in the presence of $C_6F_{13}I$ (representative of normal addition) whereas that carried out from $HC_2F_4CH_2I$ (representative of inverse addition) led to experimental $\overline{DP}_n$ values higher than the targeted ones in all cases. A low conversion of $HC_2F_4CH_2I$ was observed in contrast to that of $C_6F_{13}I$, which shows a better efficiency as the transfer agent.

## Introduction

In contrast to the radical telomerization of fluoroalkenes,[1] the controlled radical polymerization of such halogenated monomers has led to few investigations. Neither atom transfer radical polymerization (ATRP)[2] nor nitroxide mediated polymerization (NMP)[3] of fluoroolefins has been reported in the literature. However, the presence of a chain transfer agent enabled the polymerization to be controlled. Except for one survey involving xanthates,[4] several investigations (mentioned in the patent literature mainly) report industrial surveys on the iodine transfer polymerization (ITP) of fluoroalkenes and especially on vinylidene fluoride (VDF) with perfluoroalkyl iodides ($R_FI$) or with α,ω-diiodoperfluoroalkanes ($IR_FI$). Indeed, the weak $R_F$-$CF_2$−I bond, the dissociation energy of which is 45 kJ $mol^{-1}$,[1] enables an easy cleavage causing both the resulting $R_FCF_2^\bullet$ radical to be quite reactive and the perfluoroalkyl iodide to become an efficient transfer agent, hence producing a further VDF adduct with a $-CF_2I$ end group. Most chemical industries producing VDF have already protected various discoveries such as the synthesis of thermoplastic elastomers (TPE) pioneered by the Daikin Company in 1979[5] (producing Daiel TPE[6−8]) and then studied by DuPont[9,10] and developed later by Ausimont (now Solvay Solexis).[11−13] This breakthrough could be made possible by the presence of the chain transfer agent and VDF-containing (co)polymer usually made of a soft block that could initiate a further iodine transfer (co)polymerization of one (or two) monomer(s) leading to a soft-*b*-hard diblock copolymer or hard-*b*-soft-*b*-hard triblock copolymers (or thermoplastic elastomers (TPEs)) from $R_FI$ or $I-R_F-I$, respectively (Table 1).

In contrast to this industrial progress, few rigorous scientific investigations were reported in the literature. Only Tatemoto[1,5,14] supplied valuable data on the properties and applications of block copolymers, but the description lacks information on the microstructure of the obtained PVDF blocks, on the nature of the end groups, on the defects of VDF chaining of these produced blocks, and on the evidence of the controlled or "living" behavior of such a polymerization.

Since VDF is an asymmetrical monomer, the produced macroradical generated in the propagation step may add onto $CF_2$ or $CH_2$ sites, considering that an electroattractive fluorinated radical should react onto a $CH_2$ site, taking into account the polar, electronic, and steric effects.[15−17] As a matter of fact, it is known that VDF telomers, oligomers, or PVDF contain defects in their microstructures linked to the presence of reversed VDF addition since tail-to-tail, $-(CF_2CH_2-CH_2CF_2)-$, or head-to-head, $-(CH_2CF_2-CF_2CH_2)-$, chainings have been observed.[18−23] Hence, it was worth considering the consequence of these reversed additions on the control of ITP of VDF. The use of $C_6F_{13}I$ as the chain transfer agent should lead to two kinds of chains: one terminated by $-CF_2-I$ as expected, while the other one exhibits a $-CF_2CH_2-I$ end group. As a result, quantifying the content of both extremes seems possible. Then, to evaluate the difference of reactivity of both $-CF_2-I$ and $-CH_2-I$ end groups (arising from the steric and inductive effects), it proved worthwhile to use another transfer agent, $HC_2F_4CH_2I$, for ITP of VDF.

The objectives of this article concern the study of the iodine transfer polymerization (ITP) of VDF with both these different transfer agents and their influence onto the microstructure of the resulting PVDF−I (and hence the correlation between targeted and experimental average degrees of polymerization), the defects of VDF chaining, and the controlled character of ITP polymerization.

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**Table 1. Iodine Transfer Polymerization of Fluoroalkenes for the Synthesis of Fluorinated Hard-*b*-soft-*b*-hard Triblock Copolymers (n.g. Stands for Not Given)**

| soft block[a] | % comonomers in soft block | hard block | soft/hard ratio (wt %) | $T_g$ (°C) | $T_m$ (°C) | ref |
|---|---|---|---|---|---|---|
| $I[(VDF)_xHFP]_yI$ | n.g. | PVDF | n.g. | n.g. | 160 | 14 |
| $I[(VDF)_xHFP]_yI$ | n.g. | poly(E-*alt*-TFE) | n.g. | n.g. | 220 | 14 |
| $I[(CTFE)_x(VDF)_y]_zI$ | 45/55 | poly(E-*co*-CTFE) | 85/15 | −6 | 247 | 7 |
| $I[(CTFE)_x(VDF)_y]_zI$ | 45/55 | poly(E-*co*-TFE) | 90/10 | −8 | 252 | 7 |
| $I[(VDF)_x(FVA)_y]_zI$ | n.g. | PVDF | n.g. | n.g. | n.g. | 14 |
| $I[(TFE)_xP]_yI$ | 55/45 | poly(E-*co*-TFE) | 80/20 | −1 | 267 | 9 |
| $I[(VDF)_xHFP(TFE)_y]_zI$[b)c)] | 56/19/25 | PVDF | 80/20 | −12 to −15 | 165 | 11, 12 |
| $I[(VDF)_xHFP(TFE)_y]_zI$ | 35/40/25 (wt) | poly(E-*alt*-TFE) | n.g. | −8 | 222 | 14 |
| $I[(VDF)_xHFP(TFE)_y]_zI$ | 50/30/20 | poly(E-*co*-HFP-*co*-TFE) | 85/15 | n.g. | n.g. | 7 |
| $I[(VDF)_xHFP(TFE)_y]_zI$[b)] | 54/21/25 | poly(E-*alt*-TFE) | 80/20 | −13 | 266 | 11 |
| $I[(VDF)_xPMVE(TFE)_y]_zI$[b)] | 62/19/19 | PVDF | 80/20 | −30 | 160 | 11, 13 |
| $I[(VDF)_xPMVE(TFE)_y]_zI$ | 73/17/10 | poly(E-*co*-TFE) | 72/28 | −33 | 254 | 9 |
| $I[(VDF)_xPMVE(TFE)_y]_zI$[b)] | n.g. | poly(E-*co*-TFE) | n.g. | −13 to −15 | 266 | 11, 12 |
| $I[(VDF)_xPMVE(TFE)_y]_zI$[b)] | 57/23/20 | poly(E-*co*-TFE-*co*-PMVE) | 75/25 | n.g. | 180 | 13 |
| $I[(TFE)_xP(VDF)_y]_zI$ | n.g. | poly(E-*co*-TFE) | 85/15 | −13 | 262 | 9 |
| $I[(TFE)_xE(PMVE)_y]_zI$ | 45/19/36 | poly(E-*co*-TFE) | 71/29 | −16 | 245 | 9 |

[a] VDF, HFP, TFE, CTFE, PMVE, FVA, E and P represent vinylidene fluoride, hexafluoropropene, tetrafluoroethylene, chlorotrifluoroethylene, perfluoromethyl vinyl ether, perfluoro vinylacetic acid, ethylene, and propylene, respectively. [b] Also tetrapolymerization with less than 1 mol % of $H_2C{=}CH{-}C_6F_{12}{-}CH{=}CH_2$. [c] Also tetrapolymerization with less than 1 mol % of $H_2C{=}CH{-}C_6F_{12}{-}CH{=}CH_2$/$H_2C{=}CHC_6F_{12}C_2H_4I$/$IC_2H_4C_6F_{12}C_2H_4I$ mixture.

## Experimental Part

**Materials.** Vinylidene fluoride and 1,1,1,3,3-pentafluorobutane were kindly supplied by Solvay S.A., Tavaux, France, and Brussels, Belgium. Perfluorohexyl iodide (purity 99%) was kindly supplied by Arkema, France. 1,1,2,2-Tetrafluoro-3-iodopropane (99%) was purchased from Aldrich Chimie, (38299 Saint Quentin-Fallavier, France). *tert*-Butylperoxypivalate (TBPPI, purity 75%) and 2,5-bis(*tert*-butylperoxide)-2,5-dimethylhexane (DHBP, 90%) were gifts from "La Chalonnaise des Peroxydes", Chalons sur Marne, France. They were used as supplied just like acetonitrile (99%), dimethylformamide (DMF, 99%), tetrahydrofuran (THF, 99%) and methanol of analytical grade (99.8%), from Aldrich Chimie, 38299 Saint Quentin-Fallavier, France.

**Analyses.** The compositions and the structures of the oligomers obtained by ITP of VDF were determined by $^{19}F$ (200 MHz) and $^1H$ NMR (250 or 400 MHz) spectroscopies. The NMR spectra were recorded on Bruker AC 200, AC 250, and AC 400 instruments, using deuterated acetone, dimethyl sulfoxide (DMSO), and dimethylformamide (DMF) as the solvents and tetramethylsilane (TMS) (or $CFCl_3$) as the reference for $^1H$ (or $^{19}F$) nuclei. Coupling constants and chemical shifts are given in hertz and parts per million, respectively. The experimental conditions for $^1H$ (or $^{19}F$) NMR spectra were as follows: flip angle 90° (or 30°), acquisition time 4.5 s (or 0.7 s), pulse delay 2 s (or 5 s), number of scans 16 (or 64), and a pulse width of 5 $\mu$s for $^{19}F$ NMR.

**Reactions in Autoclave. Example of Iodine Transfer Polymerization (ITP) of VDF Performed in the Presence of 1,1,2,2-Tetrafluoro-3-iodopropane at 75 °C.** A 160 mL Hastelloy (HC-276) autoclave, equipped with inlet and outlet valves, a manometer, and a rupture disk, was degassed and pressurized with 30 bar of nitrogen to check eventual leaks; then, a 20 mmHg vacuum was operated for 30 min. Under vacuum were transferred into the autoclave 0.43 g ($2 \times 10^{-3}$ mol) of *tert*-butylperoxypivalate, 5.04 g ($2 \times 10^{-2}$ mol) of 1,1,2,2-tetrafluoro-3-iodopropane, and 100.0 g of 1,1,1,3,3-pentafluorobutane. Then, by mean of double weighing, 19.50 g ($30 \times 10^{-2}$ mol) of VDF was introduced in the mixture. Then, the autoclave was progressively heated to 75 °C. There was an exotherm of ca. 10 °C, followed by an increase of pressure from 20 up to 26 bar and then a sharp drop of pressure to 20 bar was noted. After reaction, the autoclave was placed in an ice bath for about 60 min, and 3.90 g of unreacted VDF was progressively released (the conversion of VDF was 80%, and the chain transfer constant (CTA) conversion was 33%). After the autoclave was opened, about 120.0 g of a brown liquid was obtained. After evaporation of 1,1,1,3,3-pentafluorobutane, the sample was dissolved in dimethylformamide (DMF), which enabled solubilization of both low average number degree of polymerization ($\overline{DP}_n$) (also soluble in acetone) and high $\overline{DP}_n$, and the polymers produced were precipitated by adding water into the DMF solution. White powders were obtained in all cases, and $^{19}F$ NMR led to a $\overline{DP}_n$ value of 35. The sample was characterized by $^{19}F$ and $^1H$ NMR spectroscopy.

The same procedure was used for the ITP reaction of VDF with perfluorohexyl iodide (Supporting Information).

NMR characteristics are reported in Tables 2 and 3.

**Table 2. Assignments of $^{19}F$ NMR Chemical Shifts in Poly(vinylidene fluorine)−I (s, Singlet; d, Doublet; t, Triplet; m, Multiplet)**

| δ (ppm) | signal | assignment |
|---|---|---|
| −38.0 | t ($^3J_{FH}$ = 7.0 Hz) t ($^4J_{FF}$ = 9.8 Hz) | -$CH_2-CF_2$I |
| −60.0 | m | -$CF_2-CF_2$I |
| −82.0 | m | $CF_3-CF_2$- |
| −91.0 | m | -$CH_2-CF_2-CH_2-CF_2$- |
| −95.7 | m | $CH_3-CH_2-CF_2$- |
| −108.0 | m | $CH_3-CF_2$- |
| | | -$CF_2-CF_2-CH_2-$I |
| | | -$CF_2-CF_2-CH_2-CF_2$- |
| −112.0 | m | $(CH_3)_3C-CF_2-CH_2-$ |
| −113.4 | m | -$CH_2-CF_2-CF_2-CH_2-CH_2$- |
| −115.7 | m | -$CH_2-CF_2-CF_2-CH_2-CH_2$- |
| −138.0 | dm | $HCF_2-CF_2$- |

**Table 3. Assignments of $^1H$ NMR Chemical Shifts in Poly(vinylidene fluorine)-I**

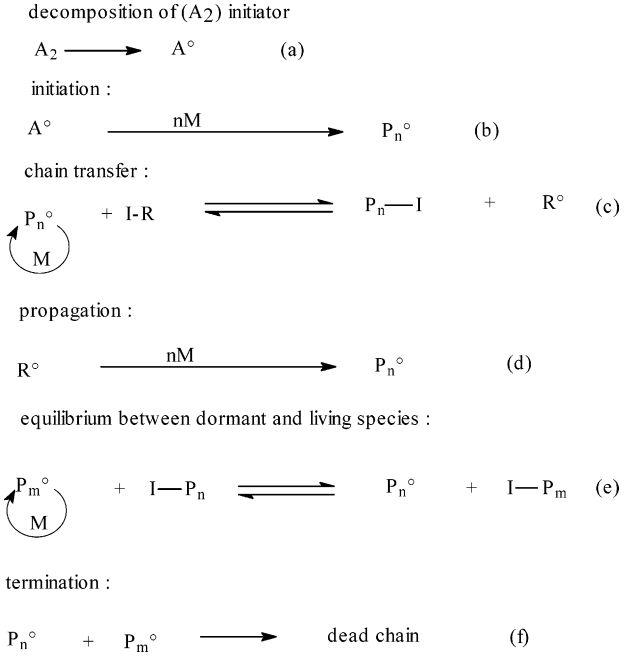
| δ (ppm) | signal | assignment |
|---|---|---|
| 1.0 | s | $(CH_3)_3CCH_2-CF_2-$ |
| 1.2 | t | $CH_3-CH_2-CF_2-$ |
| 1.3 | s | $(CH_3)_3CCF_2-CH_2-$ |
| 1.8 | t | $CH_3-CF_2-CH_2-$ |
| 2.3 | m | -$CH_2-CF_2-CF_2-CH_2-CH_2-CF_2-$ |
| 2.9 | m | -$CH_2-CF_2-CH_2-CF_2-CH_2-CF_2-$ |
| | | $CH_3-CH_2-CF_2-$ |
| | | $(CH_3)_3CCH_2-CF_2-$ |
| 3.3 | q | $C_6F_{13}-CH_2-CF_2-$ |
| 3.7 | q | -$CH_2-CF_2$-I |
| 3.9 | q | -$CF_2-CH_2$-I |
| 6.5 | t($^2J_{HF}$ = 49.6 Hz) t ($^3J_{HF}$ = 4.0 Hz) | $HCF_2CF_2$ |

[a] Key: s, singlet; t, triplet; q, quintet; m, multiplet.

## Results and Discussion

**1. Introduction of ITP.** Iodine transfer polymerization (ITP) of vinylidene fluoride deals with the "degenerative transfer" as reversible addition fragmentation transfer (RAFT)[24] or macromolecular design for interchange of xanthate.[25,26] This is an extension of the

**Scheme 1. Elementary Steps of Iodine Transfer Polymerization of M Monomer**




telomerization,[1,27] taking into account the major difference that the macromolecular chains having undergone a transfer reaction may be involved in a further reaction.

As for the telomerization, ITP requires a chain transfer agent (CTA), and in that present case, an 1-iodofluoroalkane was chosen. Scheme 1 depicts the different steps of ITP of a M monomer.

The initiating radical, A•, is generated by thermal decomposition of a conventional initiator, such as *tert*-butyl peroxypivalate or 2,5-bis(*tert*-butylperoxide)-2,5-dimethylhexane, in step a. Then, A• radical reacts with monomer (M) in step b, followed by propagation of M as shown in step c. The exchange of iodine from the transfer agent, $R_F-I$, to the propagating radical, $P_n$•, results in the formation of the polymeric alkyl iodide, $P_n-I$, and a new initiating radical, R• (step d). Large differences in the stability of the reactants and products involved in step e could result in shifting the equilibrium overwhelmingly to the right or to the left. Therefore, the ideal case is when the structure of $R_F$ closely resembles the structure of the propagating radical, resulting in a thermodynamically neutral transfer step. The exchange process described in step e is thermodynamically neutral, because $P_n$ and $P_m$ propagating chains are identical. Step e shows an equilibrium between dormant and living species, which is crucial[1,3] for a *pseudo*living behavior. As in any radical process, reaction of termination occurs, such as disproportionation and coupling of macroradicals (step f). But, to preserve the living or controlled behavior, the termination reaction in step f must be negligible compared with the transfer reactions (this condition is used for the other controlled radical polymerizations, such as ATRP, RAFT, or MADIX) and two key parameters must be taken into account:

(i) The initiator amount must be as low as possible to avoid any presence of dormant (or dead) chains but be present in an efficient amount to initiate that radical reaction. However, that amount depends on the purity of the chain transfer agent. Actually, traces of iodine in the medium may allow an overconsumption of initiator, and an inhibition time may occur.[28]

(ii) The CTA amount enables one to control the molar masses of the produced polymers. In the ideal case of a total conversion of CTA, the theoretical number-average degree of polymerization ($\overline{DP}_n$) can be assessed from eq 1:

$$\overline{DP}_n = \frac{\alpha_{VDF}[VDF]_0}{[CTA]_0} \quad (1)$$

where $[VDF]_0$, $[CTA]_0$, and $\alpha_{VDF}$ represent the monomer and CTA concentrations in feed and the VDF conversion, respectively.

The reactivity of CTA can be controlled by carrying out different reactions that vary the theoretical (or targeted) $\overline{DP}_{nS}$ and to compare them with those obtained experimentally. A satisfactory agreement between these values enables one to confirm the good reactivity of the CTA.

**2. Results.** Iodine transfer polymerization of vinylidene fluoride was initiated by *tert*-butyl peroxypivalate (TBPPI), in the presence of a iodofluorinated chain transfer agent ($C_6F_{13}I$ and $HC_2F_4CH_2I$) and in 1,1,1,3,3-pentafluorobutane at 75 °C for 4 h. After reaction and elimination of both the solvent and the CTA under vacuum, PVDF−I was precipitated from water. Its experimental $\overline{DP}_n$ value was assessed from $^{19}F$ and $^1H$ NMR spectroscopy.

**2.1. ITP of VDF with $C_6F_{13}I$.** As expected, the $^{19}F$ NMR spectrum (Figure 1) exhibits, beside the absence of the multiplet centered at −60.0 ppm attributed to $-CF_2CF_2I$ of $C_6F_{13}I$ that underwent a high field shift to −112.0 ppm, the characteristic signals of $C_5F_{11}$ end group centered at −82.0, −124.0, −126.0, and −128.0 ppm assigned to $CF_3$ and the four $CF_2$ groups, respectively.[29−31] The major signal centered at −91.0 ppm is attributed to difluoromethylene groups $-CH_2CF_2-CH_2CF_2-CH_2CF_2-$ (i.e., normal head-to-tail VDF-chaining).

The presence of the triplet ($^3J_{FH}$ = 7.0 Hz) of triplets ($^4J_{FF}$ = 9.8 Hz) centered at −38.0 ppm evidences the expected $-CH_2CF_2I$ end group (e) while both signals at −108.0 ppm (e′) correspond to the difluoromethylene in $-CH_2CF_2-CF_2CH_2I$ group,[19−23,29] arising from a reversed addition followed by a transfer step.

Indeed, Scheme 2 illustrates the different reactions that occur in ITP of VDF and enables one to understand the defects of VDF chaining. Surprisingly, the $^{19}F$ NMR spectrum (Figure 1) shows only traces of both multiplets centered at −113.0 and −116.0 ppm assigned to $-CH_2CF_2-CF_2CH_2-CH_2CF_2-$ reversed head-to-head addition, respectively, as is usually observed in VDF-containing telomers,[20−22,29] oligomers,[19,21,23] or polymers.[23,32]

The $^1H$ NMR spectrum of that same sample (Figure 2) confirms the statements above. Methylene groups located between two difluoromethylenes led to a quintet centered at about 3.0 ppm while the signals centered at 3.3, 3.6, and 3.9 ppm are attributed to methylene groups in $C_6F_{13}CH_2-$, $-(VDF)_nCH_2CF_2I$, and $-CF_2CH_2I$,[29,31,33] respectively.

As expected, $-CF_2CH_2-CH_2CF_2-$ reverse tail-to-tail additions are noted by the presence of a broad signal centered at 2.5 ppm,[19−23,32,33] although their integrals are small for low $\overline{DP}_n$ and increase for higher $\overline{DP}_n$.

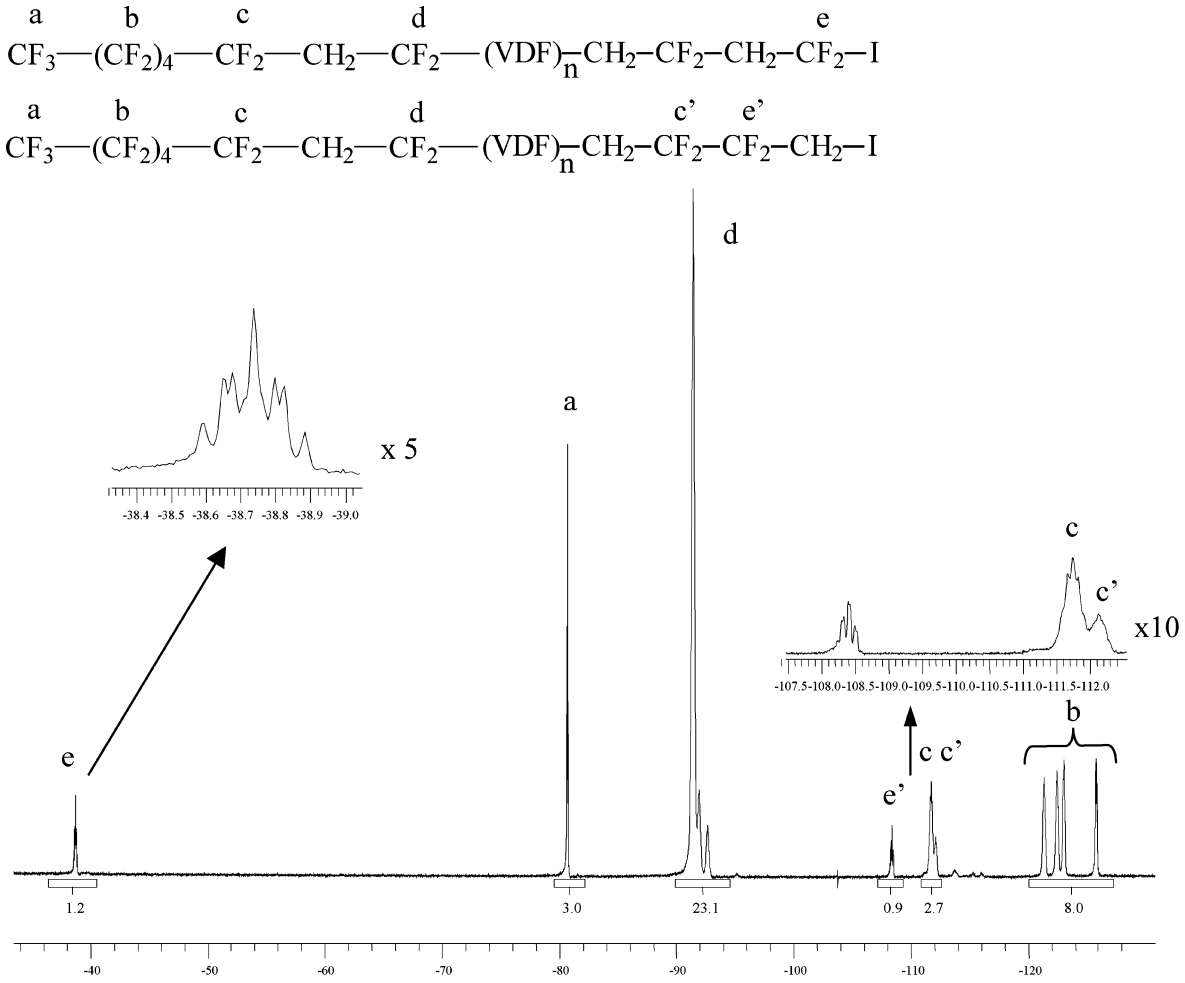
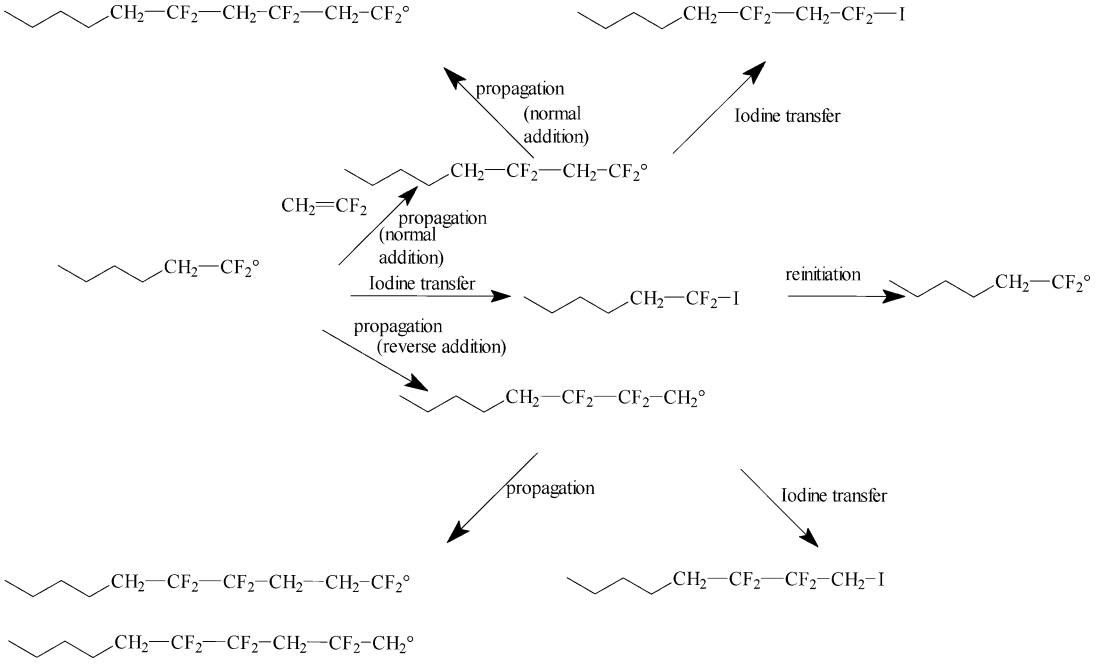



**Figure 1.** $^{19}$F NMR spectrum of the poly(vinylidene fluoride)-I (recorded in deuterated acetone; 200 MHz, 298 K) (average number degree of polymerization ($\overline{DP}_n$) = 13). Experimental conditions of iodine transfer polymerization of vinylidene fluoride with $C_6F_{13}I$: $[VDF]_0$:$[C_6F_{13}I]_0$:[*tert*-butyl peroxypivalate]$_0$ = 100.0:6.6:0.6 at 75 °C.

**Scheme 2. Different Reactions That Occur in Iodine Transfer Polymerization of Vinylidene Fluoride**




Interestingly, the absence of triplets centered at 1.2 and 1.8 ppm characteristic of methyl end groups in C*H*$_3$CH$_2$-CF$_2$– and C*H*$_3$CF$_2$CH$_2$– groups,[20,23] respectively, evidences the absence of the direct initiation of $^{\bullet}$CH$_3$

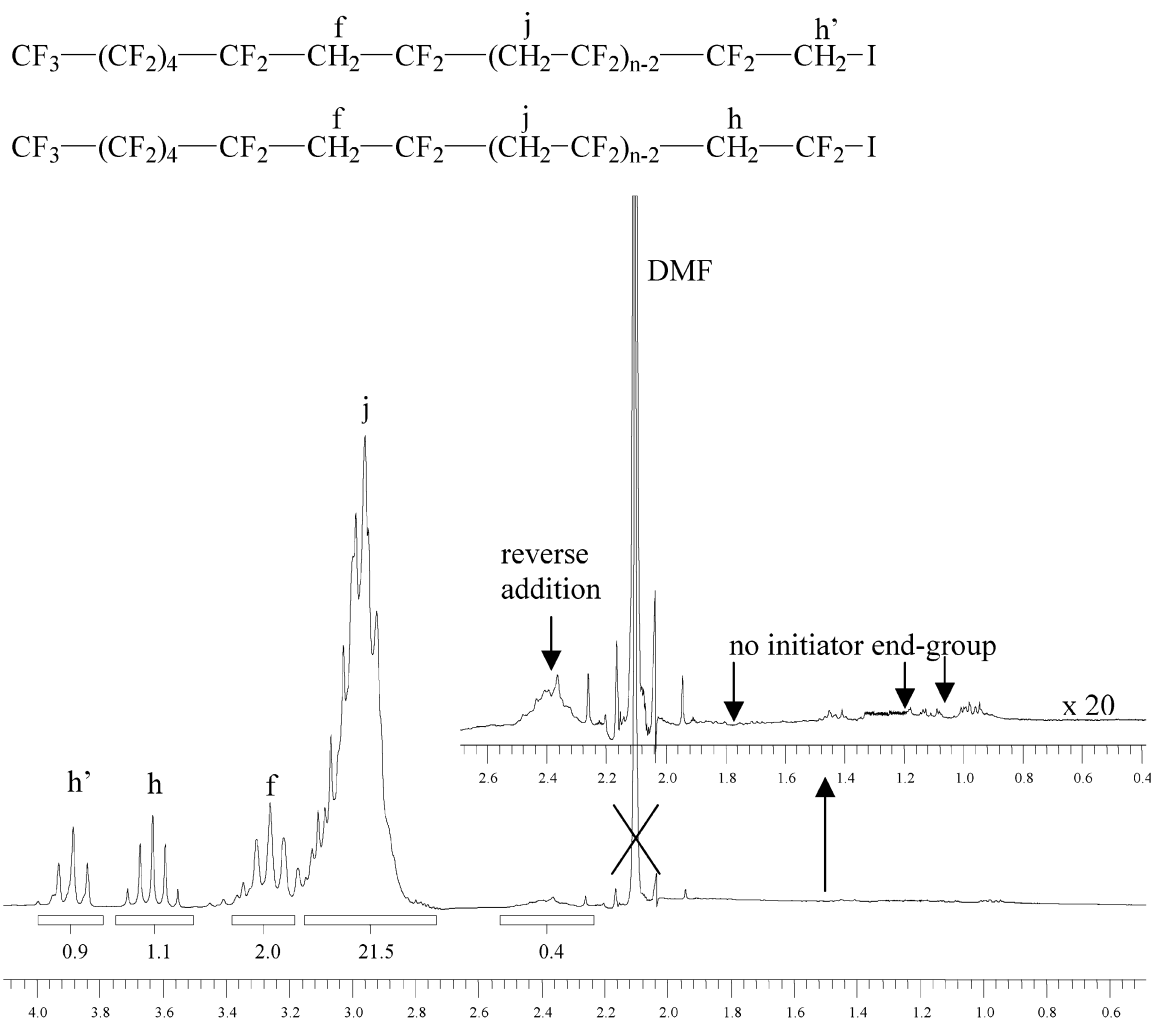



**Figure 2.** $^1$H NMR spectrum of the poly(vinylidene fluoride)−I after precipitation (recorded in deuterated acetone; 200 MHz, 298 K) (average number degree of polymerization ($\overline{DP_n}$) = 13). Experimental conditions of iodine transfer polymerization of vinylidene fluoride with $C_6F_{13}I$: $[VDF]_0$:$[C_6F_{13}I]_0$:[*tert*-butylperoxypivalate]$_0$ = 100.0:6.6:0.6 at 75 °C.

**Table 4. Summary of Average Number Degree of Polymerization ($\overline{DP_n}$) for Various Concentrations of Chain Transfer Agent (CTA: $C_6F_{13}$−I)**

| | | | | | functionality$_{exp}$[e] | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | −$CF_2$−I (%) | | −$CH_2$−I (%) | | |
| run | concentration ratios[a] $[VDF]_0$:[chain transfer agent]$_0$:[*tert*-butylperoxypivalate]$_0$ | targeted[b] $\overline{DP_n}$ (α = 100) | experimental[c] $\overline{DP_n}$ | $\alpha_{VDF}$[d] (%) | $^{19}$F | $^1$H | $^{19}$F | $^1$H | functionality$_{theo}$ -$CF_2$−I (%)[f] |
| M1 | 100.0:11.0:1.1 | 9 | 6 | 70 | 75 | 78 | 25 | 22 | 77 |
| M2 | 100.0:10.0:1.0 | 10 | 9 | 90 | 68 | 65 | 32 | 35 | 66 |
| M3 | 100.0:6.6:0.6 | 15 | 13 | 70 | 60 | 55 | 46 | 35 | 54 |
| M4 | 100.0:3.3:0.3 | 30 | 25 | 75 | 28 | 29 | 72 | 71 | 29 |

[a] Temperature: 75 °C. [b] Calculated by eq 1. [c] Determined by $^{19}$F and $^1$H NMR (eqs 2 and 3). [d] Conversion of monomer assessed by gravimetry: $\alpha_{VDF}$ = weight$_{polymer}$/(weight$_{monomer}$ + weight$_{C_6F_{13}I}$)100. [e] −$CH_2CF_2$−I or −$CF_2CH_2$−I functionalities assessed from $^{19}$F and $^1$H NMR. [f] −$CH_2CF_2$−I functionality determined from eq 6.

(arising from $(CH_3)_3CO^\bullet$ generated by *tert*-butyl peroxypivalate) and $(CH_3)_3C^\bullet$ onto VDF as previously observed.[23]

$\overline{DP_n}$ values can be assessed from $^1$H and $^{19}$F NMR spectra as follows.

(i) The first one is from $^1$H NMR data, taking into account the integrals of the signal attributed to methylene groups ($\int CH_2$) in PVDF about those of $CH_2$ adjacent to $C_6F_{13}$ end groups, as follows:

$$\overline{DP_n} = [\int CH_2^{2.5ppm} + \int CH_2^{3.0ppm} + \int CH_2^{3.3ppm} + \int CH_2^{3.6ppm} + \int CH_2^{3.9ppm}]/[\int CH_2^{3.3ppm}] \quad (2)$$

(ii) The second one comes from the $^{19}$F NMR spectrum (Figure 1) taking into account the integrals of signals of $CF_2$ assigned to PVDF centered at −91.0 ppm, −38.0 ppm and −108.0 ppm about that of $CF_3$ end group centered at −82.0 ppm, as follows:

$$\overline{DP_n} = [\int CF_2^{-91.0ppm}/2 + \int (CF_2^{-38.0ppm} + CF_2^{-108.0ppm})/2 + \int CH_2^{-112.0ppm}/2]/[\int CF_3^{-82.0ppm}/3] \quad (3)$$

Table 4 represents the experimental reactant molar ratios, the targeted and experimental $\overline{DP_n}$ values, and

the theoretical and experimental functionalities (in iodine).

Indeed, the obtained values of $\overline{DP}_n$ are slightly lower than those expected. This difference can be explained by a nontotal conversion of VDF (in the 70−90% range).

Actually, in the course of the propagation step of ITP, the reactivity of ~~$CH_2CF_2^\bullet$ macroradical onto VDF can lead either to a normal or reverse addition (Scheme 2). Transfer steps of the produced macroradicals hence yield ~~$CH_2CF_2-CH_2CF_2I$ and ~~$CH_2CF_2-CF_2CH_2I$, for which the characteristic signals of both $CF_2$ end groups appear at −38.0 and −108.0 ppm, respectively.

Therefore, the functionalities in $-CF_2I$ and $-CF_2CH_2I$ can be assessed from NMR by following eqs 4 and 5:

$$\text{functionality}^{-CF_2-I} = \frac{\int CF_2^{-38.0ppm}/2}{\int CF_2^{-82.0ppm}/2} \quad (4a)$$

Parts a and b of eq 4 enable one to determine the functionalities in $-CF_2I$ and $-CF_2CH_2I$ by $^{19}F$ NMR, respectively.

$$\text{functionality}^{-CF_2CH_2-I} = \frac{\int CF_2^{-108.0ppm}/2}{\int CF_3^{-82.0ppm}/3} \quad (4b)$$

The experimental values of such functionalities (Table 4) can be compared to those determined by $^1H$ NMR taking into account the characteristic signals of $-CF_2CH_2I$, $-CH_2CF_2I$, and $C_6F_{13}CH_2(VDF)_nI$ noted at 3.9, 3.7, and 3.3 ppm, respectively, as follows:

$$\text{functionality}^{-CF_2-I} = \frac{\int CH_2\text{-}CF_2-I^{3.7ppm}/2}{\int R_F-CH_2-CF_2-(VDF)_n-I^{3.3ppm}/2} \quad (5a)$$

$$\text{functionality}^{-CF_2CH_2-I} = \frac{\int -CF_2-CH_2-I^{3.9ppm}}{\int R_F-CH_2-CF_2\text{-}(VDF)_n-I^{3.3ppm}} \quad (5b)$$

Parts a and b of eq 5 also allow one to assess the functionalities in $-CF_2I$ and $-CF_2CH_2I$ by $^1H$ NMR, respectively.

Table 4 also lists the functionalities of PVDF−I in $-CF_2I$ and $-CF_2CH_2I$ and shows a good agreement of these values calculated from $^{19}F$ or $^1H$ NMR spectroscopy. This table also shows that the $-CF_2I$ functionality regularly decreases for higher targeted $\overline{DP}_n$. Indeed, this drop in functionality arises from the reversed addition of the macroradical onto VDF in the propagation step. The literature reports various defects of chaining, usually ranging between 6 and 9% for PVDF[32,34,35] or for oligo(VDF)[19,21,23] and 5−10% for VDF telomers,[1,20,22,29,31] although a recent work reports a value of 2.5% for fractionated $CF_3(VDF)_nI$ telomers.[33]

Equation 6 supplies the theoretical functionality linking the content of chains that do not undergo any inversion ($\psi$) and the $n$ number of VDF units, taking into account that the addition of $C_6F_{13}^\bullet$ onto VDF is regioselective and always occurs as a normal addition[29,31,33] hence showing an "$n - 1$" value in eq 6:

$$\text{theoretical functionality in } CF_2-I = (\psi)^{(n-1)} \quad (6)$$

**Table 5. Variation of the Functionality in $-CF_2-I$ for Various Fractions of Oligomers (Fractionation of Poly(vinylidene fluoride)−I (Average Degree of Polymerization, $\overline{DP}_n = 25$)'**

| fractions | initial $\overline{DP}_n$ | experimental[a] $\overline{DP}_n$ of each fraction | weight of the fraction (g) | functionality$_{exp}$ ($f_{exp}$) $-CF_2-I$ (%)[b] | |
|---|---|---|---|---|---|
| | | | | $^1H$ | $^{19}F$ |
| F1 | 25 | 5 | 10 | 0 | 0 |
| F2 | 25 | 15 | 50 | 5 | 5 |
| F3 | 25 | 35 | 40 | 50 | 45 |

[a] Assessed by $^1H$ NMR. [b] $-CH_2CF_2-I$ functionality determined by $^{19}F$ NMR(eq 4).

By variation of the $\psi$ value, the rate of reverse addition can be determined for each addition onto a further VDF (Table 4). The obtained value is close to 95% (this value gives the best fitting with the experimental values). Indeed, for a PVDF−I of $\overline{DP}_6$, 77% $-CF_2I$ end groups has been observed experimentally, while for PVDF−I of $\overline{DP}_{13}$, $-CF_2I$ theoretical (from eq 6) and experimental contents are identical (54%). These values show that the reverse addition of VDF is not disturbed by ITP. Hence, mechanism of ITP does not prevent from limiting the inversions.

Then, the fractionation of produced PVDF−I $\overline{DP}_{25}$ was carried out in acetone and then in methanol to separate higher from lower molecular weight PVDF−I (Table 5). Such a procedure enabled us to assess the distribution of oligomers bearing the $-CF_2I$ end group.

Interestingly, low $\overline{DP}_n$ fractions (i.e., F1 and F2) contain PVDF−I bearing $-CF_2CH_2I$ end group exclusively as evidenced by $^{19}F$ and $^1H$ NMR (Table 5). This observation can be explained by two features:

(i) The $-CH_2I$ end group is totally unreactive and cannot lead to any transfer reaction, thus stopping the polymerization.

(ii) $-CH_2I$ is far less reactive than $-CF_2I$; hence, the presence of the $-CF_2I$ end group in the medium still enables further transfer reactions. For a better understanding of that reaction, it was worth attempting an ITP of VDF with a chain transfer agent bearing a $-CF_2-CH_2I$ end group, described below.

**2.2. ITP of VDF in the Presence of $HC_2F_4CH_2I$.** The structure of $HCF_2(CF_2CH_2)I$ exhibits a VDF unit adjacent to an iodine end group as frequently involved in controlled radical polymerization.[1−3]

A reaction was carried out as above starting from the following initial concentration molar ratios: $[VDF]_0$:$[CTA]_0$:$[TBPPI]_0$ = 100.0:6.6:0.6. After reaction, a sample was taken off from the total product mixture and was characterized by NMR. The remaining solution was evaporated, precipitated from water, and dried under vacuum at 60 °C for 24 h. The obtained polymer was also characterized by NMR. In contrast to the absence of $C_6F_{13}I$ observed in the case above, the presence of unreacted $HC_2F_4CH_2I$ was noted by means of $^1H$ (presence of a triplet of triplets and of a quintet centered at 6.5 and 3.6 ppm, respectively) and $^{19}F$ NMR (presence of a triplet ($^3J_{FF}$ = 17.8 Hz) of quartets ($^3J_{HF}$ = 3.4 Hz) and of a doublet ($^2J_{HF}$ = 49.6 Hz) of triplets ($^3J_{HF}$ = 4.0 Hz) centered at −112.0 and −136.0 ppm, assigned to $-CF_2CH_2I$ and $HCF_2-$, respectively).

Figure 3 exhibits the $^{19}F$ NMR spectrum of the sample produced from ITP of VDF with $HC_2F_4CH_2I$ for which the characteristic signal (assigned to the $HCF_2-$ end group) of the unreacted CTA is located at −136.0 ppm. After ITP of VDF, the signal of the $HCF_2-$ group

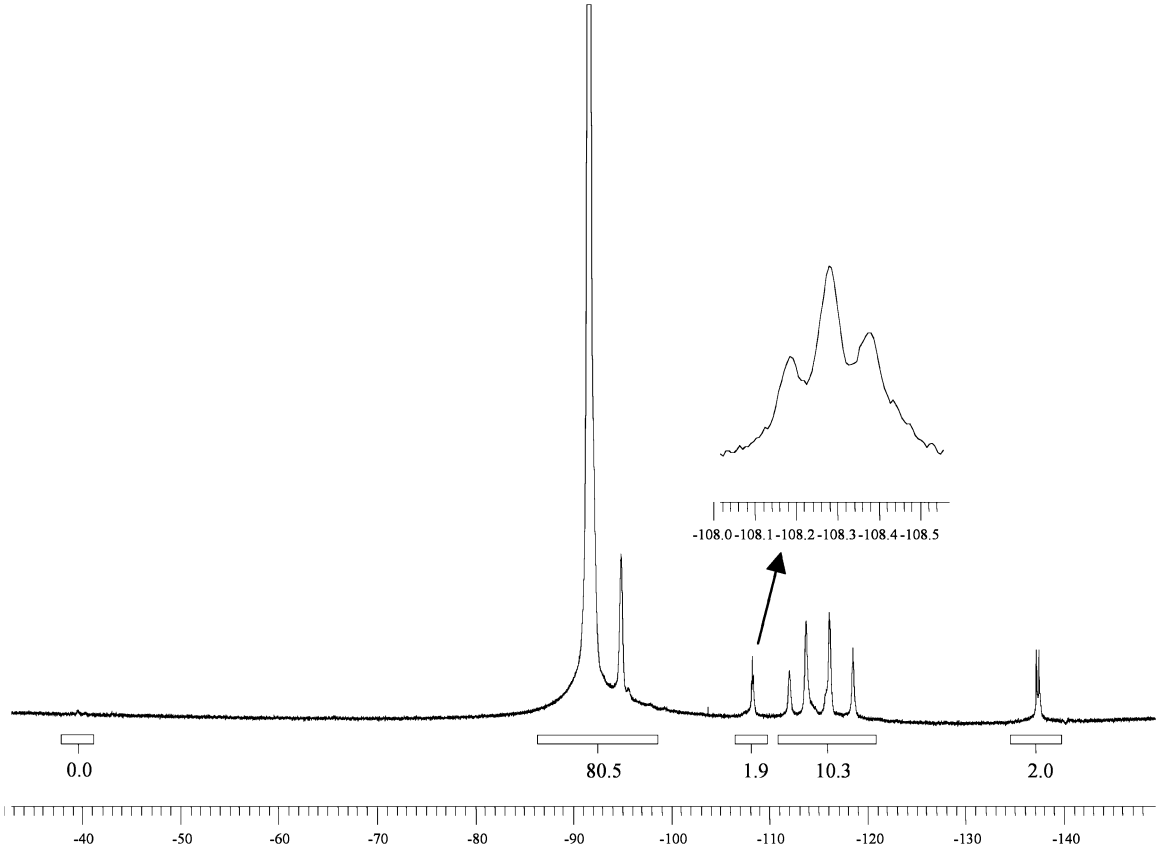



**Figure 3.** $^{19}$F NMR spectrum of poly(vinylidene fluoride)-I obtained by iodine transfer polymerization of vinylidene fluorine with $HC_2F_4CH_2I$ (after precipitation and purification) (average number degree of polymerization ($\overline{DP}_n$) = 35, calculated from eq 8) (recorded in deuterated dimethylformamide; 250 MHz, 298 K). Experimental conditions of iodine transfer polymerization of vinylidene fluoride with $HC_2F_4CH_2I$:[VDF]:[$HC_2F_4-CH_2I$]:[ *tert*-butyl peroxypivalate] = 100.0:6.6:0.6 at 75 °C.

underwent a slight high field shift from −136.0 (unreacted CTA) to −138.0 ppm. In addition, this spectrum shows that the chemical shifts assigned to $CF_2$ groups of incorporated VDF were similar to those of PVDF−I (Figure 3), just like the other methylenes in the CTA.

Thus, the $\overline{DP}_n$ value was assessed from the integrals of the characteristic signals about that of the H*C*$F_2$− end group, as follows (eq 7):

$$\overline{DP}_n = [\int CF_2^{-91.0ppm} + \int CF_2^{-95.0ppm} + \int (CF_2^{-38.0ppm} + CF_2^{-108.0ppm}) + \int CF_2^{-112.0ppm} + \int CF_2^{-115ppm}]/[\int CF_2^{-138.0ppm}] \quad (7)$$

Figure 3 shows the absence of the signal located at −38.0 ppm assigned to −C$F_2$C$H_2$I.

$^1$H NMR spectrum (Figure 4) also exhibits the characteristic signal centered at 6.5 ppm attributed to *H*C$F_2$-C$F_2$-, while the other signals assigned to the methylene groups are similar to those noted in the $^1$H NMR spectra of the above $C_6F_{13}$−PVDF−I. The signal centered at 6.5 ppm shows a complex shape, because there is an overlapping of two triplets of triplets which have different coupling constants: *H*C$F_2$C$F_2$− assigned from the chain transfer agent, which appears at 6.5 ppm, and *H*C$F_2$C$H_2$− from the transfer reaction, which appears at 6.3 ppm, as expected. However, the defects of chaining (tail-to-tail adducts evidenced by the broad multiplet centered at 2.6 ppm) exist in higher amounts in these $HC_2F_4CH_2$−PVDF−I polymers (Figure 4). The presence of signals centered at 1.0, 1.2, 1.3, and 1.8 ppm shows the direct initiation of $CH_3^\bullet$ and $C(CH_3)^\bullet$ (generated from the decomposition of *tert*-butyl peroxypivalate)[23] onto VDF. This initiator decomposition generates two radicals: $(CH_3)_3C^\bullet$ and *tert*-butoxyradicals $(CH_3)_3CO^\bullet$ that rearrange to produce $CH_3^\bullet$ radical and acetone (Scheme 3).

As shown earlier,[23] $CH_3^\bullet$ and $(CH_3)_3C^\bullet$ radicals can be added onto $CH_2$ or $CF_2$ sites of VDF. Thus, these different additions lead to four structures, ($CH_3$)$_3$C−$CH_2$−$CF_2$−, C$H_3$−$CH_2$−$CF_2$−, ($CH_3$)$_3$C−$CF_2$−$CH_2$−, and C$H_3$−$CF_2$−$CH_2$− end groups, evidenced by signals ($^1$H NMR) at 1.0, 1.2, 1.3, and 1.8 ppm, respectively (Figure 4). The structure $CH_3$−$CH_2$−C$F_2$− is confirmed by the signal centered at −95.7 ppm in the $^{19}$F NMR spectrum, while the other signals (($CH_3$)$_3$C−$CH_2$−C$F_2$-, $CH_3$−C$F_2$−$CH_2$− and ($CH_3$)$_3$C−C$F_2$−$CH_2$−) are overlapping with other signals in the $^{19}$F NMR spectrum.

As in eq 7, $\overline{DP}_n$ values were assessed from the integrals of all methylene groups, taking into account that of "labeled" *H*C$F_2$−, C$H_3$−$CF_2$−$CH_2$−, ($CH_3$)$_3$C−$CH_2$−$CF_2$−, C$H_3$−$CH_2$−$CF_2$−, and ($CH_3$)$_3$C−$CF_2$−$CH_2$− end groups (eq 8):

$$\overline{DP}_n = [(\int CH_2^{2.3ppm} + \int CH_2^{2.9ppm} + \int CH_2^{3.9ppm})/2]/[\int HCF_2^{6.5ppm} + (\int CH_3-CH_2^{1.2ppm} + \int CH_3-CF_2^{1.8ppm})/3 + (\int (CH_3)_3C-CH_2^{1.0ppm} + \int (CH_3)_3C-CF_2^{1.3ppm})/9] \quad (8)$$

The experiments were carried out at 75 and 135 °C, initiated by *tert*-butyl peroxypivalate (TBPPI) and 2,5-

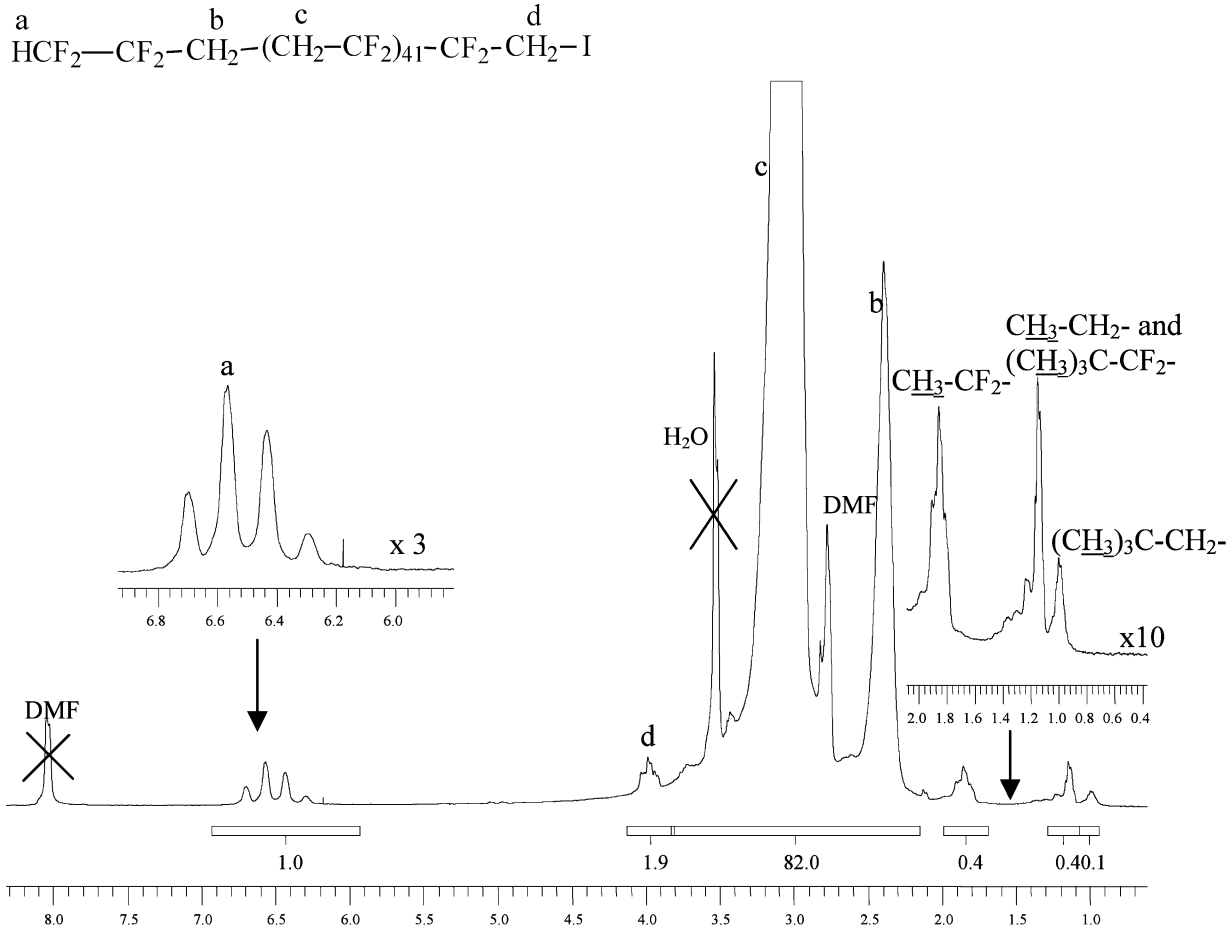
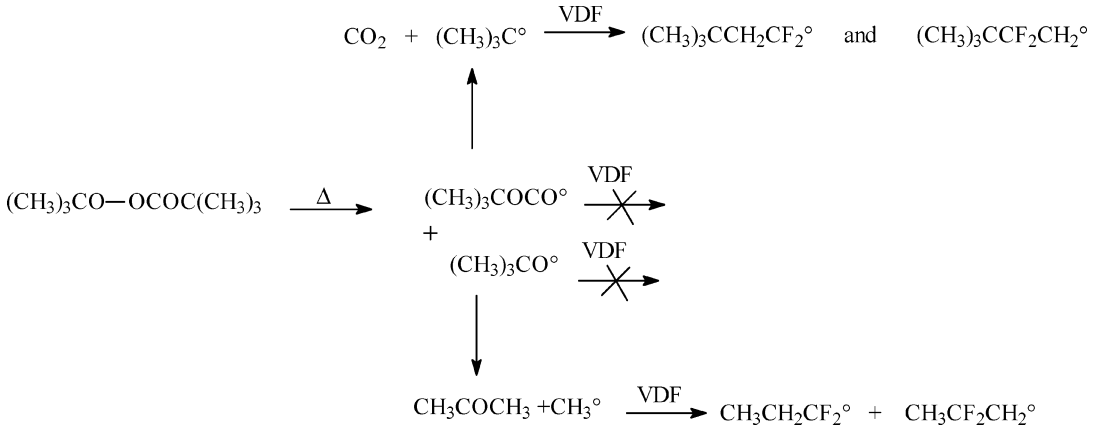



**Figure 4.** $^1$H NMR spectrum of poly(vinylidene fluoride)-I obtained by iodine transfer polymerization of vinylidene fluoride with $HC_2F_4CH_2I$ (after precipitation and purification) (Average number degree of polymerization ($\overline{DP_n}$) = 35, calculated from eq 8) (recorded in deuterated dimethylformamide (DMF); 250 MHz, 298 K). Experimental conditions of iodine transfer polymerization of vinylidene fluoride with $HC_2F_4CH_2I$:[VDF]$_0$:[$HC_2F_4CH_2I$]$_0$:[*tert*-butyl peroxypivalate]$_0$ = 100.0:6.6:0.6 at 75 °C.

**Scheme 3. Decomposition of *tert*-Butylperoxypivalate, Formation of the Radicals, and Their Addition onto Vinylidene Fluoride.[23]**




bis(*tert*-butylperoxide)-2,5-dimethylhexane (DHBP), respectively. The targeted and experimental values of $\overline{DP_n}$ for ITP reaction performed with various concentrations of $HCF_2(CF_2CH_2)I$ are listed in Table 6. A major difference is noted between targeted and obtained $\overline{DP_n}$ values. This discrepancy arises from the low CTA conversion (i.e., 33% was reacted) with respect to the low reactivity of this CTA.

A major difference is noted between the $\overline{DP_n}$ values obtained from $^1$H and $^{19}$F NMR. This difference can be explained by direct initiation of (TBPPI or DHBP) initiator. $^{19}$F NMR does not allow taking into account the chains resulting from direct initiation. The interval of confidence of $\overline{DP_n}$ values obtained from $^{19}$F NMR is about 10−15%.

$^1$H NMR enables one to quantify the chain percentage ($\epsilon$) resulting from direct initiation. Thus, the rate of direct initiation was evaluated from $^1$H NMR, by eq 9. The percentage of the CTA end chain is shown by the $HCF_2CF_2-$ signal, which appears at 6.5 ppm. This is possible since it is assumed that, under these conditions, $CF_3CH_2CF_2CH_3$ does not lead to any transfer, hence

**Table 6. Summary of Average Degree of Polymerization ($\overline{DP_n}$) for Iodine Transfer Polymerization Reaction Performed with Various Concentrations of $HC_2F_4CH_2I$, and with Two Initiators [$A_2$]: [*tert*-Butyl Peroxypivalate] at 75 °C and [2,5-Bis(*tert*-butylperoxide)-2,5-dimethylhexane] at 135 °C**

| reactions | concentration ratios $[VDF]_0:[HC_2F_4CH_2I]_0:[A_2]_0$ | $T$ (°C) | targeted[a] $\overline{DP_n}$ | experimental $\overline{DP_n}$ | $\alpha_{VDF}$[d] (%) | $\alpha_{CTA}$[e] (%) | $f_{exp}(CF_2-I)$ (%)[f] | $(\epsilon)$[g] (%) |
|---|---|---|---|---|---|---|---|---|
| M5 | 100.0:6.6:0.6 | 75 | 15 | 46[b] (35[c]) | 80 | 33 | 0 | 17 |
| M6 | 100.0:6.6:0.6 | 135 | 15 | 32[b] (28[c]) | 80 | 66 | 0 | 13 |
| M7 | 100.0:2.5:0.2 | 75 | 35 | 70[b] (60[c]) | 80 | 33 | 0 | 14 |
| M8 | 100.0:2.5:0.2 | 135 | 35 | 42[b] (38[c]) | 90 | 66 | 0 | 10 |

[a] Calculated from eq 2. [b] Determined by $^{19}F$ NMR (eq 7); determined by $^1H$ NMR (eq 8). [d] Monomer conversion measured by gravimetry (R massic yield): $R = \text{weight}_{\text{polymer}}/(\text{weight}_{\text{monomer}} + \text{weight}_{HCF_6F_2CH_2I})100$. [e] Conversion of $HC_2F_4CH_2I$; $f$, functionality in $CF_2I$ (determined by $^{19}F$ NMR (from eq 4). [g] Chain (percentage resulting from direct) initiation (eq 9).

avoiding the formation of the characteristic $-CH_2-CF_2-H$ end group, which appears as a triplet to triplets centered at 6.3 ppm.[20,21,23] This is confirmed by the absence of the characteristic doublet of multiplets centered at −114.8 ppm [20,21,23] in the $^{19}F$ NMR spectrum.

$$\epsilon = \left[\frac{\int (CH_3)_3C-CH_2{}^{1.0\text{ppm}} + \int (CH_3)_3C-CF_2{}^{1.3\text{ppm}}}{9} + \frac{\int CH_3\text{-}CH_2{}^{1.2\text{ppm}} + \int CH_3\text{-}CF_2{}^{1.8\text{ppm}}}{3}\right] \Bigg/ \left[\frac{\int (CH_3)_3C-CH_2{}^{1.0\text{ppm}} + \int (CH_3)_3C-CF_2{}^{1.3\text{ppm}}}{9} + \frac{\int CH_3-CH_2{}^{1.2\text{ppm}} + \int CH_3\text{-}CF_2{}^{1.8} + \int HCF_2{}^{6.5\text{ppm}}}{3}\right] \quad (9)$$

$\epsilon$ Values are summarized in Table 6 and show the low efficiency of $HC_2F_4CH_2I$ in contrast to that of $C_6F_{13}I$. Hence, it cannot lead to a good control of molar masses at 75 °C. This statement can be explained by the dissociation energy of $-CH_2-I$ bond which is stronger than that of $-CF_2-I$ (ca. 45 kJ $mol^{-1}$ [1]). To lower the stability of the $-CH_2-I$ bond and hence to improve the transfer step, ITP of VDF with $HC_2F_4CH_2I$ was carried out at 135 °C (Table 6). The CTA conversion increased (66%) while the control of the $\overline{DP_n}$ was slightly improved. However, $HC_2F_4CH_2I$ does not lead to any good control of the molar masses. Deeper experiments are under progress, especially involving the kinetics of ITP of VDF, to check whether this radical polymerization is controlled or *pseudo*living.

## Conclusion

Two fluoroiodinated chain transfer agents involved in the iodine transfer polymerization (ITP) of vinylidene fluoride showed different behaviors in transfer, leading to different consequences in ITP.[37] $C_6F_{13}I$ exhibits high efficiency and reactivity, thus inducing a good control of average degree of polymer in number ($\overline{DP_n}$) and a few defects of VDF chaining. Such a reaction is close to a *pseudo*living polymerization, but to check that observation, a deeper study is nesessary. In contrast, $HC_2F_4CH_2I$ behaves differently in similar conditions and leads to PVDF−I polymers containing higher defects of VDF chaining and having uncontrolled $\overline{DP_n}$ (experimental values were almost twice higher than those of the targeted ones). At higher temperatures, greater CTA conversions were noted while a slightly better control of $\overline{DP_n}$ was achieved. The microstructure of resulting PVDF−I leads to the following conclusions.

(i) ITP of VDF involving $C_6F_{13}I$ produced two structures: $C_6F_{13}-(VDF)_n-CH_2-CF_2-I$ and $C_6F_{13}-(VDF)_n-CF_2-CH_2-I$.

(ii) When the macroradical terminated by $-CH_2CF_2^\bullet$ reacts onto the $CF_2$ site of VDF, the generated $-CH_2-CF_2-CF_2-CH_2^\bullet$ (head-to-head addition) radical undergoes a transfer which is not able to reinitiate ($-CF_2-CH_2-I$), hence leading to dormant species, which stopped the reaction.

However, further investigations are required to understand ITP of VDF (i.e., to check the *pseudo*living character of ITP by establishing the molar masses vs VDF conversion linear relationship) and to study the kinetics of that polymerization. Hence, it is worth assessing the transfer constants of $C_6F_{13}I$, $HC_2F_4CH_2I$ and also $C_6F_{13}CH_2CF_2I$ and to study the "molar masses−VDF conversion" relationships in each case, under investigation.

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**Supporting Information Available:** Text giving further experimental details on the reactions in that autoclave and figures showing $^{19}F$ NMR spectra of $C_6F_{13}-I$, $C_6F_{13}-CH_2-CF_2-I$, and $HC_2F_4CH_2I$ and of the sample produced by ITP of VDF with $HC_2F_4CH_2I$. This material is available free of charge via the Internet at http://pubs.acs.org.

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