First MALDI-TOF Mass Spectrometry of Vinylidene Fluoride Telomers Endowed with Low Defect Chaining

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ABSTRACT: The radical telomerization of vinylidene fluoride (or 1,1-difluoroethylene, VDF) with iodotrifluoromethane initiated by *tert*-butyl peroxypivalate is presented. The VDF telomers obtained were characterized by ^{1}H and ^{19}F NMR spectroscopy and by matrix-assisted laser desorption−ionization time-of-flight mass spectrometry (MALDI TOF MS) that revealed low polydispersity indexes showing a pseudo-living character of this reaction regarded as an iodine transfer polymerization process. CF_3 and CF_2I end groups appear as suitable labels in the ^{19}F NMR spectra to assess the number-average molar masses of these VDF telomers ($\bar{M}_n$). Both these techniques showed a good agreement in terms of degree of telomerization, and the first examples of MALDI−TOF mass spectra of fluorotelomers are presented. Interestingly, all telomers obtained exhibit the structure $CF_3CH_2CF_2(VDF)_nI$, showing that (i) the trifluoromethyl radical preferentially attacked the methylene site of VDF with a high regioselectivity; (ii) the only transfer reaction arose from that to the CF_3I and not from the monomer, the initiator, the solvent, or the polymer; and (iii) a very low defect of VDF chaining (0.73% regarded as the lowest one noted in the literature) was observed.

1. Introduction

The telomerization of vinylidene fluoride (or 1,1-difluoroethylene, VDF) has been carried out by many authors and was also reviewed.[1] Among these various transfer agents, the iodinated telogens have drawn much attention, and Table 1 lists various investigations regarding the telomerization of VDF with such transfer agents in various initiation conditions (photochemical, thermal, in the presence of radical initiators or redox systems).

The efficient telomerizations of VDF with perfluoroalkyl iodides,[9,11,16,17,21,22] $ClCF_2CFClI$,[16] or α,ω-diiodoperfluoroalkanes[19,21,22] were achieved thanks to the low dissociation energy of the C−I bond. The telomerizations of VDF with $C_nF_{2n+1}I$ (n = 1, 3, 4, 6, or 8) catalyzed by a redox system (e.g., $FeCl_3$/Ni)[9] or photochemically induced[4−7,12] are quite selective (only the monoadduct was produced) in contrast to thermally initiated telomerizations, which led to a telomeric distribution C_nF_{2n+1} $(VDF)_pI$ (where $p = 1-5$).

However, to our knowledge, *tert*-butyl peroxypivalate has never been used to initiate the telomerization of VDF with perfluoroalkyl iodides, and we have found it interesting to use it as radical initiator.

Furthermore, iodotrifluoromethane seems to be a more active transfer agent, but to our knowledge, no articles describe its reactivity toward VDF[4−8] when this reaction was initiated by peroxides or peroxydicarbonates.

As a matter of fact, matrix-assisted laser desorption−ionization time-of-flight mass spectrometry (MALDI−TOF MS) is a very interesting technique (complementary to nuclear magnetic resonance spectroscopy) to characterize oligomers and polymers,[23] but to our knowledge, it has never been used for the analysis of fluorotelomers, although electrospray ionization was realized on VDF[24] and chlorotrifluoroethylene telomers.[25]

A few papers report the MALDI−TOF MS characterization of fluorinated polymers which are hydrophobic and insoluble in common organic solvents.[26] Marie et al.[26c] have demonstrated the influence of protocol preparation of the sample target (dried droplet, melting, matrix vapor deposition) on the quality of the spectra. Latourte et al.[26a] characterized fluorinated polymers containing a perfluorinated repeating unit or a perfluorinated end group by MALDI and ESI MS. Hence, the objective of this paper concerns the study of the telomerization of VDF with iodotrifluoromethane and the characterization by NMR and MALDI-TOF MS of these obtained telomers.

2. Results and Discussion

2.1. Synthesis of the Fluorinated Telomers. The synthesis of ω-iodinated telomers containing VDF (useful as precursors of diblock copolymers,[27] or for a curing process,[28] or which can be chemically changed into a functional group[29]) is achieved from a one-step reaction, as follows:

$$CF_3I + (n + 1)VDF \rightarrow CF_3CH_2CF_2(VDF)_nI \quad (1)$$

The chosen solvent was acetonitrile because it dissolves all the reactants well and because of its negligible transfer constant.[30] The reaction was performed in the presence of *tert*-butyl peroxypivalate as the radical initiator, in batch, and in an autoclave at 74 °C in order to have a half-life of 1 h. Organic peroxides were chosen because they are among the most widely used initiators[31] of radical polymerizations. We have utilized *tert*-

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Table 1. Telomerization of Vinylidene Fluoride with Iodinated Transfer Agents[a]

telogen	method of initiation	structure of telomers	ref
ICl	various initiations	$ClCF_2CH_2I$	2
HI	thermal	CH_3CF_2I	3
CF_3I	UV, 28 days/RT	$CF_3(VDF)_1I$	4
CF_3I	UV/0−100 °C	$CF_3(C_2F_2H_2)I$	5
CF_3I	UV/140 °C	$CF_3CH_2CF_2I$ (major) $CF_3CF_2CH_2I$ (minor)	6
CF_2HI	UV	$HCF_2CH_2CF_2I$	7
C_2F_5I	10 h/220 °C	$C_2F_5CH_2CF_2I$	8
iC_3F_7I	185−220 °C	$iC_3F_7(VDF)_nI$; $n = 1-5$	9−11
nC_3F_7I	20 h/UV/140−210 °C	$nC_3F_7(C_2F_2H_2)I$	12
$(CF_3)_3I$	thermal	$(CF_3)_3(VDF)_n$ I, $n = 1,2$	13
C_4F_9I	230 °C/15 h	$C_4F_9(VDF)_nI$	14
C_4F_9I	AIBN, scCO2	$C_4F_9(VDF)_nI$; $n = 1-9$	15
C_4F_9I	$FeCl_3$/Ni	$C_4F_9CH_2CF_2I$	9
$C_pF_{2p+1}I$ ($p = 1-8$)	180−220 °C	$C_nF_{2p+1}(VDF)_nI$; low n	9, 16, 17
$C_5F_{11}CFICF_3$	180−190 °C	$C_5F_{11}CF(CF_3)(CH_2CF_2)_nI$	17
$ClCF_2CFClI$	181°C/26 h	$ClCF_2CFCl(VDF)_nI$	16
ICH_2I	DTBP/130 °C	$ICH_2-CH_2CF_2I$ (91%)	18
ICF_2I	LTA/70 °C	$ICF_2CH_2CF_2I$	19
$I(C_2F_4)_nI$, $n = 1, 2, 3$	180 °C or rad	$I(VDF)_p(C_2F_4)_n(VDF)_qI$; variable $p + q$	20, 21
PFPE-I	DTBP, 140 °C	diblock $PFPE(VDF)_nI$, $\bar{n} = 5-50$	22

[a] RT, sc, DTBP, LTA, and PFPE mean room temperature, supercritical, di-*tert*-butyl peroxide, lead tetraacetate, and perfluoropolyether group, respectively.

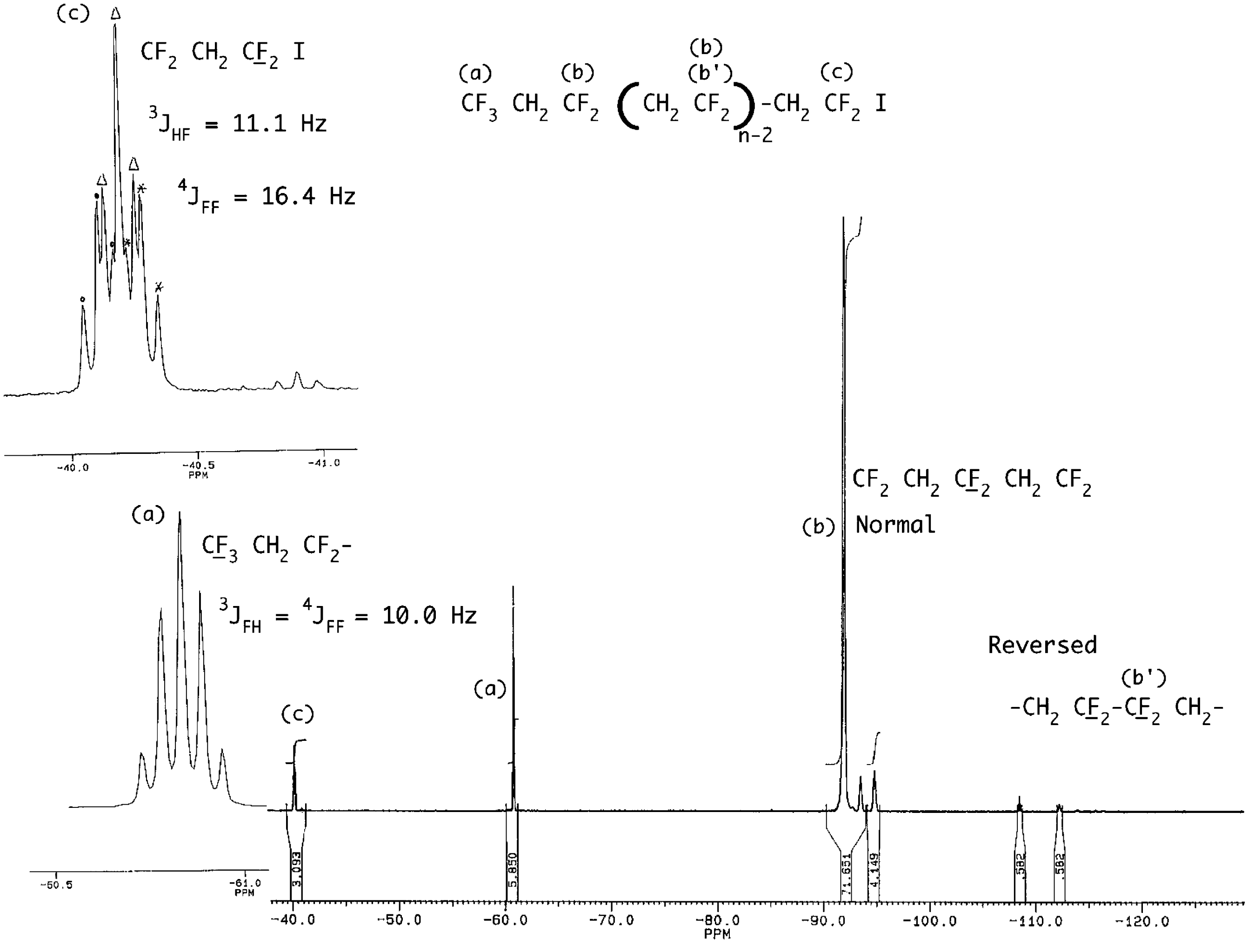


Figure 1. ^{19}F NMR spectrum of $CF_3(VDF)_{20}I$ (sample 1) recorded in deuterated DMF.

butyl peroxypivalate since it has been successful in the homopolymerization of VDF[30] and in copolymerization of VDF with other fluoromonomers.[32]

This reaction led to good yields (>65%) in shorter times (50 min). The maximum pressure of the autoclave reached 65 bar in 110 min and then dropped to 14 bar. The full details of the procedure are supplied in the experimental part. After reaction, distillation of a part of the solvent, workup, and purification of the VDF telomers by solvent fractionation[33] (precipitation in pentane), the structures of the fluoroiodinated telomers were characterized.

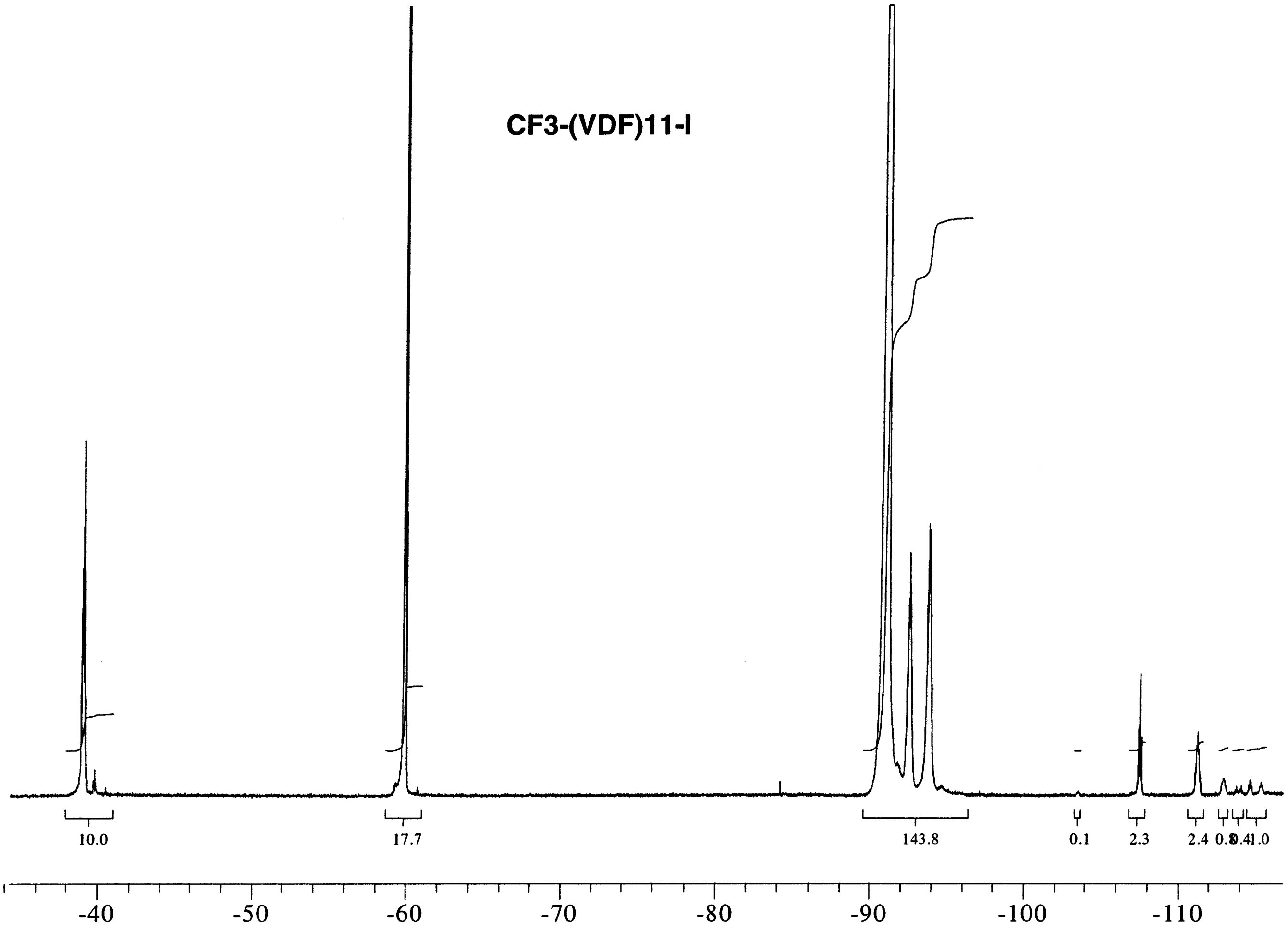


Figure 2. ^{19}F NMR spectrum of $CF_3(VDF)_{11}I$ (sample 2) recorded in deuterated DMF.

2.2. Characterization of the Fluorinated Telomers. Two distinct analytical techniques have been used for the characterization of two telomers (sample 1, $\overline{DP}_{20}$; sample 2, $\overline{DP}_{11}$) by ^{19}F and ^{1}H NMR spectroscopies and by MALDI−TOF MS.

2.2.1. Characterization by NMR. The ^{19}F NMR spectrum (Figure 1) of sample 1 exhibits the characteristic quintet (that is indeed a triplet of triplets ($^{3}J_{FH} = {}^{4}J_{FF} = 10.0$ Hz)) centered at −60.8 ppm assigned to the CF_3 end group adjacent to the CH_2CF_2 group. This shows the selective addition of $^{\bullet}CF_3$ onto the CH_2 site of VDF (as mentioned in previous works,[9,21] and not onto the difluoromethylene group as claimed by Chambers et al.[10]). Such a signal (its resonance and its shape) was already noted in previous investigations[34,35] dealing with the photochemical telomerization of VDF with aryl or alkyl trifluoromethanethiosulfonate[34] and the thermal polymerization of VDF initiated by octafluoro[2.2]-paracyclophane containing a CF_3 substituent,[35] respectively. In both cases, the $CF_3CH_2CF_2\!\sim\!\sim$ end structure was obtained.

Besides the signals in the −91 to −95 ppm range assigned to the difluoromethylene groups of the head-to-tail VDF units[9,11,16,17,22,30,36] (i.e., produced from normal VDF propagation), the ^{19}F NMR spectra (Figures 1 and 2) show the presence of the low field signal centered at −40 ppm assigned to the $\sim\!\sim CH_2CF_2I$ end group. This confirms the structure of telomers of VDF with $C_nF_{2n+1}I$ ($n = 4, 6, 8$),[9,11,17] with $I(C_2F_4)_pI$ ($p = 1, 2, 3$),[21] or with PFPE-I[22] (where PFPE stands for perfluoropolyether).

Furthermore, both expected head-to-tail additions (or normal VDF chaining, i.e., $\sim\!\sim CH_2CF_2{-}CH_2CF_2\!\sim\!\sim$) and defects of chaining arising from (i) head-to-head addition ($\sim\!\sim CH_2CF_2{-}CF_2CH_2\!\sim\!\sim$) or (ii) tail-to-tail addition ($\sim\!\sim CF_2CH_2{-}CH_2CF_2\!\sim\!\sim$) reversed additions[17,21,30,34−36] were noted, hence confirming the literature or PVDF[30,36] for which commercially available PVDF contains ca. 5−8%[37] of defect of chaining while that of fluorotelomers is about 7−12%[9,17] (although these latter ones were obtained at higher temperatures).

Surprisingly, the signals observed between −113 and −116 ppm, characteristic of the CF_2 groups of the reversed VDF units (i.e., head-to-head VDF chaining),[17,30,34,35] are almost negligible, demonstrating a certain controlled behavior of the telomerizations. However, the signal centered at −109 ppm is assigned to a reversed CF_2CH_2I end group and could evidence the nonreactivity of this group in contrast to that of CH_2CF_2I.

Several specific investigations have led to unusual low inverted VDF chaining (Table 2): (i) Chen et al.[13] synthesized VDF telomers from $(CF_3)_3CI$ at low temperature with ca. 3−4% defect. (ii) Liepens et al.[38] synthesized PVDF from the polymerization of VDF initiated by $(^{i}Bu)_3B/O_2$ from −196 °C to room temperature or by $Et_3Al/TiCl_4$ at room temperature, leading to PVDF that contained 3.2 and 2.7% of reversed

Table 2. Experimental Conditions and Defect of VDF Chaining in the Products Obtained by Polymerization or Telomerization of VDF[a]

transfer agent	experimental conditions	formulas of the products	defect of VDF chaining (%)	reference
CCl_4	di(isopropyl)peroxy dicarbonate (60 °C)	$Cl_3C(VDF)_nCl$, $n = 20$	6.5	37a
none	emulsion (30 °C)	PVDF (Kynar)	5.0	36a, 40
none	emulsion (30 °C)	PVDF	4.5	37c
CCl_4	di(isopropyl)peroxy dicarbonate (60 °C)	$Cl_3C(VDF)_nCl$, $n = 9$	4.0	37a,b
none	suspension (30 °C)	PVDF(KF polymer)	3.7	36c
IC_4F_8I	$(R_{F,Cl}CO_2)_2$ (50−60 °C)	I−PVDF−I (ITP)	3.4−4.7	37c
$(CF_3)_3CI$	radicals (20−50 °C)	$(CF_3)_3C(VDF)_nI$	3 to 4	13
none	$(^iBu)_3B/O_2/{-}196$°C to RT	PVDF	3.2	38
none	$(Cl_3CCO_2)_2$ (50 °C)	$P(C_2D_2F_2)$ chemically changed into PVDF	2.8	39
none	$Et_3Al/TiCl_4$/RT	PVDF	2.7	38
CF_3I	*tert*-butyl peroxypivalate 74°C	$CF_3(VDF)_nI$	0.73 and 1.80	this work

[a] RT stands for room temperature.

addition, respectively. (iii) Cais and Kometani[39] achieved the radical polymerization of 1,1-difluoro-2,2-dideuterioethylene initiated by bis(trichloromethyl) peroxydicarbonate at 60 °C, leading to poly(CD_2CF_2) with 97.16% normal addition. The selective reduction of all the deuterium atoms yielded PVDF containing 2.84% of reversed VDF chaining. (iv) Okui[37a,b] achieved the radical telomerization of VDF with carbon tetrachloride and produced $Cl_3C{-}(VDF)_n{-}Cl$ that contained 4% and 6.5% of reversed adduct when average *n* was 9 and 20, respectively. Hence, the temperature seems to have a crucial effect on the amount of reversed adducts (the lower the temperature, the lower this amount).

As for our study, the percentage of defects of VDF chaining can be assessed from the following ratio that takes into account the integrals of the signals centered at −40, −91 to −95, and −109 ppm mentioned above:

$$\%\ \text{defect of VDF chaining} = \frac{I_{-109}}{I_{-109} + I_{-91\text{ to }-95} + I_{-40}} \qquad (2)$$

The calculation of the defects of chaining of $CF_3(VDF)_n{-}I$ was 0.73% and 1.80% for the fluoroiodotelomers 1 and 2, respectively. Compared to those determined in the surveys above, our results show that the lowest reversed VDF addition has been achieved.

Interestingly, in contrast to Liepens et al.[38] and Cais and Kometani,[39] who carried out these reactions at low temperature (−196 °C) or at to room temperature, our telomers produced at 74 °C have also shown a very low inverted VDF content. Yet, Bovey[40] mentioned that the lower the temperature, the lower the amount of reversed addition.

Interestingly, the absence of the doublet ($^2J_{FH}$ ca. 50 Hz) of multiplets, centered at −114.9 ppm and characteristic of a CH_2CF_2H end group, demonstrates the lack of transfer to the solvent, to the initiator, to the polymer, or to the monomer. This is also confirmed by the ^1H NMR spectra that does not contain the characteristic triplet of triplets centered at 6.3 ppm assigned to the terminal proton in the $\sim\!\sim CH_2CF_2H$ group.[30,36] The ^1H NMR spectra of VDF telomers also show the expected broad quintet and small multiplet centered at 2.65 and 2.35 ppm, assigned to normal head-to-tail VDF chaining and reversed tail-to-tail VDF units, respectively. The latter one is rather small and confirms the poor amount of $CF_2CH_2{-}CH_2CF_2{-}$ tail-to-tail defect of chaining. The presence of the triplet ($^3J_{HF} = 15.2$ Hz) centered at 3.4 ppm indicates an inverted VDF unit bearing the iodine atom (i.e., CF_2CH_2I end group) as shown in the literature.[9,17,20]

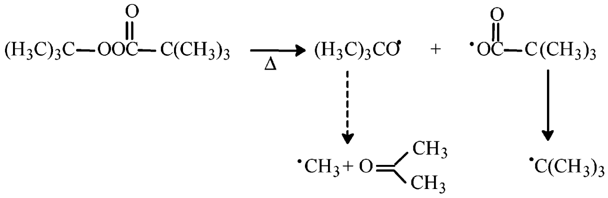
The number-average molar masses of these VDF telomers, $\bar{M}_n$, could be assessed by two techniques of analysis: by NMR and MALDI−TOF mass spectrometry.

Hence, $\bar{M}_n$ can be determined by taking into account the integrals I_1, I_2, I_3, and I_4 of the ^{19}F NMR signals centered at −40.2, −60.8, −91 to −95, and −109 ppm, respectively:

$$\bar{M}_n = 64\,\frac{(I_1 + I_3 + I_4)/2}{I_2/3} + 195.9 \qquad (3)$$

Hence, from the integrals of the chemical shifts in Figures 1 and 2, we have found that the number-average molar masses of both samples 1 and 2, $\bar{M}_n$, were 1424.8 and 1067.5, respectively.

Good yields were obtained in the presence of *tert*-butyl peroxypivalate. Yet, this initiator exhibits a half-life of 1 h at 74 °C, and it generates three (or four) types of radical, as follows:



$$(H_3C)_3C{-}OOC(=O){-}C(CH_3)_3 \xrightarrow{\Delta} (H_3C)_3CO^{\bullet} + {}^{\bullet}OC(=O){-}C(CH_3)_3 \qquad (4)$$
$$(H_3C)_3CO^{\bullet} \dashrightarrow {}^{\bullet}CH_3 + O{=}C(CH_3)_2 \qquad {}^{\bullet}OC(=O){-}C(CH_3)_3 \rightarrow {}^{\bullet}C(CH_3)_3$$

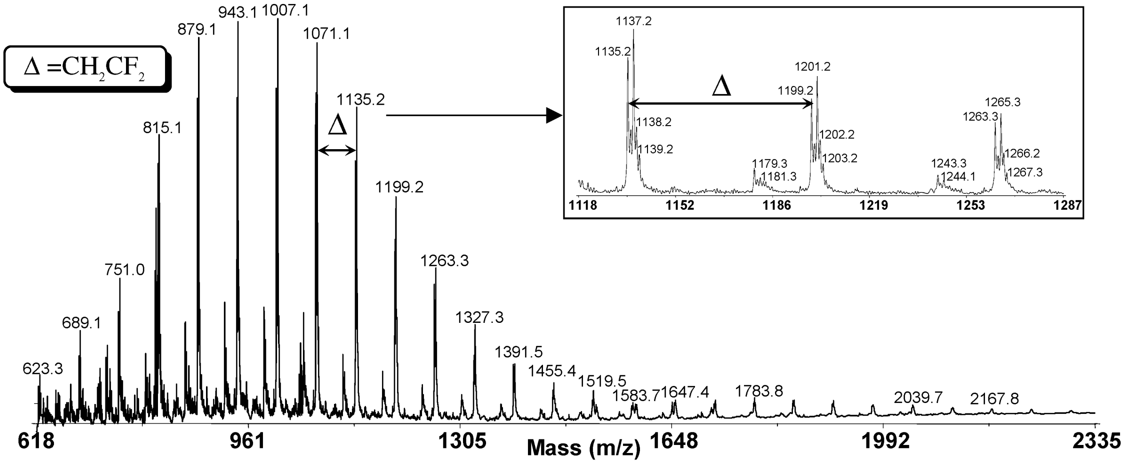
The formation of the methyl radical from the *tert*-butoxyl one can occur from 100 to 120 °C,[30,41] but it is not obvious at 75 °C since, to our knowledge, it is not quoted in the literature. However, the presence of these different kinds of radicals produced in the course of the reaction may provide a good efficiency of telomerization based on previous works.[42]

Interestingly, the absence of signals at 1.10, 1.18, 1.22, and 1.80 ppm (assigned to $(CH_3)_3CCH_2CF_2\sim\!\sim$, $CH_3CH_2CF_2\sim\!\sim$, $(CH_3)_3CCF_2CH_2\sim\!\sim$, and $CH_3CF_2CH_2\sim\!\sim$, respectively) in the ^1H NMR spectra of PVDFs prepared from the radical polymerization of VDF initiated by *tert*-butyl peroxypivalate[30] evidences the high efficiency of CF_3I a transfer agent.

Second, the structure of the telomers and the values of $\overline{DP}_n$ can also be assessed from the MALDI−TOF MS.

2.2.2. MALDI−TOF Mass Spectrometry. Several mass spectrometric techniques can be used to characterize vinylidene fluoride telomers. Among them, fast

(a) $CF_3(CH_2CF_2)_{11}I$ (SAMPLE 2)



(b) $CF_3(CH_2CF_2)_{20}I$ (SAMPLE 1)

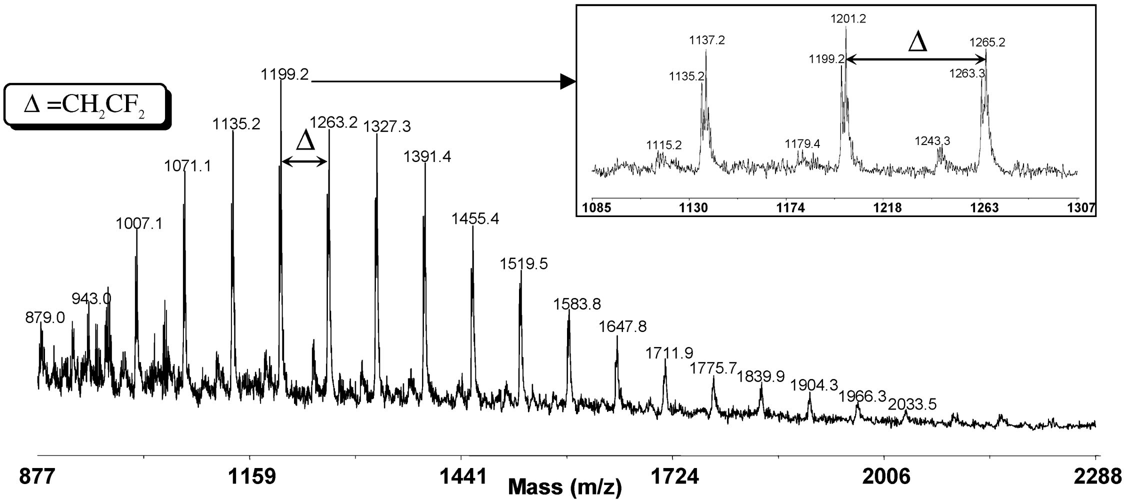


Figure 3. Positive-ion MALDI−TOF mass spectrum of (a) $CF_3(VDF)_{11}I$ (sample 2) and (b) $CF_3(VDF)_{20}I$ (sample 1) in 2,3,4,5,6-pentafluorcinnamic acid (PFCA). The telomers are Ag^+-cationized (addition of AgTFA in telomer solution). The inset shows expanded zones of spectra. The data were acquired in a linear mode.

atom bombardment (FAB) and liquid secondary ion (LSI) mass spectrometry have extensively been applied onto low molecular weight polymers such as those studied in this paper (<5000 g/mol). However, these techniques are limited to polar polymers that are miscible with the polar liquid matrices, and moreover they lead to species fragmentation and hence to complex spectra. Electrospray ionization (ESI) mass spectrometry is not widely used to analyze fluorinated polymers because of the production of multiply charged ions which greatly complicate the interpretation of the spectra. Therefore, MALDI−TOF mass spectrometry has been chosen. It is established as a powerful technique to analyze polymers since this technique supplies information about the end groups, the base units, the molecular weights, and distributions for monodispersed macromolecules. It has many advantages over other methods such as size exclusion chromatography (SEC), a popular method for polymer characterization which unfortunately needs standards of the same structure as that of the samples. Finally, the associated time-of-flight (TOF) mass spectrometer is ideal for polymer analysis because of theoretically unlimited mass range.

In this work, the VDF telomers were soluble in dimethylformamide, dimethylacetamide, and dimethyl sulfoxide, only. The analyses were carried out on a Voyager-DE STR instrument in the linear mode using 2,3,4,5,6-pentafluorocinnamic acid (PFCA) as the matrix. Silver trifluoroacetate was added as the cationization agent. Consequently, a silver cation is complexed with each of the sample molecules.

In the obtained MALDI−TOF mass spectra of two analyzed telomers, sample 2 (Figure 3a) and sample 1 (Figure 3b) ($\overline{DP}$ was assessed by NMR), separate telomers were clearly resolved. The difference of mass between peaks was 64 g/mol, corresponding to one VDF unit (CH_2CF_2). The end groups, deduced of monoisotopic mass, correspond to the expected ones (I and CF_3 group). Interestingly, it was noted the absence of oligomers obtained by coupling reactions (i.e., no $CF_3(VDF)_nCF_3$ was formed). In the expanded zones of the figures, the peaks at minus 20 g/mol with regard to major populations can be attributed to a loss of HF.

This observation mentioned by Marie et al.[24] and Chen et al.[43] and shown in our PSD spectrum (Figure 4) is ascribed to fragmentation induced by the analysis technique used. The same remark could be applied to the analysis of the telomer leading to a loss of HI (−128 g/mol). This loss cannot be evidenced in

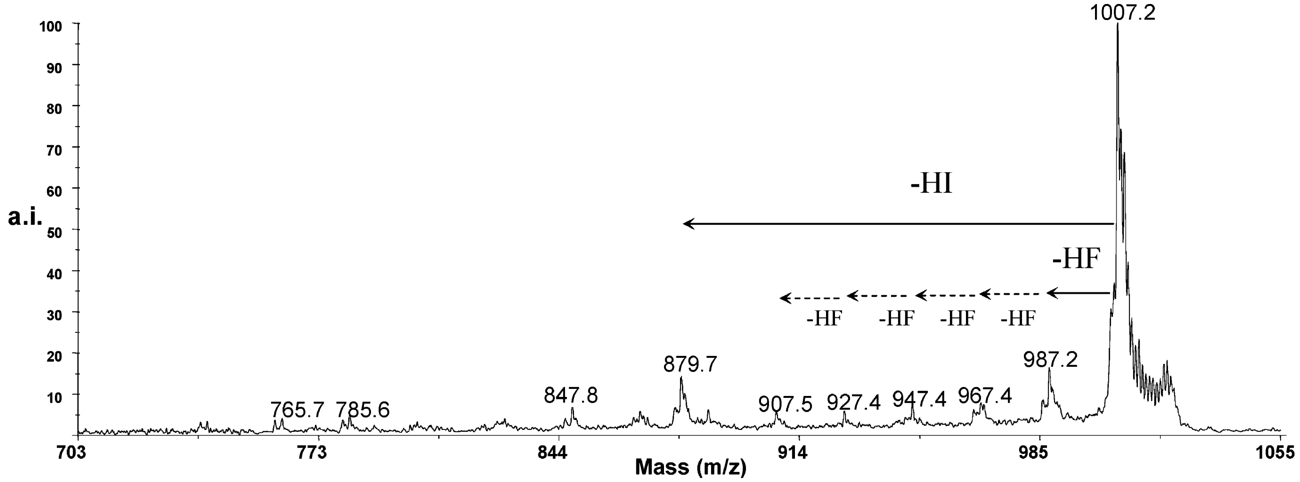


Figure 4. Post source decay MALDI−TOF mass spectrum of $CF_3(VDF)_{11}I$. The most intense fragment peaks correspond to the loss of HF and HI groups.

Figure 3 since the molar mass of this molecule equals two CH_2CF_2 monomer units (2×64 g/mol). There was an overlapping of peaks. However, as the PSD spectrum shows this loss of 128 g/mol, it really exists and is again caused by the ionization/desorption process of the MALDI−TOF analysis. Moreover, an evidence of this fragmentation caused by the MALDI−TOF technique was provided by NMR which does not indicate any transfer reaction (except that to the transfer agent). Hence, it is noteworthy mentioning that the association of both NMR and MALDI−TOF spectrometry is very interesting because they are complementary to each other.

In Figure 3b, the distribution ranges between 9-mers and the 27-mers (sample 1). It is centered at 14-mers and is calculated as follows:14×64.01 (CH_2CF_2) + 195.9 (CF_3I) + 106.9 (Ag) = 1198.9 *m/z* instead of 1199.20 obtained experimentally. As an indication, the calculated number-average molar masses, M_n, is 1240 g/mol (with a narrow PDI = 1.09), which is close to the NMR value (1531.8 g/mol, including silver).

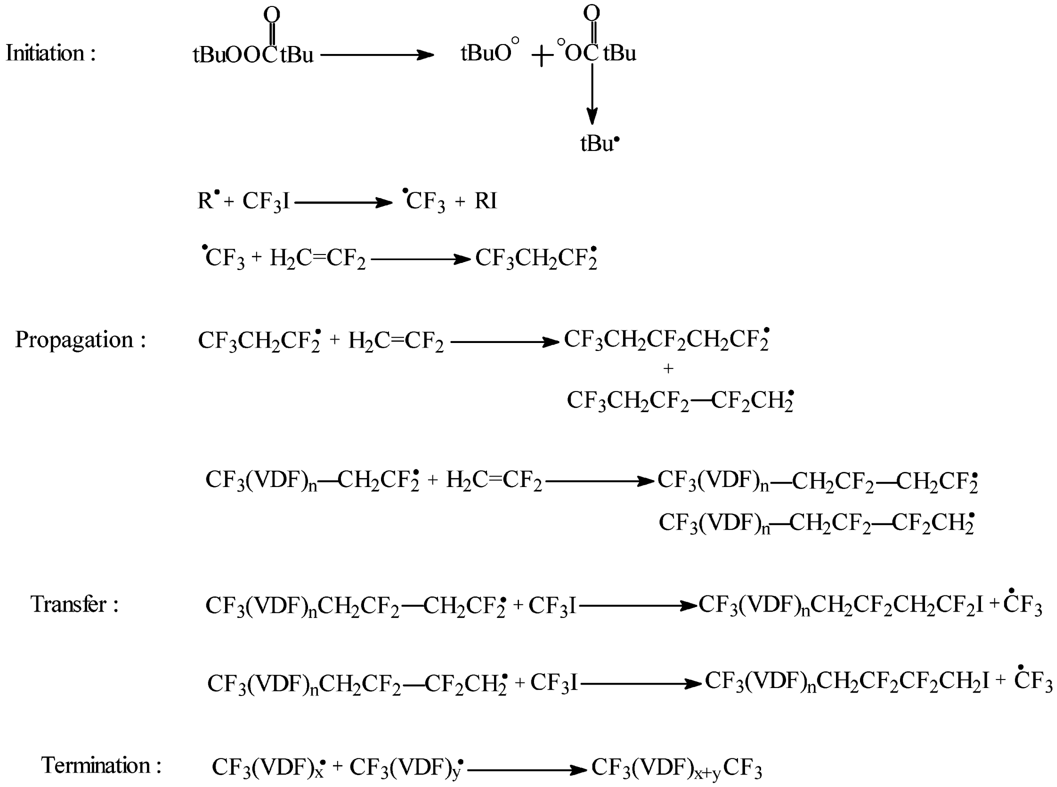
In Figure 3a, the distribution is spread from 5- to 21-mers and the center is at 11-mers (sample 2). M_n value obtained by MALDI−TOF MS (1050 g/mol) is also close to that assessed from ^{19}F NMR (1174.4 g/mol, including silver). Good agreement between both techniques shows that the ion yield in MALDI is satisfactory. Furthermore, it is noted that there is no mass discrimination effect because of the low polydispersity indexes of the telomers.

According to the observations noted above, the mechanism of the telomerization of VDF with iodotrifluoromethane, initiated by *tert*-butyl peroxypivalate at 74 °C, can be suggested as depicted in Scheme 1. It indicates the following features: (i) as soon as the radicals are generated from the initiator, they selectively react with CF_3I but do not initiate any oligomerization (or polymerization) of VDF; (ii) the transfer to CF_3I is highly efficient; (iii) a few reversed VDF additions were noted, and when this step occurred, the transfer reaction leading to $CF_3(CH_2CF_2)_n-CF_2CH_2I$ was preferable to the propagation step; (iv) the coupling reaction (i.e., the recombination of $CF_3(VDF)_n^\bullet$ radicals) did not happen. However, because of the controlled behavior of this telomerization, it can be assumed, as Tatemoto[37c,d] reported earlier, that an iodine transfer polymerization may occur or a stepwise telomerization of VDF, leading to the formation of pseudo-living PVDF telomers. Further investigations are in progress.

3. Conclusion

Iodotrifluoromethane is an efficient transfer agent in the telomerization of vinylidene fluoride (VDF) initiated by *tert*-butyl peroxypivalate at 74 °C, offering $CF_3(VDF)_nI$ telomers in good yields. This reaction was clean and did not lead to the formation of any oligomers arising from the direct addition of radicals (generated from the initiator) to VDF, and the telomers were well-identified. From a mechanistic point of view, it is confirmed that the trifluoromethyl radical (produced from CF_3I) selectively reacted onto the methylene side of VDF and did not undergo any hydrogen abstraction or any transfer to the monomer, to the solvent, or to the polymer. In addition, the CF_3 and CF_2I end groups were useful labels for the assessment of the molecular weights of the resulting telomers from ^{19}F NMR. Interestingly, these fluorotelomers contain defects of VDF chaining as low as 0.73% (to date, the lowest reported in the literature), and it was suggested that, when an inversion of chaining did occur, the transfer step occurred immediately. Further studies are necessary to find an initiator that decomposes at a lower temperature that may still lower the defect of chaining. Further, the values of the number-average molar masses of these telomers, being assessed by ^{19}F NMR or MALDI−TOF MS, were in good agreement. In addition, this latter technique enables one to assess the polydispersity indexes (PDI), and in this present case, narrow PDIs of the fractionated telomers were obtained. However, further investigations are required to check whether a certain livingness occurred in the course of the reaction although the hypothesis of a stepwise telomerization cannot be rejected. This is why we have decided to study the use of $C_nF_{2n+1}I$ or $IC_nF_{2n}I$ transfer agents in the iodine transfer polymerization of VDF. Interestingly, this present telomerization led to a wide range of oligo(VDF)s of various molecular weights. They can act as original standards being able to be utilized in GPC characterization since presently only PMMA and polystyrene (PS) standards are available for the assessment of the molecular weights of fluoropolymers and are inappropriate as mentioned by Ming et al.[26d] Moreover, these telomers terminated by a CF_2I group can be chemically changed into original hydroxylated telomers

Scheme 1. Mechanism of the Radical Telomerization of Vinylidene Fluoride with Iodotrifluoromethane as the Transfer Agent Initiated by *tert*-Butyl Peroxypivalate at 74 °C



that are interesting precursors of original VDF macromonomers involved as surface modifiers[29] or for the preparation of PVDF-*b*-PS, or PVDF-*b*-PMMA block copolymers[27] under investigations.

4. Experimental Part

4.1. General Comments. CF_3I was purchased from Fluorochem (UK) and acetonitrile from SDS, Peypin (France). VDF was kindly supplied by Solvay Solexis SA while *tert*-butyl peroxypivalate was offered by La Châlonnaise des Peroxydes, Châlons sur Marne, France.

The products were characterized by ^{1}H and ^{19}F NMR spectroscopies at room temperature (ca. 23 °C). ^{19}F NMR and ^{1}H NMR spectra were recorded on Bruker AC-200, -250, or WM-360 instruments, using deuterated acetone or DMF and tetramethylsilane or $CFCl_3$ as solvents and internal references, respectively.

The experimental conditions for recording ^{1}H (and ^{19}F) NMR spectra were as follows: flip angle = 90° (and 30°), acquisition time = 4.5 s (and 0.7 s), pulse delay = 2 s (and 5 s), number of scans = 16 (and 64), and pulse width = 5 μs (for ^{19}F NMR).

The telomerization of VDF with CF_3I was carried out in a 160 mL Hastelloy (HC-276) autoclave equipped with inlet and outlet valves, a manometer, and a rupture disk, where were placed 0.802 g (12 mmol) of *tert*-butyl peroxypivalate and 60.3 g of degassed acetonitrile. Then, the autoclave was cooled, degassed, and pressurized with 20 bar of nitrogen to check for eventual leaks. Vacuum (20 mmHg)/nitrogen cycles were performed to remove oxygen. Then, the autoclave was left under vacuum for 15 min, after which, by double weighing, 30 g (0.150 mol) of CF_3I was first introduced in the autoclave, followed by 32 g (0.50 mol) of VDF. Then, the autoclave was progressively heated to 74 °C, and from 70 °C, an exotherm of ca. 82 °C was observed followed by an increase of the pressure from 33 to 65 bar and then a fall of pressure to 14 bar.

After reaction, the autoclave was placed in an ice bath for about 30 min, and 21 g of unreacted VDF and CF_3I was progressively released (the minimum conversion of VDF was 66%). After opening the autoclave, 85 g of a slurry composed of yellow liquid and yellow solid particles was obtained. The autoclave was rinsed with acetone, and the mixture was stirred for 20 min. The filtration of the solid phase led to a gray precipitate after drying (sample 1, $\overline{DP}_{20}$ assessed by ^{19}F NMR and MALDI−TOF MS) and an orange filtrate (whose ^{19}F NMR and MALDI−TOF mass spectroscopy led to sample 2, $\overline{DP}_{11}$). This latter was concentrated (removal of acetone) and precipitated from pentane. The precipitate was then dissolved and again precipitated from methanol to lead to two fractions: that from the filtrate yielded a VDF telomer with $\overline{DP}_{12}$ while that from the precipitate supplied a fluorotelomer of $\overline{DP}_{16}$.

The matrix-assisted laser desorption−ionization time-of-flight mass spectrometer (MALDI-TOF-MS) used to acquire the mass spectra was a Voyager-DE STR (Applied Biosystems, Framingham, MA). This instrument was equipped with a nitrogen laser (wavelength 337 nm) to desorb and ionize the samples. The accelerating voltage used was 20 kV. The spectra were the sum of 300 shots, and an external mass calibration was used. Samples were prepared by dissolving the product in DMF at a concentration of 1 g/L. The matrix used for all experiments was 2,3,4,5,6-pentafluorocinnamic acid (PFCA) purchased from Fluka (Milwaukee, WI) and used directly without further purification. This solid matrix was dissolved in hexafluoro-2-propanol (HFIP) with a 10 g/L concentration. 1 μL of the matrix solution, then 1 μL of product solution, and 1 μL of AgTFA were placed onto MALDI.

Metastable ions, analyzed by the post source decay method (PSD), were generated by laser-induced decomposition of the selected precursor ions. No additional collision gas was applied. Precursor ions were accelerated to 20 kV and selected in a time ion gate. The masses of the fragments were analyzed after the ion reflector passage.

Average molar masses ($\bar{M}_n$, $\bar{M}_w$) were determined directly from the *m*/*z* domain according to the following equations:

$$\bar{M}_n = \sum N_i M_i / \sum N_i$$

$$\bar{M}_w = \sum N_i (M_i)^2 / \sum N_i M_i$$

where M_i and N_i stand for the mass of a molecular ion with a degree of polymerization i and the number of molecules of M_i mass, respectively. Indeed, N_i is assumed to be proportional to the intensity of the signal in the MALDI mass spectrum. The ratio of both averages represents the polydispersity index Ip:

$$Ip = \bar{M}_w/\bar{M}_n$$

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Supporting Information Available: Small overview on the telomerization of vinylindene fluoride. This material is available free of charge via the Internet at http://pubs.acs.org.

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