Radical Homopolymerization of Vinylidene Fluoride Initiated by *tert*-Butyl Peroxypivalate. Investigation of the Microstructure by ^{19}F and ^{1}H NMR Spectroscopies and Mechanisms

J. Guiot, B. Ameduri,* and B. Boutevin

Laboratory of Macromolecular Chemistry, UMR (CNRS) 5076, Ecole Nationale Supérieure de Chimie de Montpellier, 8 Rue Ecole Normale, 34296 Montpellier Cedex 5, France

Received February 19, 2002; Revised Manuscript Received August 1, 2002

ABSTRACT: The radical polymerization in solution of vinylidene fluoride (VDF) initiated by different peroxides (*tert*-butyl peroxide and *tert*-butyl peroxypivalate) and by azo-*tert*-butane is presented. Various reaction temperatures and times and solvents were chosen to monitor the polymerization in terms of initiating radical generated from these initiators and transferring agents. Homopolymers thus obtained were characterized by ^{19}F and ^{1}H NMR spectroscopies. Different VDF telomers were synthesized (e.g., $C_4F_9(CH_2CF_2)_3H$, $C_6F_{13}CH_2CF_2CH_2CH_3$, and $CH_3CF_2(CH_2CH_2)_2I$) as models to explain the microstructure of these PVDFs. They enable one to identify without any ambiguity most different signals observed in ^{1}H and ^{19}F NMR spectra of PVDFs. From those assignments, an overall reactional mechanism was proposed that allows one to explain each step of polymerization of VDF. In particular, an interpretation of the polymer microstructures and of end groups arising from the radical initiator and from eventual transfers is suggested.

Introduction

Polyvinylidene fluoride (PVDF or PVF_2) exhibits various interesting properties (chemical inertness, resistance to acids, and piezo- and pyroelectrical properties)[1−5] and has thus found numerous applications[6] in the semiconductor industry,[7,8] in the nuclear industry,[9] and in paints and coatings.[10] This polymer is usually obtained by radical homopolymerization of VDF according to various processes such as suspension,[1,11] emulsion,[12−16] and solution.[15,17] Different initiators have successfully been used, in particular *tert*-butyl peroxide, dicumyl peroxide, and *tert*-butyl perbenzoate.[16] Fluorinated initiators have also been involved in such a polymerization, such as bis(perfluorophenyl) peroxide or bis(ω-hydrooctafluorovaleryl) peroxide.[17] However, the homopolymerization of VDF initiated by *tert*-butyl peroxypivalate has been scarcely investigated.[18] Hence, the objective of this present article deals with that reaction under radical conditions involving this initiator. First, the microstructure of these homopolymers is studied to assign all the signals noted in their ^{1}H and ^{19}F NMR spectra. These attributions enable us to propose a mechanism of radical homopolymerization of VDF.

Experimental Part

(a) Reactants and Methods of Analyses. Vinylidene fluoride (VDF) was kindly donated by Solvay S. A. (Brussels, Belgium). Acetonitrile (SDS, Peypin, France) was distilled over calcium hydride and then degassed from an argon flow for 10−15 min, prior to use. Azo-*tert*-butane and *tert*-butyl peroxide were supplied by Aldrich while *tert*-butyl peroxypivalate (in a 75% solution of decane) was kindly donated by "La Chalonaise des Peroxydes". These three initiators were used without any purification. CH_3CF_2I was synthesized by addition of HI onto VDF.[19] C_4F_9I and $C_6F_{13}I$ were kindly donated by the Atofina Co. NMR spectra were recorded on Bruker AC 200 and AC 250 instruments, using deuterated chloroform or acetone as the solvents and TMS ($CFCl_3$) as the references for ^{1}H (^{19}F) nuclei. The letters s, d, t, q, and m stand for singlet, doublet, triplet, quintet, and multiplet, respectively. Coupling constants and chemical shifts are given in hertz (Hz) and ppm, respectively. The experimental conditions to record ^{1}H (or ^{19}F) NMR spectra were the following: flip angle, 90° (30°); acquisition time, 4.5 s. (0.7 s); pulse delay, 2 s (5 s); number of scans, 16 (64); a pulse width of 5 μs for ^{19}F NMR. Size exclusion chromatography (or GPC) analyses were carried out at 40 °C onto type 2HR5E and 1HR2E columns with DMF/LiBr in 0.1 mol L^{-1} as eluent with an isocratic pump.

(b) Homopolymerizations. The homopolymerizations of VDF were performed in thick borosilicate Carius tubes in a batch process (length, 130 mm; internal diameter, 10 mm; thickness, 2.5 mm; for a total volume of 8 cm^3). After the initiator and acetonitrile were placed, the tube was connected to a vacuum line and purged several times by evacuating and flushing with helium. After five thaw-freeze cycles at least, to get rid of oxygen, VDF was trapped under vacuum, in the tube frozen in liquid nitrogen, after a release into an intermediate metallic container calibrated for pressure. The required amount of VDF introduced into the tube was assessed by the relative drop of pressure in this release container, initially fed by a cylinder of 300 g of VDF. A beforehand calibration curve-weight of trapped VDF (in g) vs drop of pressure (in bar) was determined (for 0.75 g of VDF, a difference of pressure of 0.50 bar was required). The tube, under vacuum and immersed in liquid nitrogen, was sealed and placed into the cavity of a shaking oven at the temperature and for the time required. After reaction, the tube was frozen in liquid nitrogen and then opened, but the conversion rate of the VDF could not be assessed. Hence, the yield of the reaction is not given in this paper. Then, the homopolymer was precipitated from 100 mL of cold pentane. After this precipitation, the solution was removed, and the insoluble product was dried at 80 °C under vacuum for 4 h at least. NMR characteristics are described in the text (Tables 1 and 2).

(c) Synthesis of M_1 Model (1,1,1,2,2,3,3,4,4,6,6,8,8,10,-10-Pentadecafluorodecane) and M_4 Model (1,1,1,2,2,3,3,-4,4,6,6,8,8,9,9-Pentadecafluorodecane). First, 100.0 g (0.29 mol) of C_4F_9I was introduced into a 500 mL hastelloy (HC 276) autoclave equipped with outlet and inlet valves, a security disk, and a manometer, cooled in an acetone/liquid nitrogen

* To whom correspondence should be sent. E-mail: ameduri@cit.enscm.fr.

10.1021/ma0202641 CCC: $22.00
Published on Web 10/02/2002

Table 1. Assignments of ^{19}F NMR Chemical Shifts in PVDF Polymers

δ (ppm)	signal	assignment
−80.3	multiplet	$(CH_3)_3C-O-C\mathbf{F_2}CH_2-$
−91.0	multiplet	$-CF_2CH_2-C\mathbf{F_2}CH_2-CF_2-$
−92.2	multiplet	$(CH_3)_3C-CH_2C\mathbf{F_2}-CH_2CF_2-$
−92.4	multiplet	$HCF_2CH_2-C\mathbf{F_2}CH_2-$
−94.8	multiplet	$-CF_2CH_2-C\mathbf{F_2}CH_2-CH_2CF_2-CF_2-$
−95.7	multiplet	$CH_3-CH_2C\mathbf{F_2}-CH_2CF_2-$ and $NC-CH_2-CH_2C\mathbf{F_2}-$ (supposed)
−107.5	multiplet	$CH_3C\mathbf{F_2}-CF_2CH_2-CF_2-$
−112.3	*t*, $^3J_{FH} = 16.6$ Hz	$(CH_3)_3C-C\mathbf{F_2}CH_2-CF_2-$
−113.4	multiplet	$-CH_2C\mathbf{F_2}-CF_2CH_2-CH_2-$
−113.7	multiplet	$CH_3CF_2-C\mathbf{F_2}CH_2-CF_2-$
−114.5	*dm*, $^2J_{FH} = 55.0$ Hz	$HC\mathbf{F_2}CH_2-CF_2CH_2-$
−115.7	multiplet	$-CH_2CF_2-C\mathbf{F_2}CH_2-CH_2-$
−150.0	multiplet	$NC-CH_2-C\mathbf{F_2}CH_2-$ (supposed)

Table 2. Assignments of ^1H NMR Chemical Shifts in PVDF Polymers

δ (ppm)	signal	assignment
1.00	*t*, $^3J_{HH} = 7.5$ Hz	$C\mathbf{H_3}-CH_2CF_2-CH_2CF_2-$
1.05	singlet	$(C\mathbf{H_3})_3C-CH_2CF_2-CH_2CF_2-$
1.20	singlet	$(C\mathbf{H_3})_3C-CF_2CH_2-$
1.30	singlet	$(C\mathbf{H_3})_3C-O-CF_2CH_2-$
1.55	*t*, $^3J_{HF} = 18.6$ Hz	$C\mathbf{H_3}-CF_2CH_2-CH_2CF_2-$
1.80	*tt*, $^3J_{HF} = 19.4$ Hz, $^4J_{HF} = 1.6$ Hz	$C\mathbf{H_3}CF_2-CF_2CH_2-CF_2-$
2.30	multiplet	$-CF_2C\mathbf{H_2}-C\mathbf{H_2}CF_2-CH_2-$, $CH_3-C\mathbf{H_2}CF_2-CH_2CF_2-$ and $(CH_3)_3C-C\mathbf{H_2}CF_2-CH_2CF_2-$
2.90	multiplet	$-CH_2CF_2-C\mathbf{H_2}CF_2-CH_2-$
6.30	*tt*, $^2J_{HF} = 55.2$ Hz, $^3J_{HH} = 4.4$ Hz	$\mathbf{H}CF_2CH_2-CF_2CH_2-$

bath. After 3 cycles, N_2 gas/vacuum, 32.0 g (0.5 mol) of VDF was introduced by double weighing. The autoclave was then heated in a silicone bath at 210 °C for 15 h. After reaction, the vessel was cooled to room temperature and then put into ice; the unreacted VDF was carefully released and the autoclave opened. Solid iodine from the total product mixture was filtered off and mono- and diadducts $[C_4F_9(VDF)_xI$, $x = 1$ and 2] were distilled. The next pure fraction was the triadduct (Bp = 55−58 °C/24 mmHg), yield = 47%. Then, 10.7 g (20.0 mmol) of this fraction was dropwise added to 6.4 g of tributyl stannane (22.0 mmol) for 30 min under nitrogen. After separation of both phases, the lower one contained the expected fluorinated carbides (M_1 and M_4 models) with 95% purity (GC). The yield was 41% for M_1 model vs 4% for M_4 model).

•M_1 Model: $C_4F_9-CH_2CF_2-CH_2CF_2-CH_2CF_2-H$. ^{19}F NMR (acetone-d_6): $\delta = -81.0$ (s, $C\mathbf{F_3}-CF_2-CF_2-CF_2-CH_2-$, 3F), −88.3 (s, $C_4F_9-CH_2-C\mathbf{F_2}-CH_2-$, 2F), −92.4 (s, $-CH_2-C\mathbf{F_2}-CH_2-CF_2H$, 2F), −112.6 (s, $CF_3-CF_2-CF_2-C\mathbf{F_2}-CH_2-$, 2F), −114.7 (dtt, $^2J_{FH} = 45.2$ Hz, $^3J_{FH} = 19$ Hz, $^4J_{FH} = 5.8$ Hz, $-CH_2-CF_2-CH_2-C\mathbf{F_2}H$, 2F) −124.4 (s, $CF_3-CF_2-C\mathbf{F_2}-CF_2-CH_2-$), −125.9 (s, $CF_3-C\mathbf{F_2}-CF_2-CF_2-CH_2-$, 2F).

^1H NMR (acetone-d_6): $\delta = 2.7$ (m, $C_4F_9-C\mathbf{H_2}-CF_2-C\mathbf{H_2}-CF_2-C\mathbf{H_2}$-, 6H), 6.3 (dt, $^2J_{HF} = 55.2$ Hz, $^3J_{HH} = 4.8$ Hz, $-CH_2-CF_2-CH_2-CF_2\mathbf{H}$, 2H).

•M_4 Model: $C_4F_9-CH_2CF_2-CH_2CF_2-CF_2CH_3$. ^{19}F NMR (acetone-d_6): $\delta = -81.0$ (s, $C\mathbf{F_3}-CF_2-CF_2-CF_2-CH_2-$, 3F), −87.4 (s, $C_4F_9-CH_2-C\mathbf{F_2}-CH_2-$, 2F), −112.6 (s, $CF_3-CF_2-CF_2-C\mathbf{F_2}-CH_2-$, 2F), −113.8 (s, $-CH_2-C\mathbf{F_2}-CF_2-CH_3$, 2F), −107.5 (s, $-CH_2-CF_2-C\mathbf{F_2}-CH_3$, 2F), −124.4 (s, $CF_3-CF_2-C\mathbf{F_2}-CF_2-CH_2-$, 2F), −125.9 (s, $CF_3-C\mathbf{F_2}-CF_2-CF_2-CH_2-$, 2F).

^1H NMR (acetone-d_6): $\delta = 2.7$ (m, $C_4F_9-C\mathbf{H_2}-CF_2-C\mathbf{H_2}-CF_2-$, 4H), 1.8 (tt, $^3J_{HF} = 19$ Hz, $^4J_{HH} = 1.7$ Hz, $-CH_2-CF_2-CF_2-C\mathbf{H_3}$, 3H).

(d) Synthesis of M_2 Model: 1,1,1,2,2,3,3,4,4,5,5,6,6,8,8-Pentadecafluorodecane ($C_6F_{13}—CH_2—CF_2—CH_2—CH_3$). First, 100.0 g (0.22 mol) of $C_6F_{13}I$ was introduced into the autoclave. It was closed, cooled, and put under vacuum/liquid N_2 as above. Then 17.9 g (0.28 mol) of VDF was condensed in, and the autoclave was heated to 200 °C for 15 h. After reaction and cooling in ice, the autoclave was degassed and opened. I_2 formed was filtered off and the monoadduct $C_6F_{13}CH_2CF_2I$ was distilled (bp = 66−69 °C (22 mmHg), yield = 66%). Then, 75.2 g (0.13 mmol) of this telomer was put into a 160 mL autoclave that was cooled and degassed as above. Then 3.6 g (0.13 mol) of VDF was condensed in it as above, and the mixture was heated to 205 °C for 24 h. After filtration of the total product mixture, the substrate was distilled. Bp = 69−72 °C (23 mmHg), and $C_6F_{13}CH_2CF_2CH_2CH_2I$ was obtained in 30% yield; 10.7 g (20.1 mmol) of this compound was dropwise added into 6.4 g (22.0 mmol) of tributylstannane under nitrogen and stirring. After phase separation, the lower phase (dark liquid) was the expected carbide (95% pure), and the overall yield was 17%.

^{19}F NMR (acetone-d_6): $\delta = -80.8$ (s, $C\mathbf{F_3}-CF_2-CF_2-CF_2-$, 3F), −96.1 (hept, $-CH_2-C\mathbf{F_2}-CH_2-CH_3$, 2F) −111.5 (s, $C_4F_9-CF_2-C\mathbf{F_2}-CH_2-$, 2F), −121.0 (s, $C_4F_9-C\mathbf{F_2}-CF_2-CH_2-$, 2F), −122.1 (s, $CF_3-CF_2-CF_2-C\mathbf{F_2}-CF_2-CF_2-$, 2F), −122.6 (s, $CF_3-CF_2-C\mathbf{F_2}-CF_2-CF_2-$, 2F), −125.6 (s, $CF_3-C\mathbf{F_2}-CF_2-CF_2-CF_2-$, 2F).

^1H NMR (acetone-d_6): $\delta = 1.07$ (t, $^3J_{HH} = 7.5$ Hz, $C_6F_{13}-CH_2-CF_2-CH_2-C\mathbf{H_3}$, 3H), 2.1 (tq, $^3J_{HF} = 17.0$ Hz, $^3J_{HH} = 7.5$ Hz, $C_6F_{13}-CH_2-CF_2-C\mathbf{H_2}-CH_3$, 2H), 3.0 (q, $^3J_{HF} = 17.0$ Hz, $C_6F_{13}-C\mathbf{H_2}-CF_2-CH_2-CH_3$, 2H).

(e) Synthesis of M_3 Model: 1-Iodo-5,5-difluorohexane ($CH_3—CF_2—CH_2—CH_2—CH_2—CH_2—I$). First, 3.5 g (18.2 mmol) of CH_3CF_2I prepared by addition of VDF into HI, 0.07 g (0.35 mmol) of *tert*-butyl cyclohexyl peroxydicarbonate, and 40.1 g of *tert*-butyl alcohol were introduced in a 160 mL autoclave. It was cooled and flushed as above, and 2.0 g (70 mmol) of ethylene was condensed into it. Then, the mixture was heated to 60 °C for 8 h. After reaction, the total product mixture (purple liquid) was directly analyzed by gas chromatography and characterized by ^1H and ^{19}F NMR (the yield was 24%).

^{19}F NMR (acetone-d_6): $\delta = -89.6$ (hex, $^3J_{FH} = 18$ Hz, $CH_3-C\mathbf{F_2}-CH_2-CH_2-$, 2F).

^1H NMR (acetone-d_6): $\delta = 1.58$ (t, $^3J_{HF} = 18.6$ Hz, $C\mathbf{H_3}-CF_2-CH_2-CH_2-$), 2.5 (m, $CH_3-CF_2-C\mathbf{H_2}-C\mathbf{H_2}-C\mathbf{H_2}-CH_2-I$), 3.1 (m, $CH_2-CH_2-CH_2-C\mathbf{H_2}-I$).

Results and Discussion

The homopolymerization of VDF, initiated by a radical initiator (A_2), is based on a five-step process, as follows:

Initiation $A_2 \rightarrow 2A^\bullet$

$$A^\bullet + VDF \rightarrow A-VDF^\bullet$$

Propagation $A-VDF^\bullet + VDF \rightarrow A-VDF-VDF^\bullet$

$$A-(VDF)_{n-1}-VDF^\bullet + VDF \rightarrow A-(VDF)_n-VDF^\bullet$$

Termination

$$A-(VDF)_n-VDF^\bullet + A-(VDF)_p-VDF^\bullet \rightarrow A-(VDF)_{n+p+2}-A$$

Transfer

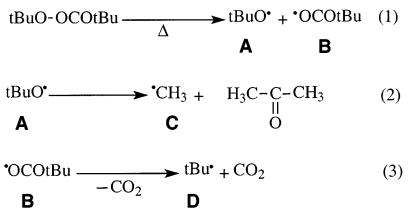
$$A-(VDF)_n-VDF^\bullet + X-Y \rightarrow A-(VDF)_{n+1}-X + Y^\bullet$$

Reinitiation $Y^\bullet + VDF \rightarrow Y-VDF^\bullet$

The transfer may occur to the initiator, to the monomer (although, to our knowledge, no work has reported such a behavior), to the solvent, and to the polymer.[20]

Hence, to assess the microstructure of PVDF (i.e., to assign all the signals observed in the ^{1}H and ^{19}F NMR spectra), we have found it interesting to investigate the possible decompositions of *tert*-butyl peroxypivalate leading to various radicals which further initiate the radical homopolymerization of VDF.

This initiator first undergoes a homolytic cleavage of O−O bond, hence generating two radicals (**A** and **B**, eq 1). tBuO$^\bullet$ (**A**) may rearrange to produce $^\bullet$CH$_3$ radical and acetone (eq 2), while the decarboxylation reaction of $^\bullet$OCOtBu[21] (**B**) yields tBu$^\bullet$ radical as follows:[22]



As a consequence, *tert*-butyl peroxypivalate can lead to four types of radicals (**A**, **B**, **C**, and **D**). To enable one to obtain a nonambiguous assignment of the signals in the ^{1}H and ^{19}F NMR spectra of PVDF initiated by tBuOOCOtBu, several key reactions were performed in which VDF was initiated by various compounds generating certain radicals exclusively. We chose two initiators mainly: *tert*-butyl peroxide, tBu−O−O−tBu (DTBP) and azo-*tert*-butane, tBu−N=N−tBu (ATB).

Actually, the formation of **A** and **C** radicals can be achieved from DTBP since it is known that this initiator leads to two **A** radicals that may undergo a rearrangement into **C** radicals.[23,24]

To initiate the polymerization of VDF in the presence of radical **D**, ATB can be regarded as an interesting starting material since it generates the tBu$^\bullet$ radical (**D**) after losing N_2.[25] Consequently, various homopolymerizations of VDF initiated by DTBP and ATB were investigated as first model reactions. Then, under the same conditions, *tert*-butyl peroxypivalate was used, and the ^{1}H and ^{19}F NMR spectra of all homopolymers produced were compared. These assignments hence enable one to further propose a mechanism of initiation of the VDF homopolymerization by *tert*-butyl peroxypivalate.

(I) Attributions of NMR Signals. (A) Homopolymerization of VDF Initiated by *tert*-Butyl Peroxide. *tert*-Butyl peroxide (DTBP) was used as the initiator at 100 and 150 °C. Actually, it is well-known that the generated tBuO$^\bullet$ can undergo a rearrangement into $^\bullet$CH$_3$ and acetone, according to the experimental conditions[23,24] that it was required to revisit below.

(A-1) Reaction Temperature: 100 °C. First, four homopolymerization reactions of VDF initiated by DTBP were carried out in acetonitrile for 66 h (attempts 1−4 in Table 3). After precipitation from pentane and filtration, the homopolymers thus formed were characterized by ^{1}H and ^{19}F NMR (Figures 1 and 2, respectively.).

All the ^{1}H NMR spectra show the presence of the characteristic multiplet centered at 2.9 ppm assigned to methylene groups of $-CF_2CH_2-CF_2CH_2-CF_2CH_2-$ sequence resulting from the normal tail-to-head VDF addition. Such a structure was confirmed by the characteristic signal at −91.0 ppm in the ^{19}F NMR spectra attributed to the difluoromethylene group in $-CH_2CF_2-CH_2CF_2-CH_2CF_2-$. These spectra also exhibit expected

Table 3. Initial Molar Compositions and Experimental Conditions of the Radical Polymerization of Vinylidene Fluoride (VDF) Co

expt no.	initiator	C_0[a] (%)	time (h)	temp (°C)	solvent
1	tBu−OO−tBu	1.2	66	100	CH_3CN
2	tBu−OO−tBu	9.0	66	100	CH_3CN
3	tBu−OO−tBu	19.4	66	100	CH_3CN
4	tBu−OO−tBu	47.3	66	100	CH_3CN
5	tBu−OO−tBu	50.1	216	50	CH_3CN
6	tBu−N=N−tBu	50.2	72	120	CH_3CN
7	tBu−N=N−tBu	25.0	72	120	CH_3CN
8	tBu−OO−CO−tBu	9.8	16	50	CH_3CN
9	tBu−OO−CO−tBu	20.1	16	50	CH_3CN
10	tBu−OO−CO−tBu	10.4	16	100	CH_3CN
11	tBu−OO−CO−tBu	19.9	16	100	CH_3CN
12	tBu−OO−tBu	1.6	66	100	$CH_3CO_2CH_3$
13	tBu−OO−tBu	1.2	66	100	C_6F_{14}

[a] C_o stands for the initial $[initiator]_o/[VDF]_0$ molar ratio.

multiplets centered at −94.8, −113.4, and −115.7 ppm, corresponding to $-CH_2CF_2-CF_2CH_2-CH_2CF_2-CH_2-CF_2-$; $-CH_2CF_2-CH_2CF_2-CF_2CH_2-$, and $CH_2CF_2-CF_2CH_2-CH_2CF_2-$, respectively. All these three signals arise from the inversion of a VDF base unit in the polymeric chain, regarded as a head-to-head VDF addition.

Actually, tail-to-tail VDF additions were identified in the ^{1}H NMR spectra by the presence of a multiplet centered at 2.3 ppm assigned to both methylene groups in a role (as an inversed addition). These ^{1}H and ^{19}F NMR spectroscopic analyses were in good agreement with those reported in the litterature.[26−30] The normal to inversed addition ratio could hence be assessed from the integrals of the characteristic peaks, indicated in Table 2, in both ^{1}H (eq 4) and ^{19}F (eq 5) NMR spectra, as follows:

$$\text{mole fraction of normal VDF sequence (from } ^1\text{H NMR)} = \frac{I_{2.9} + I_{2.3}/2 + I_{1.05}/9 + I_{1.00}/3}{2\,I_{1.8}/3 + I_{2.3} + I_{2.9}} \quad (4)$$

$$\text{mole fraction of normal VDF sequence (from } ^{19}\text{F NMR)} = [I_{-91.0} + I_{-92.2} + I_{-92.4} + I_{-94.8} + I_{-95.7} + I_{-113.4} + I_{-113.7} + I_{-114.5}]/[I_{-80.3} + I_{-91.0} + I_{-92.2} + I_{-92.4} + I_{-94.8} + I_{-95.7} + I_{-107.5} + I_{-112.3} + I_{-113.4} + I_{-113.7} + I_{-114.5} + I_{-115.7}] \quad (5)$$

where I_n represents the integral of the signal centered at n ppm. These formula represent the sum of the integrals of the peaks assigned to normal VDF adducts over the sum of the integrals of the peaks belonging to VDF (normal and reversed base units). Obviously, the signals attributed to the end group arising from the initiators are not considered in eq 4 (^{1}H NMR).

In addition, the ^{1}H NMR spectra show a triplet ($^2J_{HF}$ = 55.2 Hz) of triplets ($^3J_{HH}$ = 4.4 Hz) centered at 6.30 ppm attributed to the terminal proton in $-CH_2CF_2H$ end group arising from a transfer to the polymer, as observed by various research groups.[20,28,30] The ^{19}F NMR spectra confirm such an observation since the doublet ($^2J_{HF}$ = 55.0 Hz) of multiplets centered at −114.5 ppm corresponds to $-CH_2CF_2H$.

Incidently, all ^{19}F NMR spectra display a signal at −92.4 ppm, and we found it interesting to synthesize models, the NMR chemical shifts of which could enable us to supply accurate assignments. Hence, 1,1,1,2,2,3,3,-

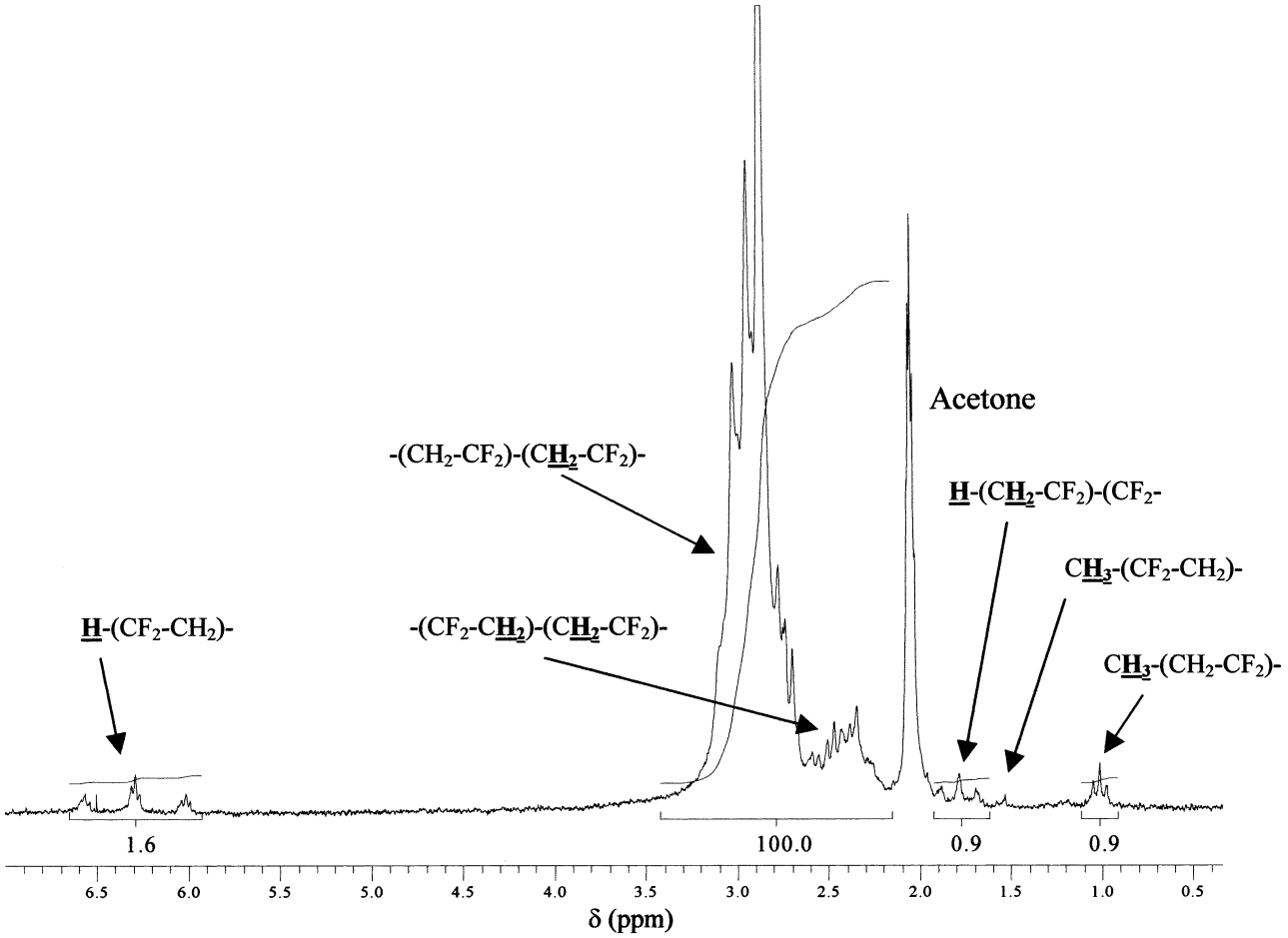


Figure 1. ^{1}H NMR spectrum of PVDF homopolymer (experiment 2) initiated by *tert*-butyl peroxide at 100 °C for 66 h.

4,4,6,6,8,8,10,10-pentadecafluorodecane ($C_4F_9CH_2CF_2$-$CH_2CF_2CH_2CF_2H$) was prepared by thermal telomerization of VDF with 1-iodoperfluorobutane, followed by the selective reduction of the iodine atom of the distilled VDF triadduct, as follows:

$$C_4F_9I + n\text{VDF} \xrightarrow[15\ h]{200\ °C} C_4F_9(\text{VDF})_nI$$

A telomeric distribution was noted by gas chromatography (GC), showing the formation of the first four telomers. The yield of the reaction was 95%, and the total product mixture was distilled, leading to several fractions analyzed by GC. The pure fraction attributed to the telomer containing three VDF base units was characterized by ^{19}F NMR. Indeed, the distilled triadduct was composed of a mixture of three isomers: C_4F_9-$CH_2CF_2-CH_2CF_2-CH_2CF_2I$ (88%), $C_4F_9CH_2CF_2-CH_2$-$CF_2-CF_2CH_2I$ (9%), and $C_4F_9CH_2CF_2-CF_2CH_2CF_2CH_2I$ (3%).

The selective reduction of the iodine terminal atom was carried out in the presence of tributyl stannane, as reported by Newman[31] or in a previous work:[29]

$$C_4F_9(C_2H_2F_2)_3I \xrightarrow{SnBu_3H} C_4F_9(C_2H_2F_2)_3H$$

with

M_1 model: $C_4F_9CH_2CF_2-CH_2CF_2-CH_2CF_2H$

M_4 model: $C_4F_9CH_2CF_2-CH_2CF_2-CF_2CH_3$

The overall yields of M_1 and M_4 from C_4F_9I were 41 and 5%, respectively. ^{19}F NMR characterization of M_1 model shows, by the signal centered at −114.7 ppm, a peak centered at −92.4 ppm assigned to the difluoromethylene group in the $HCF_2CH_2-CF_2CH_2-CF_2CH_2$ sequence.

The ^{1}H NMR spectra of the homopolymers exhibit the triplet ($^3J_{HH}$ = 7.5 Hz) centered at 1.0 ppm. It can be expected that this signal arises from the methyl end group of the $CH_3CH_2CF_2$ sequence. To prove the assignment of this peak, the M_2 model was synthesized by thermal telomerization of VDF with $C_6F_{13}I$, followed by an ethylenation step on the obtained monoadduct then followed by a selective reduction, as follows:

$$C_6F_{13}I \xrightarrow{\text{VDF}} C_6F_{13}CH_2CF_2I \xrightarrow{H_2C=CH_2} C_6F_{13}CH_2CF_2C_2H_4I \xrightarrow{SnBu_3H} \underset{M_2}{C_6F_{13}CH_2CF_2CH_2CH_3}$$

The VDF monoadduct shows the above formulas arising from the regioselective addition of $C_6F_{13}^{\bullet}$ onto the methylene group of VDF.[29] The ethylenation of this monoadduct was carried out in the presence of CuCl/ethanol amine catalyst, and the reduction of the iodine atom into the corresponding derivative occurred quantitatively in the presence of tributyl stannane. The overall yield of M_2 from $C_6F_{13}CH_2CF_2I$ was 17%.

The ^{1}H NMR spectrum of M_2 (Figure 3) shows a triplet ($^3J_{HH}$ = 7.5 Hz) centered at 1.05 ppm assigned to the CH_3 end group. Its ^{19}F NMR spectrum (Figure 4)

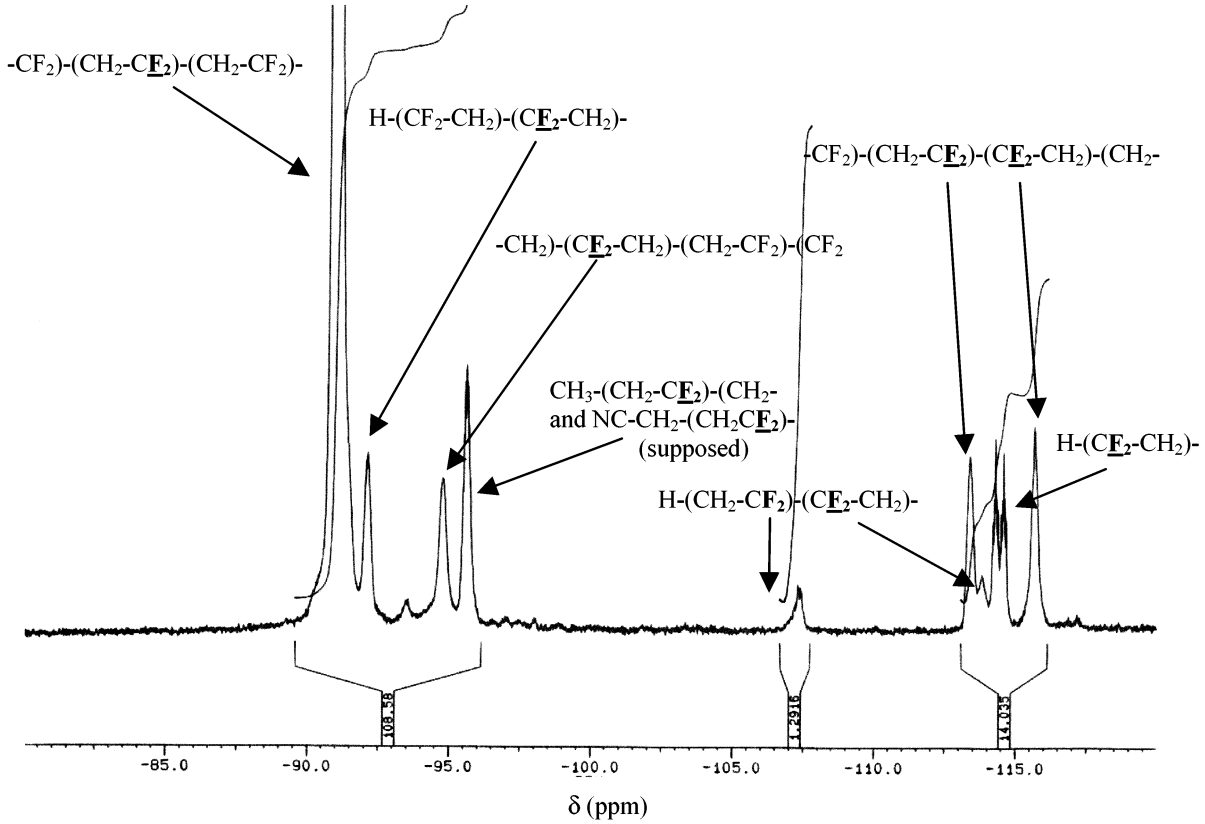


Figure 2. ^{19}F NMR spectrum of PVDF homopolymer (experiment 2) initiated by *tert*-butyl peroxide at 100 °C for 66 h.

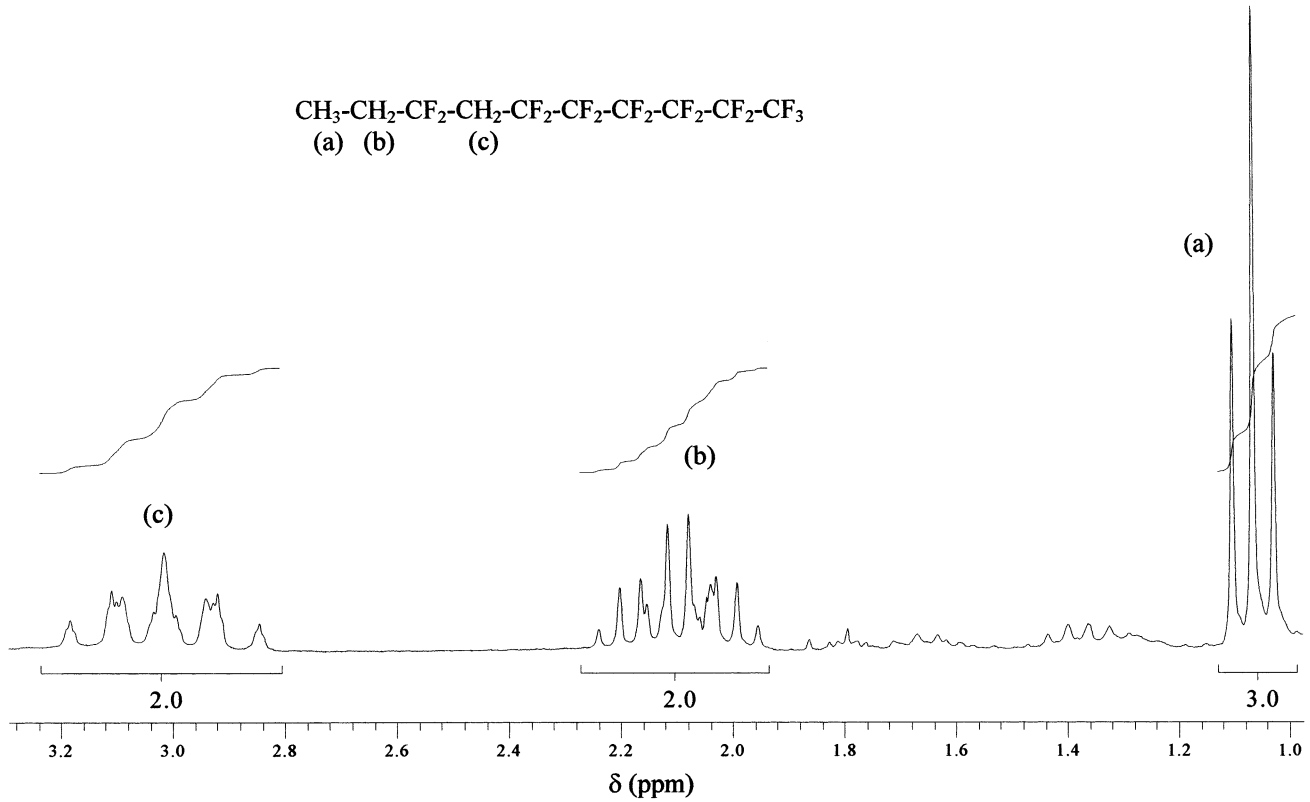


Figure 3. ^{1}H NMR spectrum of the M_2 model: 1,1,1,2,2,3,3,4,4,5,5,6,6,8,8-pentadecafluorodecane ($C_6F_{13}-CH_2-CF_2-CH_2-CH_3$).

shows a signal at −96.1 ppm. Besides, all the spectra of our PVDF samples show a peak centered at −95.7 ppm. By comparison of the electronic environment of the difluoromethylene group of the M_2 model for which both methylene groups are adjacent and that of CF_2 arising from PVDF in the $CH_3CH_2CF_2CH_2CF_2-$ structure, it is observed that the CF_2 group of the M_2 model has a C_5F_{11} group in the γ-position while that coming from PVDF has VDF units in the γ-position. This difference could explain the slight shift (−96.1 and

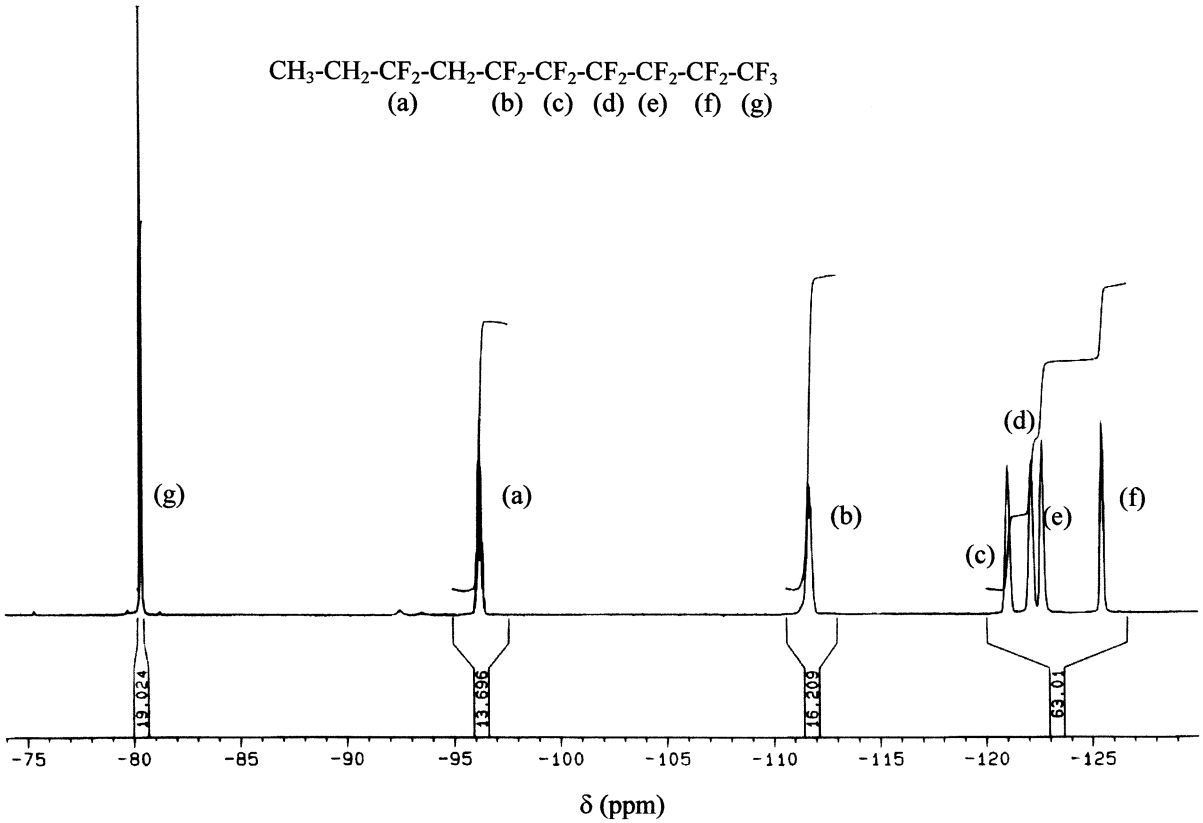


Figure 4. ^{19}F NMR spectrum of the M_2 model: 1,1,1,2,2,3,3,4,4,5,5,6,6,8,8-pentadecafluorodecane ($C_6F_{13}-CH_2-CF_2-CH_2-CH_3$).

−95.7 ppm) existing between ^{19}F NMR chemical shifts corresponding to fluorine atoms of both CF_2 groups. Thus, the signal centered at −95.7 ppm can be attributed to CF_2 group in a $C_2H_5CF_2CH_2CF_2-$ sequence.

As mentioned above, a $^{\bullet}CH_3$ radical arising from tBuO−OtBu can start the initiation by reacting onto the methylene side of VDF. Besides, Walton et al.[32] and later Sass et al.[33] demonstrated that the $^{\bullet}CH_3$ radical can be added in a small way (ca. 10%) onto the CF_2 side of this fluoroalkene so that the following sequences may be obtained: $CH_3(CF_2CH_2)(CH_2CF_2)-$ (A type) or $CH_3(CF_2CH_2)(CF_2CH_2)-$ (B type). Considering that a low probability of structure formation containing a double inversion is possible, structure B can be neglected. In addition, Duc et al.[30] have shown that, in the course of the telomerization reaction of VDF with methanol, the direct initiation of *tert*-butyl peroxide via $^{\bullet}CH_3$ radical onto VDF was not regioselective. Hence, to assess the presence of that type of end group ($CH_3-CF_2CH_2-CH_2CF_2-$) and thus the characteristic ^{19}F NMR chemical shifts, the synthesis of the M_3 model was realized. 1-Iodo-5,5-difluorohexane ($CH_3CF_2CH_2CH_2-CH_2CH_2I$) ($M_3$) was produced by telomerization of ethylene with 1-iodo-1,1-difluoroethane[34] (obtained by reaction of HI onto VDF[19]) as follows:

$$CH_3CF_2I + H_2C{=}CH_2 \xrightarrow[8\ h/60\ ^{\circ}C]{\text{percarbonate/tBuOH}} CH_3CF_2(CH_2CH_2)_nI; \quad n = 1 \text{ or } 2$$

Characterizing the total product mixture by gas chromatography shows both the total conversion of CH_3-CF_2I starting reagent and the production of ca. 90% of the monoadduct and ca. 10% of diadduct (M_3).

Its ^{19}F NMR spectrum confirms the quantitative conversion of the iodinated reactant (absence of the peak centered at −30.5 ppm assigned to CF_2I) and exhibits two multiplets centered at −89.5 ppm (corresponding to 7.5% of the total product mixture) and at −90.6 ppm (92.5%). This demonstrates, in comparison with the gas chromatogram, that the chemical shift of the CF_2 group in the diethylenated telomer (M_3) appears at −89.5 ppm.

Its ^1H NMR spectrum displays two triplets having the same coupling constants ($^3J_{HH}$ = 18.6 Hz) centered at 1.62 and 1.58 ppm. The respective integrals are in a 14:1 ratio (in favor of the former triplet) indicates that the signal assigned to CH_3 end- group of M_3 model is centered at 1.58 ppm. Interestingly, all the ^1H NMR spectra of 1−4 samples (Table 3) show a signal of low intensity centered at 1.55 ppm. As a result, this multiplet corresponds to the methyl end group in $CH_3-CF_2-CH_2-CH_2CF_2$ sequence.

As a matter of fact, all the spectra also exhibit a triplet ($^3J_{HF}$ = 19.4 Hz) of triplets ($^4J_{HF}$ = 1.6 Hz) centered at 1.8 ppm; the higher coupling constant indicates that the methyl end group is linked to a $-CF_2-CF_2-$ group as previously shown.[30]

To confirm this statement, 1,1,1,2,2,3,3,4,4,6,6,8,8,9,9-pentadecafluorodecane ($C_4F_9-CH_2CF_2-CH_2CF_2-CF_2-CH_3$) ($M_4$ model) produced in the course of the synthesis of M_1 model has also been characterized by NMR. Its ^1H NMR spectrum shows the presence of a triplet ($^3J_{HF}$ = 19.2 Hz) of triplets ($^4J_{HF}$ = 1.7 Hz) centered at 1.8 ppm. This confirms that the methyl end group of $CH_3-CF_2CF_2CH_2-$ sequence gives a triplet of triplets centered at 1.8 ppm. Furthermore, two distinct signals, centered at −107.5 and −113.7 ppm, are also present in all the ^{19}F NMR spectra. Interestingly, both signals of the M_4 model are centered at −113.7 and −107.5 ppm

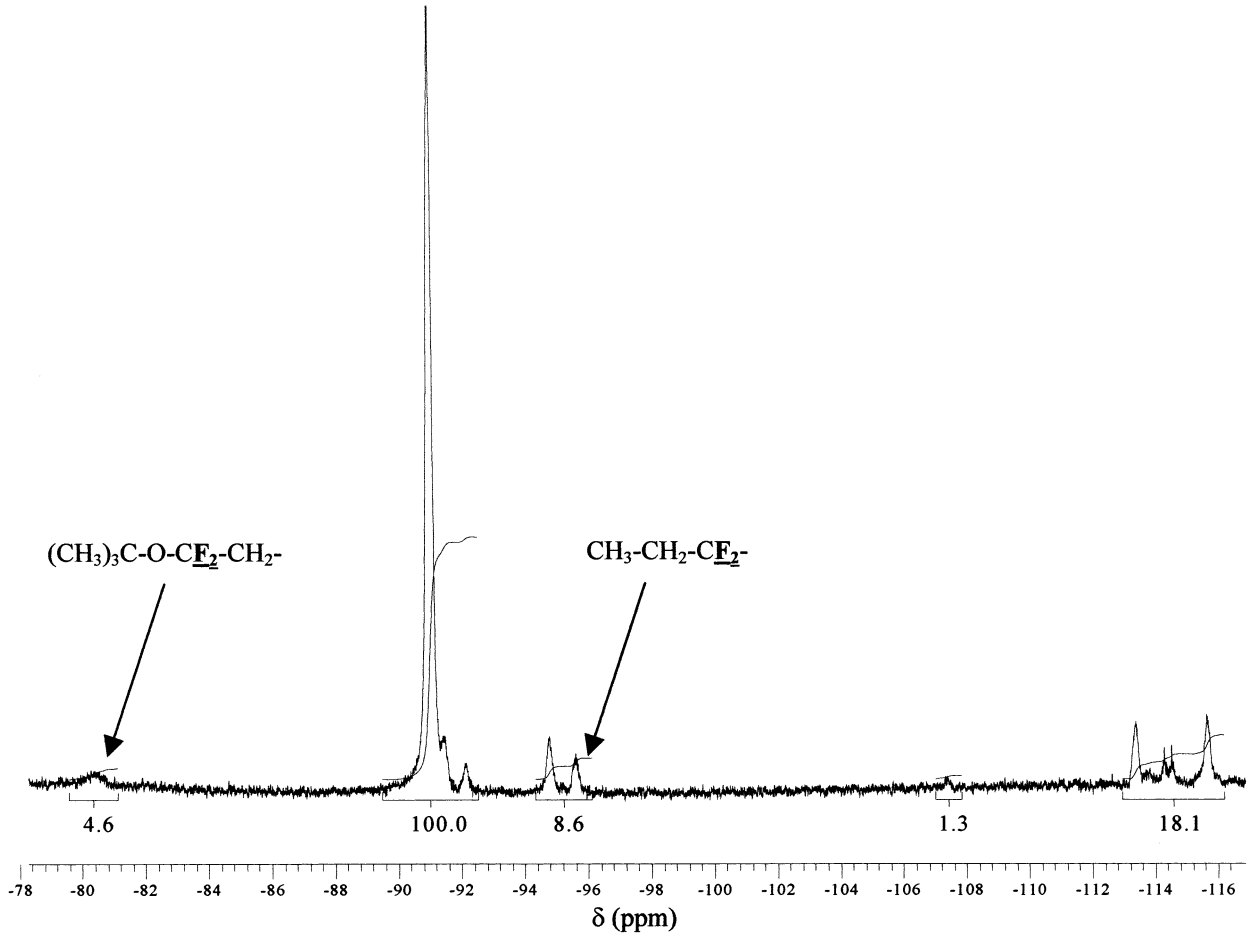


Figure 5. ^{19}F NMR spectrum of PVDF homopolymer (experiment 5) initiated by *tert*-butyl peroxide at 50 °C for 216 h.

and hence confirm the presence of the $CH_3CF_2CF_2CH_2$-CF_2- structure in the polymer. This sequence can be obtained from the transfer of a proton onto the $-CH_2$-$CF_2-CF_2CH_2^{\bullet}$ macroradical.

Finally, all ^{19}F NMR spectra exhibit the presence of a multiplet centered at −150 ppm, discussed later.

Hence, the main signals present in the ^{19}F and ^{1}H NMR spectra of polymers (produced from the homopolymerization of VDF initiated by *tert*-butyl peroxide at 100 °C) have been assigned. Regarding the assessment of the molar masses of this PVDF, it is known that several techniques can be possible: (1) size exclusion chromatography, which is not adequate because of the lack of PVDF standards; (2) viscosimetry, which would be an elegant method since K and α are known[35,36] but, in this case, a high content of inititator was used, hence reducing the molar mass; (3) NMR spectroscopy taking into account the end groups arising from the initiator or from transfer. Actually, less ambiguity is supplied from the transfer end group that enables the determination of molar masses. As mentioned above, in the ^{1}H NMR spectrum (Figure 1), the signals correponding to the transfer are centered at 6.3 and 1.8 ppm, and they represent one ($CH_2-CF_2-\boldsymbol{H}$) and three $-(CF_2-C\boldsymbol{H_3})$ protons, respectively. Thus, the average degree of polymerization in number, $\overline{DP_n}$, can be calculated as the ratio of the integrals of the peak attributed to the $-CH_2$ group belonging to VDF over those of the end group (taking into account a factor of 2 related to both end groups).

$$\overline{DP_n} = \frac{2[I_{2.9}/2 + I_{2.3}/2 + I_{1.8}/3]}{I_{1.0}/3 + I_{1.05}/9 + I_{1.2}/9 + I_{1.3}/9 + I_{1.55}/3 + I_{1.8}/3 + I_{6.3}} \quad (6)$$

where I_n represents the integral of the signal centered at n ppm.

The same calculation can be possible from ^{19}F NMR spectrum (Figure 2), obtained from the integrals of all peaks divided by those of signals assigned to CF_2 adjacent to an end group (as the peaks centered at −107.5 and −113.7 ppm represent two CF_2 groups with the same end group, it must appear once only; this is also the same for both multiplets signals centered at −92.4 and −114.5 ppm).

$$\overline{DP_n} = 2[I_{-80.3} + I_{-91.0} + I_{-92.2} + I_{-92.4} + I_{-94.8} + I_{-95.7} + I_{-107.5} + I_{-112.3} + I_{-113.4} + I_{-113.7} + I_{-114.5} + I_{-115.7}]/[I_{-80.3} + I_{-92.2} + I_{-95.7} + I_{-107.5} + I_{-112.3} + I_{-114.5} + I_{-150.0}] \quad (7)$$

As a matter of fact, these both determinations are approximate since possible branching occurs.[20]

It was thus interesting to perform the same study, but investigated at 50 °C.

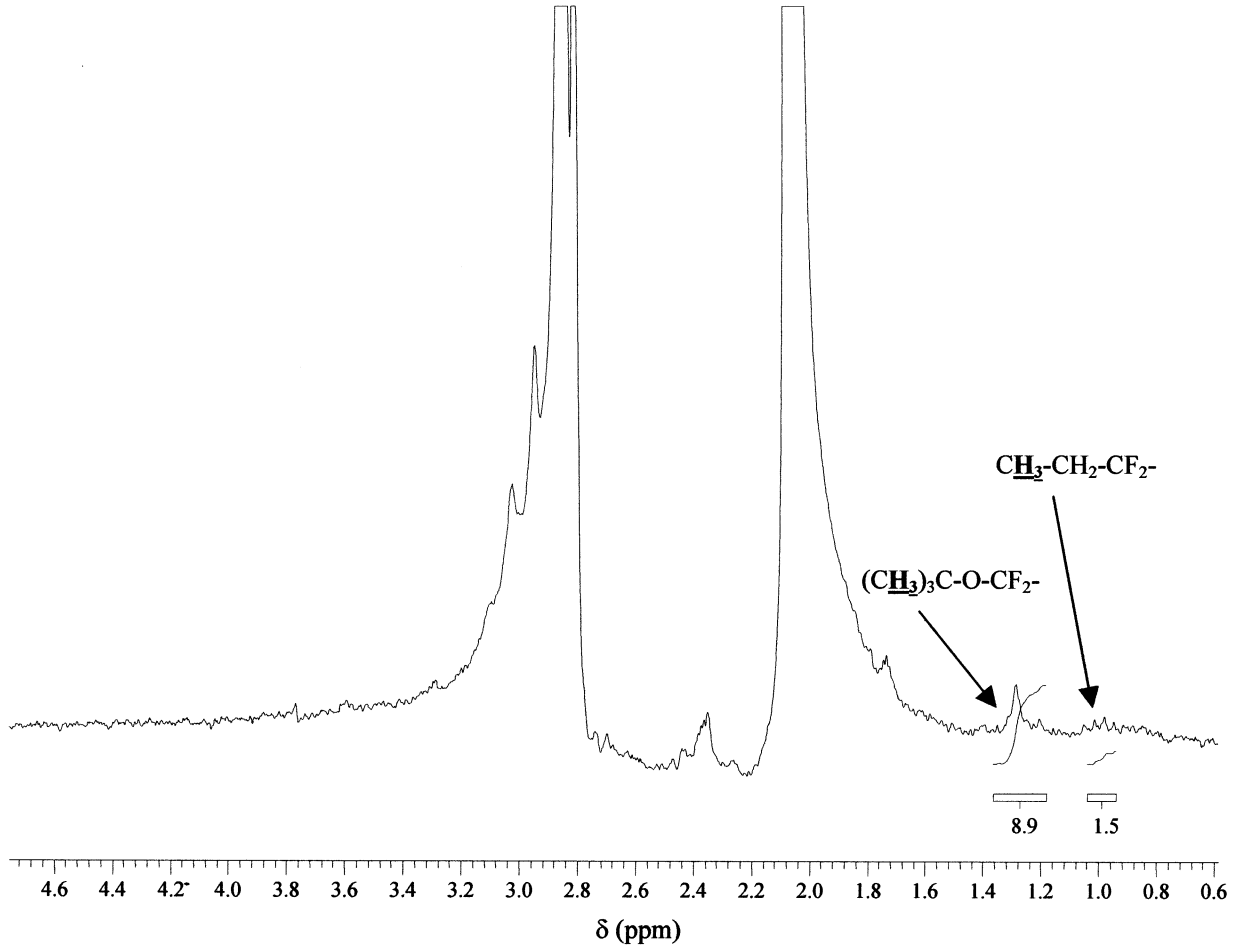


Figure 6. ^{1}H NMR spectrum of PVDF homopolymer (experiment 5) initiated by *tert*-butyl peroxide at 50 °C for 216 h.

(A-2) Reaction Temperature: 50 °C. It is well-known that *tert*-butyl peroxide has a half-life of 1 h at 146 °C.[37] Consequently, we have found it interesting to carry out homopolymerization of VDF at 50 °C in the presence of a high amount of that initiator (C_0 = 50%) for about 9 days (Table 3).

After reaction and treatment, the samples were characterized by ^{19}F and ^{1}H NMR. The former series (Figure 5) shows the characteristic signals centered at −91.0, −94.8, −113.4, and −115.7 ppm. In the ^{1}H NMR spectra (Figure 6), expected multiplets were present at 2.3 and 2.9 ppm while a further singlet was noted at 1.3 ppm. Such an observation was compared to the results obtained by Cuthbertson et al.[38] who described the addition of tBuO$^{\bullet}$ onto VDF, the monoadduct being trapped by a nitroxide. These authors supplied the ^{1}H NMR data of both molecules: tBuO−CH_2CF_2−ONR_2 (M_5) and tBuO−CF_2CH_2−ONR_2 (M_6). The chemical shifts of *tert*-butoxy end groups in the ^{1}H NMR spectra of both M_5 and M_6 molecules are 1.10 and 1.35 ppm, respectively. This Australian team also showed that the CH_2 group (in M_5) gives a triplet ($^{3}J_{HF}$ = 9.5 Hz) centered at 3.65 ppm. Hence, it can be considered that the signal centered at 1.3 ppm in the ^{1}H NMR spectrum of the PVDF corresponds to methyl groups of tBu in tBu−OCF_2CH_2 sequence.

In addition, the ^{19}F NMR spectra indicate another signal centered at −80 ppm attributed to the difluoromethylene of the sequence above. This confirms Moggi investigation's,[39] who showed that the signal assigned to a CF_2 group adjacent to both an oxygen atom and a methylene group (OCF_2CH_2) is centered at ca. −80 ppm.

A further investigation concerns the homopolymerization of VDF initiated by the azo-*tert*-butane (tBu−N=N−tBu).

(B) Homopolymerization of VDF with Azo-*tert*-butane. This initiator exhibits a high activation energy of 180.0 kJ mol.$^{-1}$ [25] and a half-life of 10 h at 160 °C. Hence, a high amount of initiator was used (25% and 50%) to be sure that a part of it is decomposed and thus initiates the homopolymerization of VDF. Actually, at 120 °C for 72 h, 3.6% only of the initial amount of initiator has reacted. Table 3 lists the results obtained in acetonitrile in these conditions with initial molar concentrations of tBu−N=N−tBu of 50% and 25% (attempts 6 and 7, respectively).

The ^{19}F (Figure 7) and ^{1}H (Figure 8) NMR spectra of the obtained polymers display the expected chemical shifts as assigned above. Interestingly, the ^{19}F NMR spectrum also shows the presence of a triplet ($^{3}J_{HF}$ = 16.6 Hz) centered at −112.3 ppm, assigned to a difluoromethylene group coupling with a methylene or a difluoromethylene group, only. However, as we cannot get the tBu−CF_2CF_2 structure, thus the tBu−CF_2CH_2 end group, arising from the radical addition of tBu$^{\bullet}$ onto CF_2 of VDF, is produced. Moreover, the comparison of the relative integrals of that signal above about the integrals of the other signals for both samples indicates 1.4% and 0.7% for attempts 6 (c_o = 50%) and 7 (c_o = 25%), respectively. This statement confirms that this peak corresponds to a tBu−CF_2CH_2 end group.

Further, it is noted that the higher the initial amount of initiator, the greater the integral of the signal centered at −92.2 ppm.

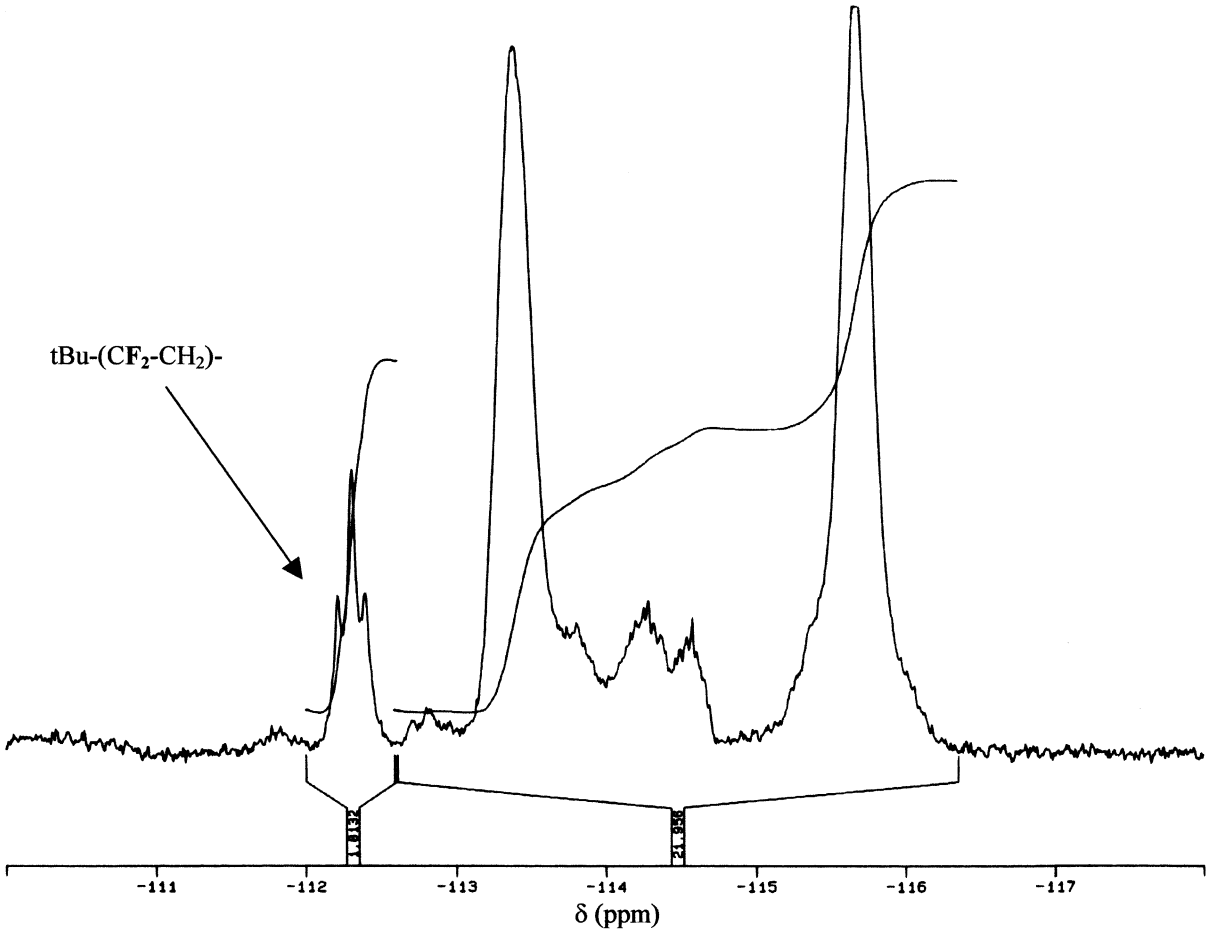


Figure 7. ^{19}F NMR spectrum expansion of the −110 to −118 ppm range of PVDF homopolymer (experiment 7) initiated by azo-*tert*-butane at 120 °C for 72 h.

Regarding the signals arising from the proton transfer to CF_2 group, two characteristic peaks centered at −92.4 and −114.5 ppm were noted. However, the latter has a low intensity. That of the former can be also neglected because of overlapping with the multiplet centered at −92.2 ppm. The relative intensity of that peak is 11.4% of the total number of fluorine atom for attempt 6 vs 6.8% for attempt 7. It can thus be deduced that it corresponds to a CF_2 group of a VDF unit having reacted with tBu• as follows: tBu−CH_2CF_2−.

Furthermore, by comparing the relative integrals of signal centered at −92.2 ppm (assigned to CF_2 in tBu−CH_2CF_2−) with that centered at −112.3 ppm (tBu−CF_2-CH_2−), it was found that 89% of the tBu• radicals react with CH_2 in attempt 6 vs 90% in attempt 7.

However, signals having low integrals cannot be assigned: in particular, a triplet (J = 16 Hz) centered at −50.6 ppm, a singlet at −150 ppm, and two multiplets centered at −94.3 and −95.6 ppm. Nevertheless, one of these signal could be assigned to the CF_2 group of VDF unit located in β position about the tBu end group:

tBu-CF_2CH_2−CH_2CF_2− structure

In the ^1H NMR spectra, it the presence of two singlets centered at 1.05 and 1.20 ppm was noted, the respective intensities of which for the total number of protons are 5.5 and 1.2% for attempt 6 and 3.6 and 0.7% for attempt 7. This can be assumed by considering that the signals corresponding to methylene groups belong to the *tert*-butyl end group. Hence, these integrals allowed us to conclude that the peaks centered at 1.05 and 1.20 ppm are assigned to t*Bu*−CH_2CF_2 and t*Bu*−CF_2CH_2 end groups, respectively.

Similarly, as in ^{19}F NMR spectra, an estimation of the addition of tBu• radical onto the methylene side of VDF was assessed to 82% and 84% from the results of experiments performed in experiments 6 and 7, respectively.

Finally, after the NMR assignments of the various hydrogenated or fluorinated groups of PVDF produced from the initiations in the presence of *tert*-butyl peroxide and azo-*tert*-butane, it was worth investigating that from *tert*-butyl peroxypivalate.

(C) Radical Homopolymerization of VDF Initiated by *tert*-Butyl Peroxypivalate. As mentioned above, the thermal decomposition of tBu−OO−CO−tBu can generate a •OCOtBu radical type, but its initiation for the radical homopolymerization of VDF is questionable. Hence, this fluoroalkene was reacted at 50 and 100 °C in the presence of that initiator. As in the latter temperature, it is assumed that CO_2 can be produced from •OCOtBu, two experiments were realized at these above temperatures, with initial molar initiator concentrations of 10 and 20% for 16 h (experiments 7−10).

As *tert*-butyl peroxypivalate exhibits a half-life of 24.2 h at 50 °C,[37] it can be deduced that, in 16 h, only 36.7% of the initial amount of initiator was decomposed.

The NMR spectra of the PVDFs arising from these four homopolymerization reactions show the presence of the expected characteristic signals at 2.3 and 2.9 ppm

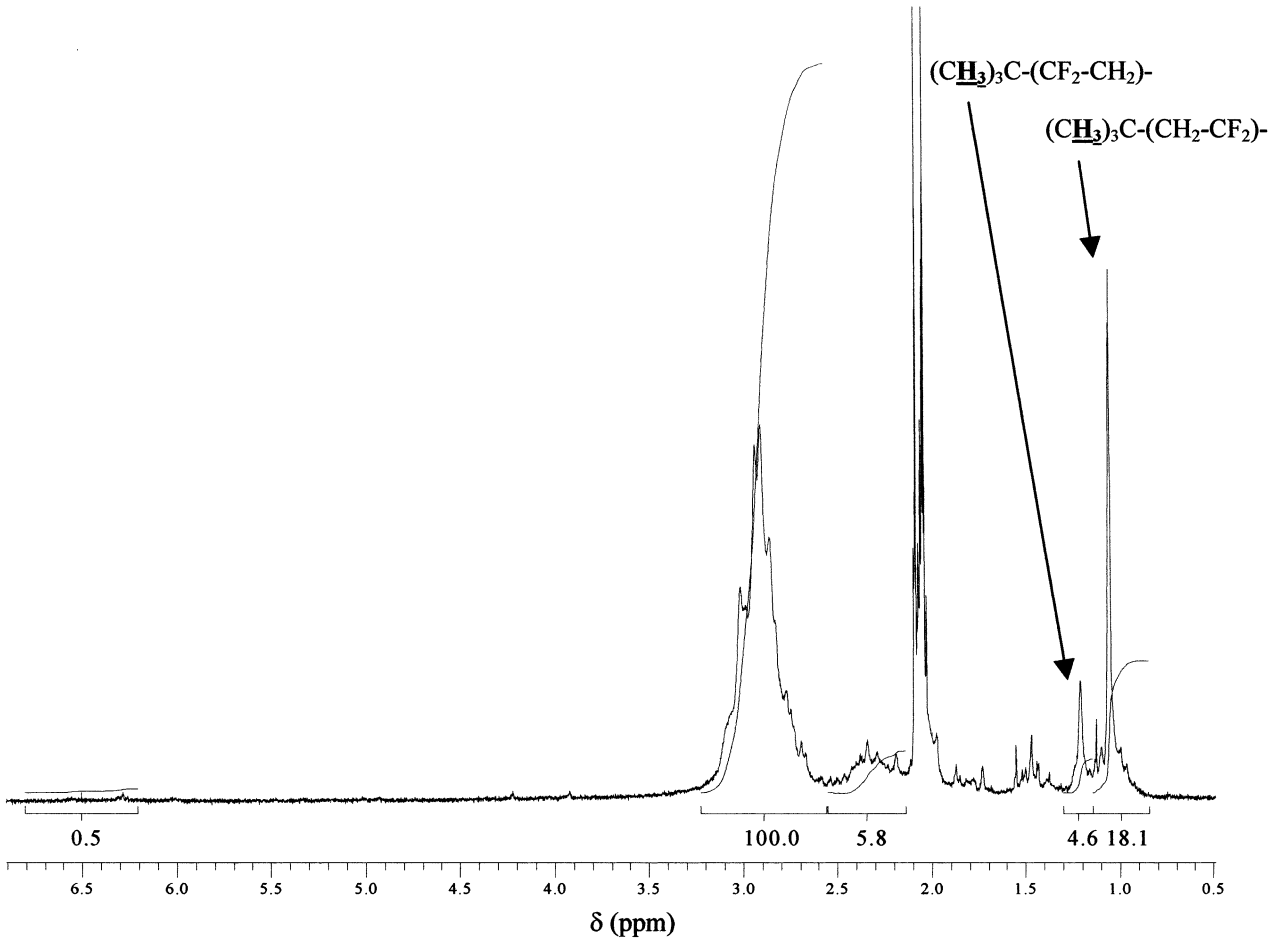


Figure 8. ^{1}H NMR spectrum of PVDF homopolymer (experiment 7) initiated by azo-*tert*-butane at 120 °C for 72 h.

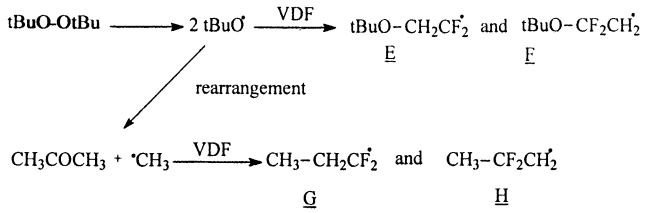
and at −91.0, −94.8, −113.4 and −115.7 ppm, respectively, for the ^{1}H (Figure 9) and ^{19}F (Figure 10) NMR spectra. In addition, the characteristic $-CF_2H$ end group, coming from the proton transfer to the macroradical, was indicated by the triplet of triplets centered at 6.3 ppm and the multiplet centered at −114.5 ppm, on the ^{1}H and ^{19}F NMR spectra, respectively. Further, the signal centered at −95.7 ppm in the ^{19}F NMR spectra was assigned to $CH_3-CH_2CF_2-$ groups (the triplet centered at 1.0 ppm attributed to the methyl end group was overlapping with the broad signal). The ^{19}F NMR spectra also exhibit the presence of multiplets of low integrals centered at −107.5 and −113.7 ppm assigned to the $-CH_2CF_2-CH_2CF_2-CF_2CH_3$ sequence.

In addition, the triplet ($^3J_{FH}$ = 16.6 Hz) centered at −112.3 ppm indicates the presence of a $tBuCF_2CH_2-$ end group, while the signal centered at −92.2 ppm corresponds to the $tBuCH_2CF_2-$ sequence. However, comparing the respective integrals of these peaks enables us to deduce that tBu• radical is preferentially added (ca. 90%) onto the methylene group of VDF. That statement was also confirmed from the integral ratio of both singlets at 1.05 and 1.20 ppm noted on the ^{1}H NMR spectra.

A peak centered at −150 ppm was also observed in the ^{19}F NMR spectra. Having assigned main signals noted in the ^{1}H and ^{19}F NMR spectra of PVDFs, it was worth proposing a mechanism of radical homopolymerization of VDF.

(II) Mechanism of Homopolymerization. (A) Mechanism of Initiation. The mechanism of initiation were determined for each initiators.

(A-1) Initiation from *tert*-Butyl Peroxide (DTBP). At 50 and 100 °C, DTBP undergoes a thermal decomposition by homolytical cleavage of the O−O bond according to the following reaction scheme



Four types of initiations are thus possible, generating four different end groups (**E**−**H**).

(a) For Reactions Realized at 50 °C (Experiment 5). The presence of two peaks centered at 1.0 and 1.3 ppm in the ^{1}H NMR spectrum and two peaks located at −80.3 and −95.7 ppm in the ^{19}F NMR spectrum indicate that the tBuO• radical initiates onto the CF_2 site of VDF only and H_3C• is added mainly onto the CH_2 side. For the tBuO• radical, this observation confirms the results obtained by Elson et al.[40] who have shown that the photolysis of *tert*-butyl peroxide in the presence of VDF afforded a product correponding to the addition of *tert*-butoxy radical onto the difluoromethylene side, only. This is also in good agreement with the results of Cuthberson et al.,[38] who have demonstrated that the selectivity of addition of this radical depends on the temperature according to the following equation: $\ln(k_t/k_h) = (1.06 \pm 0.01) - (800 \pm 40)/T$ where T, t, and h

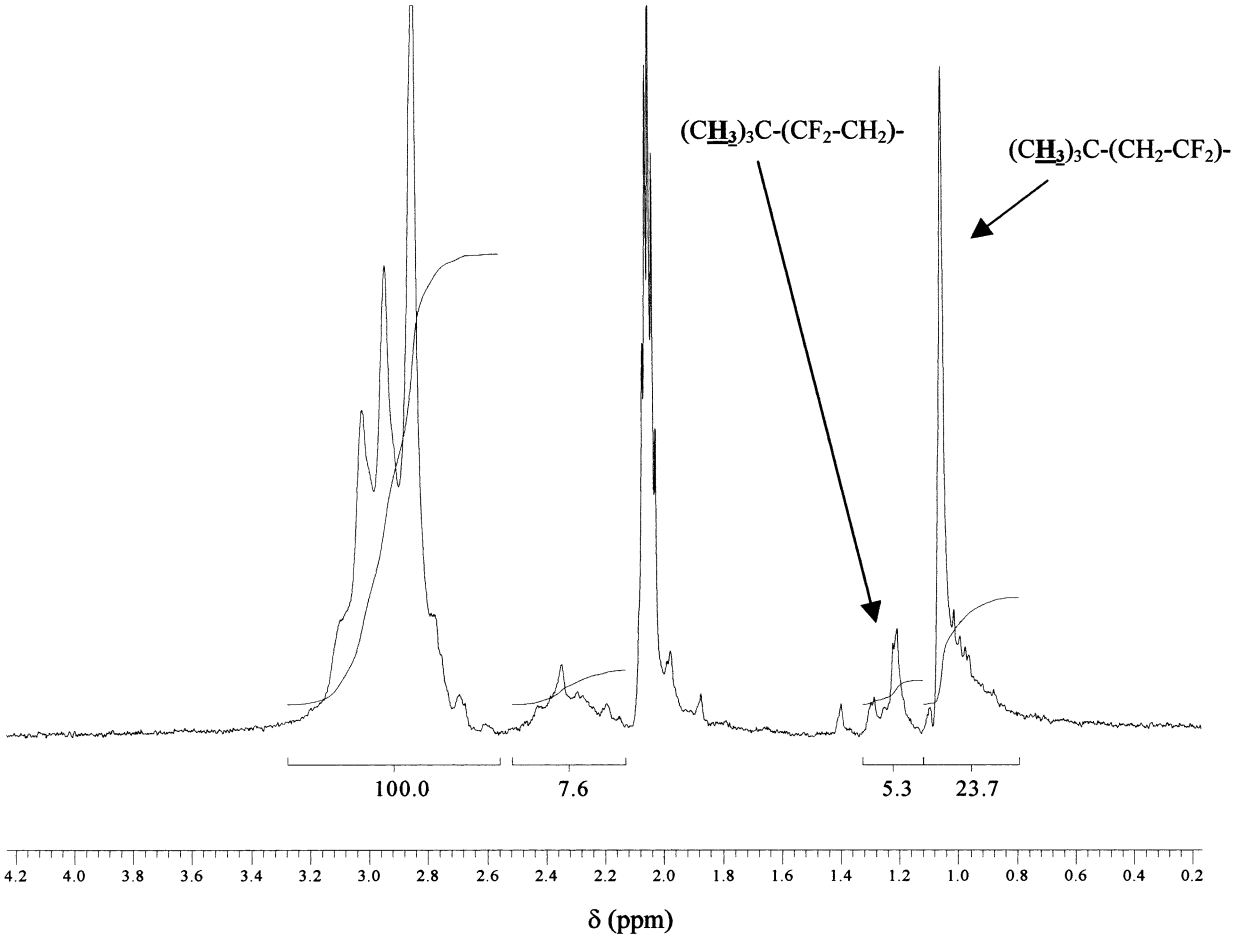
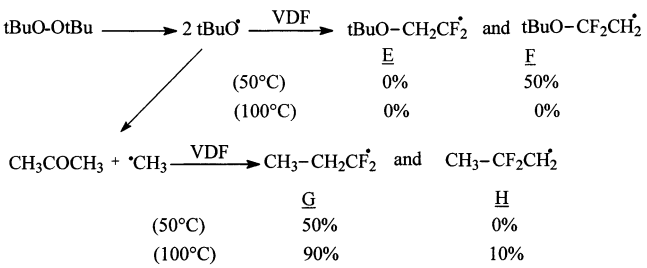


Figure 9. ^{1}H NMR spectrum of PVDF homopolymer (experiment 9) initiated by *tert*-butyl peroxypivalate at 50 °C for 16 h.

stand for the temperature (in K), the addition rate of tBuO$^\bullet$ onto CH_2, and the addition rate of tBuO$^\bullet$ onto CF_2, respectively. Using such an equation enables one to deduce a k_h/k_t ratio of 4 at 50 °C.

(b) At 100 °C (Experiments 1−4). It is noted that, in the ^{1}H NMR spectrum, the absence of both signals centered at 1.1 and 3.6 ppm assigned to nine protons of *tert*-butyl end group and to those of the methylene group adjacent to tBuO indicated that this PVDF did not exhibit the **E** sequence. Hence, it can be deduced that the initiation of tBuO$^\bullet$ radical toward the CH_2 site of VDF did not occur. Similarly, the absence of the peaks centered at +1.3 and −80.3 ppm reveal that the tBuO$^\bullet$ radical does not initiate onto the CF_2 group of VDF. Under these conditions, the initiation exclusively occurs by $^\bullet CH_3$ radical as shown by the presence of peaks centered at 1.0 (**G** structure) and 1.55 ppm (**H** structure) that is mainly favored to a CH_2 site of a VDF unit.

Hence at 50 and 100 °C, the end groups arising from the initiator are the following:



(A-2) Initiation by Azo-*tert*-butane. The initiator undergoes a double homolytic thermal cleavage that generates two tBu$^\bullet$ radicals and a molecule of nitrogen as follows:

$$tBu{-}N{=}N{-}tBu \xrightarrow[\Delta]{} 2\ tBu^\bullet + N_2$$

In a second step, these radicals were added onto VDF, hence generating two fluorinated radicals, as follows:

$$tBu^\bullet \xrightarrow{VDF} tBu{-}CH_2CF_2^\bullet + tBu\text{-}CF_2CH_2^\bullet$$

As a consequence, two initiations are possible leading to two types of end groups. Further, as indicated above, it was noted that tBu$^\bullet$ radical mainly attacks the methylene side of VDF (80−85%), according to the integrals of the characteristic peaks in the NMR spectra.

(A-3) Initiation by *tert*-Butyl Peroxypivalate. As observed above, this initiator can generate four types of radicals: tBuO$^\bullet$, $^\bullet$OCOtBu, $H_3C^\bullet$, and tBu$^\bullet$.

At 50 °C, the first one does not react onto VDF as evidenced by the absence of any signal centered at 1.3 and 3.6 ppm in the ^{1}H NMR spectrum.

Similarly at 50 °C (attempts 8 and 9) or 100 °C (attempts 10 and 11), the second radical does not enable the initiation of VDF (the proof was also given from NMR spectra). It undergoes a decarboxylation to lead to tBu$^\bullet$.

In contrast, the $H_3C^\bullet$ radical initiates the homopolymerization of VDF, mainly by reacting on the methylene group of VDF.

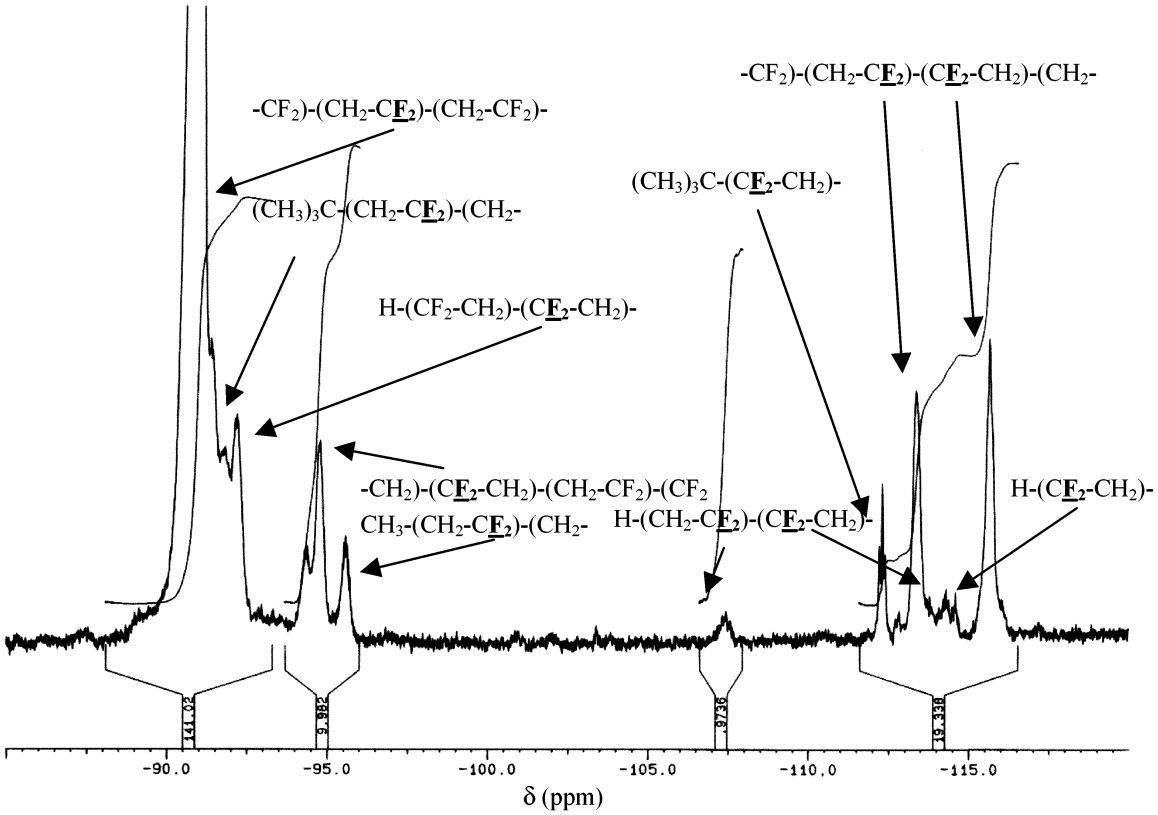
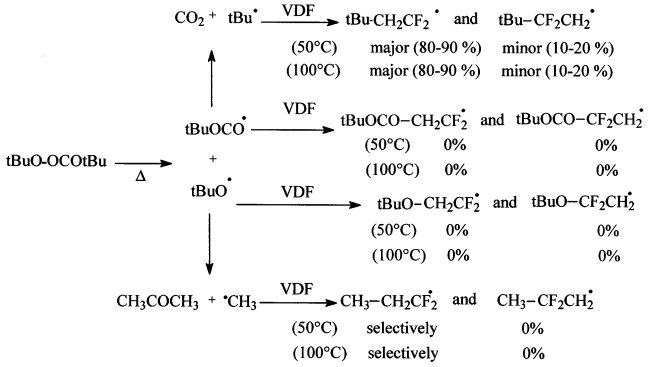


Figure 10. ^{19}F NMR spectrum of PVDF homopolymer (experiment 9) initiated by *tert*-butyl peroxypivalate at 50 °C for 16 h.

Finally, tBu• radical can also be added, mainly onto the CH_2 of the VDF side (80−90%).

As above, in the case of *tert*-butyl peroxide, the integrals of the characteristic signals assigned to all the groups enabled us to propose the following tendency:



(B) Mechanism of Propagation. In all the spectra, the integrals of the multiplets corresponding to normal head-to-tail additions are favored (90−95%) about those of the inversed adducts (head-to-head and tail-to-tail: 5−10%),[27−30] as follows:

$$A(VDF)_nCH_2CF_2^{\bullet} \xrightarrow[90-95\%]{H_2C=CF_2} A(VDF)_nCH_2CF_2-CH_2CF_2^{\bullet}$$

$$A(VDF)_nCH_2CF_2^{\bullet} \xrightarrow[5-10\%]{F_2C=CH_2} A(VDF)_nCH_2CF_2-CF_2CH_2^{\bullet}$$

(C) Mechanisms of Transfer. The assignments of the peaks in the NMR spectra have also shown the presence of transfer of protons that can occur either onto a macroradical exhibiting a $-CH_2CF_2^{\bullet}$ end group or a $-CF_2CH_2^{\bullet}$ inverse unit. These transfers may arise either from the acetone generated in the course of the thermal rearrangement of tBuO• or from a transfer to the solvent or to the polymer, as follows:

$$\sim\sim CH_2CF_2-CH_2CF_2^{\bullet} + R-H \rightarrow \sim\sim CH_2CF_2-CH_2CF_2H + R^{\bullet}$$

$$\sim\sim CH_2CF_2-CF_2CH_2^{\bullet} + R-H \rightarrow \sim\sim CH_2CF_2-CF_2CH_3 + R^{\bullet}$$

To assess the ability of the solvent to promote a transfer, two homopolymerization reactions were realized under conditions similar to those of attempt 1 (1% of tBu−O−O−tBu, 66 h, 100 °C), but methyl acetate (attempt 12) and perfluorohexane (attempt 13) were used as the solvents.

The study of the signals corresponding to $-CH_2CF_2H$ and $-CF_2CF_2CH_3$ sequences, arising from the transfers of protons onto the growing macromolecular radical, shows that a slight transfer occurred when perfluorohexane was involved as the solvent. Hence, it can be deduced that the acetone generated from the radical coming from tBuO• rearrangement provokes a little transfer; this may also be explained by the fact that a small amount of acetone was produced. In contrast, when methyl acetate was used as the solvent, it was noted that the integrals of the peaks corresponding to $-CF_2H$ and $-CF_2CH_3$ end groups were greater. However, such an observation is in contradiction with the investigations of Russo et al.[28] showing that, at 55 °C, the transfer constant to methyl acetate was 1.63×10^{-3} while that of acetone was estimated at 4.21×10^{-3}.

To confirm our results, size exclusion chromatography (or GPC) analyses were done on these three samples. It was noted that samples 1, 12 (from methyl acetate), and 13 (from perfluorohexane) have molar masses of 15 000, 9600, and 19 000, respectively. Such observations are in good agreement with the above results: transfer reactions limit the propagation step and hence lower the molar masses.

Considering that the transfer step may occur from the solvent (i.e., acetonitrile), the following equations can be suggested:

$$\sim\sim CH_2CF_2-CH_2CF_2^{\bullet} + H-CH_2CN \rightarrow \sim\sim CH_2CF_2-CH_2CF_2H + {}^{\bullet}CH_2CN$$

$$\sim\sim CH_2CF_2-CF_2CH_2^{\bullet} + H-CH_2CN \rightarrow \sim\sim CH_2CF_2-CF_2CH_3 + {}^{\bullet}CH_2CN$$

In addition, a signal centered at −150 ppm that appears in all ^{19}F NMR spectra was not present in those arising from samples 12 and 13. It could be supposed that $^{\bullet}CH_2CN$ radical also can be added onto VDF to produce either $NCCH_2CH_2CF_2^{\bullet}$ or $NCCH_2CF_2CH_2^{\bullet}$ radicals. Hence, the former structure might be represented by a signal centered at −95.7 ppm while the latter one could have a chemical shift at −150 ppm

(D) Termination Step. As known, in the course of the polymerization of VDF, recombination only occurs,[1] as follows:

$$A(VDF)_n^{\bullet} + {}^{\bullet}(VDF)_pA \rightarrow A(VDF)_{n+p}A$$

(E) Reinitiation. Some radicals can be produced by transfer reactions, for example from $CH_3COCH_2^{\bullet}$ or $CNCH_2^{\bullet}$ radicals (see above). Hence, these radicals could initiate polymerization reactions as follows:

$$CH_3COCH_2^{\bullet} \xrightarrow{VDF} CH_3COCH_2-CH_2CF_2^{\bullet} + CH_3COCH_2-CF_2CH_2^{\bullet}$$

$$NCCH_2^{\bullet} \xrightarrow{VDF} NCCH_2-CH_2CF_2^{\bullet} + NCCH_2-CF_2CH_2^{\bullet}$$

The former reaction was reported by Pianca et al.[20]

Conclusions

^{1}H and ^{19}F NMR spectroscopies of various PVDFs synthesized by radical polymerization of VDF initiated by *tert*-butyl peroxide, azo-*tert*-butane, and *tert*-butyl peroxypivalate were investigated. Interestingly, the use of model molecules prepared by telomerization reactions or ethylene end-capping enabled one to assign most of the chemical shifts of the different signals observed in the ^{1}H and ^{19}F NMR spectra of the PVDFs. Hence, attributions of end groups gave us much information on the mechanisms and, in particular, on the initiation and transfer steps. This study has also shown that *tert*-butoxy radical mainly reacts onto CF_2 side of the VDF, in contrast to the methyl and *tert*-butyl radicals, which can be mainly added onto the CH_2 of VDF. Furthermore, when *tert*-butyl peroxypivalate was used as the initiator, several radicals were generated but only methyl and *tert*-butyl ones initiated the homopolymerization of VDF. These spectral characterizations and the understanding of the mechanisms are particularly interesting for investigations regarding the copolymerization and the terpolymerization of VDF with other monomers,[41−44] under progress.

Acknowledgment. The authors thank the Solvay S.A. Co. (Brussels, Belgium, and especially Dr. T. Lannuzel) for its financial help and for the gift of VDF, and the Atofina Co. for supplying perfluoroalkyl iodides. In addition, pertinent comments, from the reviewer, have been appreciated.

References and Notes

(1) Timmerman, R. *J. Appl. Polym. Sci.* **1962**, *6*, 456−460.
(2) Görlitz, M.; Minke, R.; Trautvetter, W.; Weisberger, G. *Angew. Makromol. Chem.* **1973**, *29/30*, 137−162.
(3) Lovinger, A. J. *Developments in Crystalline Polymers I*; Applied Science Publishers: London, 1981; p 195.
(4) Nguyen, T. *J. Macromol. Sci.—Rev. Macromol. Chem., Part C* **1985**, *25*, 227.
(5) Dohany, J. E.; Humphrey, J. S. *Encycl. Polym. Sci. Eng.* **1989**, *17*, 532−548.
(6) Seiler, D. A. PVDF in the Chemical Process Industry. In *Modern Fluoropolymers*; Scheirs, J., Ed.; Wiley: New York,-1997; Chapter 25, pp 487−505.
(7) Governal, R. A. Ultrapure Water: a battle every step of the way. *Semicond. Int.* **1994**, *July*, 176−180.
(8) Henley, M. Market review: semiconductor industry expansion should continue *Ultrapure Water* **1995**, *May/June*, 15−20.
(9) Robinson, D.; Seiler, D. A. Potential Applications For Kynar Flex PVDF in the nuclear industry. *Proceedings American Glovebox Society, 1993 National Conference, Linings, Coatings, and Materials*, Seattle, WA, August 16−19, 1993, Section 3C, 10−14.
(10) Moggi, G.; Caratto, A.; Bonardelli, P.; Monti, C. US Patent 4,739,024 (Montefluos S.P.A), 1988.
(11) Fr. Patent 1,419,741 (Kureha Chemical Industry Co.), 1965; *Chem. Abstr.* **1966**, *65*, 9049b.
(12) Hauptschein, M. US Patent 3,193,539 (Pennsalt Chemicals Corp), 1965; *Chem. Abstr.* **1965**, *63*, 13443c.
(13) Br. Patent 1,179,078 (Daikin Kogyo Co), 1970; *Chem. Abstr.* **1970**, *72*, 56095p.
(14) McCain, G. H.; Semanack, J. R.; Dietriech, J. J. Fr. Patent 1,530,119 (Diamond Alkali Co.), 1968; *Chem. Abstr.* **1969**, *71*, 3923e.
(15) Br. Patent 1,057,088 (Kali-Chemie, A.G.), 1967; *Chem. Abstr.* **1967**, *66*, 66041h.
(16) Iserson, H. US Patent 3,245,971 (Pennsalt Chemicals Corp.), 1966; *Chem. Abstr.* **1966**, *64*, 19822a.
(17) Carlson, D. P. Ger. Offen. 1,806,426 (E. I. du Pont de Nemours and Co.), 1969; *Chem. Abstr.* **1969**, *71*, 13533s.
(18) Lasson, P. Fr. Patent 0,417,585 B1 (Solvay, S.A), 1994.
(19) Rondestvedt, C. S. *J. Org. Chem.* **1977**, *42*, 1985−1990.
(20) Pianca, M.; Barchiesi, E.; Esposto, G.; Radice, S. *J. Fluorine Chem.* **1999**, *95*, 71−84.
(21) Davids, W. H., Jr.; Pryor, W. A. *J. Am. Chem. Soc.* **1977**, *99*, 6365−6372.
(22) Nakamura, T.; Suyama, S.; Busfield, W. B.; Jenkins, I. D.; Rizzardo, E.; Thang, S. H. *Polymer* **1999**, *40*, 1395−1401.
(23) Griffiths, P. G.; Rizzardo, E.; Solomon, D. H. *J. Macromol. Sci. Chem.* **1982**, *17*, 45−50.
(24) Schwetlick, K.; Karl, R.; Jentzsch, R. *J. Prakt. Chem.* **1963**, *22*, 113−224.
(25) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99−150.
(26) Yagi, T.; Tatemoto, M. *Polym. J.* **1979**, *11*, 429−436.
(27) Ferguson, C.; Brame, E. G., Jr. *J. Phys. Chem.* **1979**, *83(11)*, 1397−1401.
(28) Russo, S.; Behari, K.; Chengji, S.; Pianca, M.; Barchiesi, E.; Moggi, G. *Polymer* **1993**, *34*, 4777−4781.
(29) Balague, J.; Ameduri, B.; Boutevin, B.; Caporiccio, G. *J. Fluorine Chem.* **1995**, *70*, 215−223.
(30) Duc, M.; Ameduri, B.; Boutevin, B.; Kharroubi, M.; Sage, J. M. *Macromol. Chem. Phys.* **1998**, *199*, 1271−1289.
(31) Neumann, W. P. *Synthesis* **1987**, *8*, 665−683.
(32) Walton, J. C.; Low, H. C.; Tedder, J. M. *J. Chem. Soc., Faraday Trans 1* **1976**, *72*, 1707−1714.
(33) Sass, V. P.; Serov, S. I.; Sokolov, S. V. *Zh. Org. Khim. (Eng. Ed.)* **1977**, *13*, 2140−2142.
(34) Ameduri, B.; Boutevin, B. Manuscript in preparation.

(35) Welch, G. J. *Polymer* **1974**, *15*, 429−436.
(36) Ali, S.; Raina, A. K. *Makromol. Chem.* **1978**, *179*, 2925−2931.
(37) *Organic Peroxides*: *half-life times*; Technical brochure; Internox, The Akzo-Nobel Co.: 1991.
(38) Cuthbertson, M. J.; Rizzardo, E.; Solomon, D. H. *Aust. J. Chem.* **1985**, *38*, 315−324.
(39) Moggi, G.; Modena, S.; Marchionni, G. *J. Fluorine Chem.* **1990**, *49*, 141−146.
(40) Elson, I. H.; Mao, S. W.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 335−341.
(41) Ameduri, B.; Boutevin, B.; Bauduin, G.; Kostov, G.; Petrova, P. *Macromolecules* **1999**, *32*, 4544−4550.
(42) Ameduri, B.; Boutevin, B.; Kostov, G.; Petrova, P. *Des. Monomers Polym.* **1999**, *2*, 277−285.
(43) Guiot, J.; Ameduri, B.; Boutevin, B. *J. Polym. Sci., Part A: Polym. Chem.*, in press.
(44) Souzy, R.; Guiot, J.; Ameduri, B.; Boutevin, B.; Paleta, O. *Collect. Czech. Chem. Commun.*, in press.

MA0202641