Synthesis and Properties of Novel Fluorotelechelic Macrodiols Containing Vinylidene Fluoride, Hexafluoropropene and Chlorotrifluoroethylene

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ABSTRACT: The dead-end radical copolymerization of 1,1-difluoroethylene (or vinylidene fluoride, VDF or VF_2) with hexafluoropropene (HFP) initiated by hydrogen peroxide for obtaining original fluorinated telechelic elastomers is presented. The influence of the process (solution or emulsion) and the nature and amounts of solvents were studied. Various initial $[H_2O_2]_i/[\text{fluoroolefins}]_i$ molar ratios, ranging from 5 to 40%, were used, showing that the higher the hydrogen peroxide amount, the lower the molecular weights of the polymers obtained leading to fluorinated telechelics. Hence, low molecular weight copolymers, the $\overline{M}_n$ of which ranged from 800 to 3200, were synthesized. A careful structural analysis of these fluorinated telechelics was performed and enabled one to determine the fluorinated base units of both alkenes in the copolymers. Interestingly, these liquid to oily products exhibited low glass transition temperatures (from −80 to −40 °C). The mechanism of the reaction was approached and showed that the hydroxyl radical generated from hydrogen peroxide reacted to the hydrogenated carbon atoms of VDF but also to the fluorinated carbons of VDF and HFP, yielding COOH end groups, and is discussed. The selective reduction of these carboxylic end groups was achieved in the presence of lithium aluminum hydride leading to fluorinated telechelic diols.

Introduction

Fluoropolymers exhibit a unique combination of high thermal stability,[1−4] chemical inertness (to acids, bases, solvents and petroleum), low dielectric constants and dissipation factors, low water absorptivities, excellent weatherabilities, and very interesting surfaces properties.[1−4] Their high stability allows their use in numerous applications such as aerospace, aeronautics,[5] engineering, optics,[6−10] textile finishing,[10] military use,[11] and microelectronics.

However, fluorinated homopolymers (e.g., polyvinylidene fluoride, poly(tetrafluoroethylene), or polychlorotrifluoroethylene) exhibit a too high crystallinity rate that induces high costs in the processing at the molten state, poor solubility in organic common solvents and difficult cross-linking.

Interestingly, fluorinated elastomers[12−17] (Table 1) have shown enhanced properties and can solve both first drawbacks, but curability still remains a disadvantage, although cross-linkings from polyamines,[13,17] polyphenols,[13,17,18] peroxides,[13,17,19] or electron beam[17,20] are possible.

Two possibilities enable these polymers to improve their vulcanization. The first one lies in the use of cure site monomer(s) (CSM)[13,17,21−23] in the ternary or quaternary copolymerization, although the availability of these monomers is not easy.

This CSM possess bromine or iodine atoms[17] or hydroxyl,[17] carboxyl,[17] nitrile,[17] or mercapto[24] end groups that can further react in a specific reaction (e.g., with melamine or isocyanate reactants in the case of hydroxyl end group) with peroxides/triallyl (iso)cyanurate in the case of brominated elastomers[13,17,24] or with nonconjugated diene.[17,23]

The second issue consists of using fluorinated telechelics. These α,ω-difunctional compounds are powerful intermediates for polycondensation or polyaddition reactions.[14,16,25,26]

Except for commercially available perfluoropolyethers (Krytox,[27] Fomblin Z-deal and Z-Dol,[28] Demnum,[29] or Aflunox[30] produced by DuPont, Ausimont, Daikin, or Nippon Mektron companies, respectively), few telechelic elastomers have been obtained: they can be achieved from the polymerization of functional vinyl ether,[31] from fluorinated α,ω-diiodides.[26] Nevertheless, an elegant way deals with the radical copolymerization of vinylidene fluoride (VDF) with hexafluoropropene (HFP) initiated from functional initiator as pioneered by Rice and Sandberg.[32,33] However, the synthesis of the initiator is difficult (several steps), and several hazards arising from the poor thermal stability of the initiator are a limitation.

Surprisingly, hydrogen peroxide which is cheap, reactive, and able to generate hydroxyl radicals, has scarcely been used as a potential initiator in radical polymerization of fluoroalkenes (tetrafluoroethylene[34,35] mainly), while synthesized α,ω-poly(acrylamide) diols[36] or commercially available hydroxytelechelic polybutadienes[37−40] are easily achieved.

Hence, the objective of this article concerns the obtaining of original telechelic fluorinated elastomers from the radical copolymerization of VDF and HFP initiated by hydrogen peroxide.

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Table 1. Main Commercially Available Fluoroelastomers[a]

	HFP	PMVE	CTFE	P	HPFP
VDF	Daiel 801 (Daikin) Fluorel (3M/Dyneon) Tecnoflon (Ausimont) SKF-26 (Russia) Viton A (DuPont)		Kel F (Dyneon) SKF-32 (Russia) Voltalef (Atofina)		Tecnoflon SL (Ausimont)
TFE		Kalrez (DuPont)		Aflas (Asahi Glass)	
VDF + TFE	Daiel 901 (Daikin) Fluorel (Dyneon) Tecnoflon (Ausimont) Viton B (DuPont) + ethylene: Tecnoflon (Ausimont) + X: Viton GH (DuPont)	Viton GLT (DuPont)			Tecnoflon T (Ausimont)

[a] Key: CTFE, chlorotrifluoroethylene, $F_2C{=}CFCl$; HFP, hexafluoropropene, $F_2C{=}CF{-}CF_3$; HPFP, 1-hydropentafluoropropene, $FHC{=}CF{-}CF_3$; P, propene, $H_2C{=}CHCH_3$; PMVE, perfluoromethyl vinyl ether, $F_2C{=}CFOCF_3$; TFE, tetrafluoroethylene, $F_2C{=}CF_2$; VDF, vinylidene difluoride (1,1-difluoroethylene), $F_2C{=}CH_2$; X, cure-site monomer, $F_2C{=}CFOR_FG$ (G: CN, Br, OPh).

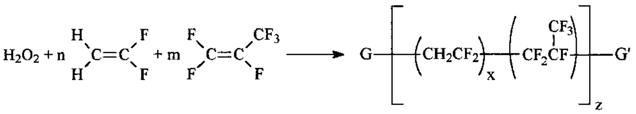
Experimental Part

(a) Materials. Hexafluoropropene (HFP), vinylidene fluoride (VDF), and chlorotrifluoroethylene (CTFE) were kindly supplied by Solvay SA. Hydrogen peroxide, lithium aluminum hydride, and acetonitrile were supplied by Aldrich and were used as received.

(b) Syntheses of Copolymers. The reactions were conducted in a 500 or 1000 mL Hastelloy C 276 autoclave (PARR) equipped with a valve, a manometer, a relief disk, and a temperature probe. After the introduction of the nonvolatile reactants, the vessel was closed, frozen in an acetone/liquid nitrogen mixture, and then placed under vacuum for several minutes. The required amounts of HFP, CTFE, or VDF were then introduced by doubled weighing in that order. The autoclave was left to warm to room temperature and then was placed either in a silicone bath (500 mL) or in a mantle (1 L) and progressively heated to the required temperature.

Caution! This procedure has to be performed carefullysince traces of metallic salt (especially iron) may enhance the decomposition rate of H_2O_2, resulting in a fast increase of hazardous pressure. The homolytic scission of H_2O_2 bond, catalyzed by iron salts, is a well-known reaction, which has been studied by Fenton. This phenomenon can be limited by the use of a Hastelloy autoclave instead of an iron one.

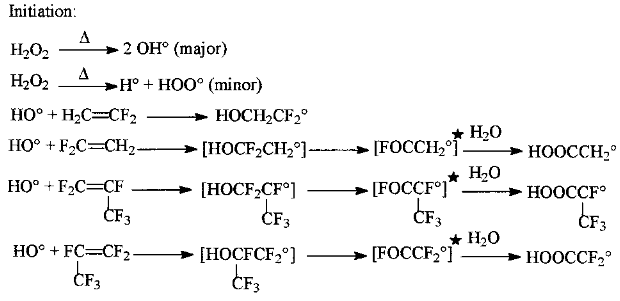
Scheme 1. Synthesis of a Copolymer Containing VDF and HFP Intiated by Hydrogen Peroxide



$H_2O_2 + n\,H_2C{=}CF_2 + m\,F_2C{=}CF(CF_3) \longrightarrow G{-}[(CH_2CF_2)_x{-}(CF_2CF(CF_3))]_z{-}G'$

where G represents hydroxyl or carboxylic functions
where G' represents hydroxyl, hydroxymethyl or carboxylic functions
where the formula with x and z means PVDF blocks linked by HFP units

Scheme 2. Initiation Step in the Copolymerization of VDF and HFP Initiated by Hydrogen Peroxide



Initiation:

$H_2O_2 \xrightarrow{\Delta} 2\,OH^\circ$ (major)

$H_2O_2 \xrightarrow{\Delta} H^\circ + HOO^\circ$ (minor)

$HO^\circ + H_2C{=}CF_2 \longrightarrow HOCH_2CF_2^\circ$

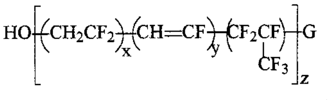
$HO^\circ + F_2C{=}CH_2 \longrightarrow [HOCF_2CH_2^\circ] \longrightarrow [FOCCH_2^\circ]^\star \xrightarrow{H_2O} HOOCCH_2^\circ$

$HO^\circ + F_2C{=}CF(CF_3) \longrightarrow [HOCF_2CF^\circ(CF_3)] \longrightarrow [FOCCF^\circ(CF_3)]^\star \xrightarrow{H_2O} HOOCCF^\circ(CF_3)$

$HO^\circ + FC(CF_3){=}CF_2 \longrightarrow [HOCF(CF_3)CF_2^\circ] \longrightarrow [FOCCF_2^\circ]^\star \xrightarrow{H_2O} HOOCCF_2^\circ$

The radicals with a star directly led to carboxylic functions in the presence of water.

Scheme 3. General Formula of Nonreduced Products Containing VDF and HFP



$HO{-}[(CH_2CF_2)_x{-}(CH{=}CF)_y{-}(CF_2CF(CF_3))]_z{-}G$

where G represents hydroxymethyl or carboxylic function.

The fluoroolefin conversion was determined by double weighing under slight vacuum. Although it gives an overestimation of the real fluoroolefin conversion, it is difficult to get a better estimation because of the partial solubility of the liquid phase of the fluoroolefins in reaction medium. The size exclusion chromatography was performed in THF as solvent at a flow rate of 0.8 mL/min and did not indicate the presence of byproducts coming from the possible oxidation of fluorinated olefins by hydrogen peroxide. The solvent was then removed by heating (40 °C) under slight vacuum, and the oligomers were purified by precipitation from cold pentane.

(c) Determination of the Acid Content. The carboxylic functions of different copolymers were titrated by a KOH (0.5 N) solution. In an Erlenmeyer, an *m* amount of copolymer was weighed and then diluted into THF. Phenolphthalein was added (0.002 g), and the COOH content was assessed from the following equation:

$$I_{\mathrm{COOH}} = \frac{N_{\mathrm{b}} V_{\mathrm{b}}}{m}$$

where N_b and V_b stand for the concentration of KOH used and the volume of base employed for the titration, respectively.

(d) Reduction of Carboxylic Functions. The reduction of carboxylic end groups according to the following procedure: after introducing 4*x* mol of $LiAlH_4$ into a three necked round-bottom flask fitted with a reflux condenser, a nitrogen inlet, a magnetic stirrer, and a dropping funnel, anhydrous THF was introduced. Then, *x* mol of the product was dissolved into anhydrous THF, the solution was dropwise added, and then the temperature was raised to 90 °C. The reduction reaction was allowed to proceed for 3 h, and at the end of the reaction, the excess of $LiAlH_4$ was neutralized by an excess of HCl (10% in water) leading to a solid complex. The mixture was then filtered, separating the complex of residual $LiAlH_4$. Then, the solvent was evaporated and the fluorinated oligomers were precipitated into cold pentane.

(e) Characterization by NMR Spectroscopy. The produced fluorinated copolymers were characterized by ^1H and ^{19}F nuclear magnetic resonance (NMR) spectroscopies. The spectra were recorded on a Bruker AC 200 or Bruker A-250 MHz instrument at room temperature in deuterated acetone or DMF, using tetramethylsilane (TMS) or $CFCl_3$ as internal reference for ^1H and ^{19}F NMR spectroscopies, respectively. The experimental conditions for recording ^1H (^{19}F) NMR spectra were as follows: flip angle 90° (30°); acquisition time 4.5 s (0.7 s); pulse delay 2 s (5 s); 64 (128) scans and pulse width of 5 μs for ^{19}F NMR.

(f) Assessment of the Glass Transition Temperature by Differential Scanning Calorimetry (DSC). DSC measurements were carried out on a Perkin-Elmer Pyris 1 DSC. The temperature was calibrated with ultrapure indium, octane, and dodecyloctane. The samples were heated from

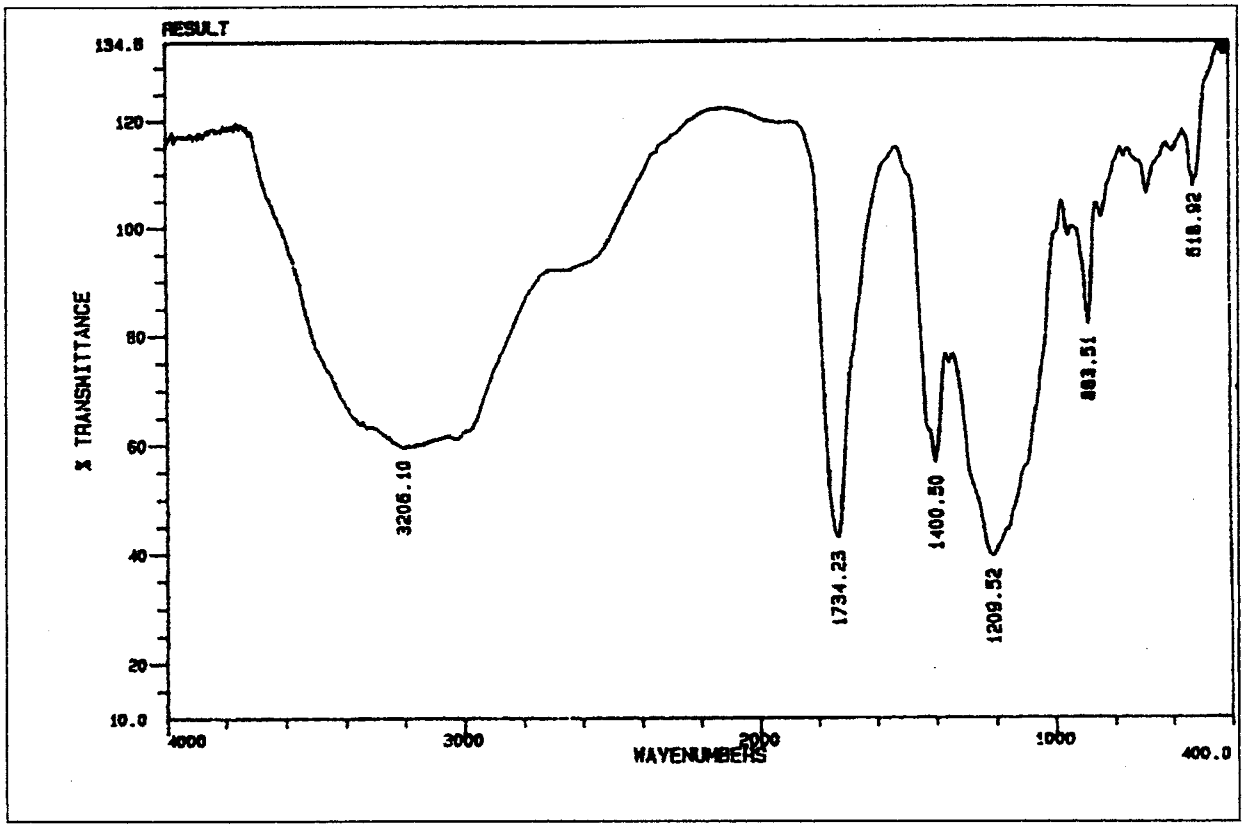


Figure 1. IR spectrum of a carboxyhydroxy telechelic copolymer containing VDF and HFP.

Table 2. Synthesis and Characterization of Fluorinated Telechelics Containing Vinylidene Fluoride (VDF) and Hexafluoropropylene (HFP) by Dead-End Copolymerization of These Fluoroalkenes Initiated by Hydrogen Peroxide. ($C_i = [H_2O_2]_i/[(VDF)_i + (HFP)_i]$)

init. HFP (mol %)	init. VDF (mol %)	solv	T (°C)	solv amt (g)	time (h)	F-olefins convn (%)	P_{max} (bar)	ΔP (bar)	C_i^{α} (%)	mass yield (%)	mol % VDF in copo.	mol % HFP in copo.	COOH before redcn (±0.15)	T_g (°C)	state	M_n	n	m	r
40.5	59.5	MeCN + F	110 113	260 100	8	30	35	11.0	8	11	42	58	1.90		liquid	1000	3	5	0
26.6	73.4	^{i}PrOH	90	160	8	37			10	24	52	48			liquid	780	3	3	1
27.2	72.8	AcOMe	110	450	8	38	35	7.8	27	18	45	55	1.90		liquid	900	3	4	1
47.0	53.0	MeCN	110	250	8	37	30	11.0	32	17	75	25	1.97	−41	oily	1500	13	4	2
29.1	70.9	MeCN	110	450	8	73	22	10.6	38	42	78	22	1.95	−56	oily	1000	8	2	2
31.0	69.0	MeCN	110	550	8	88	20	10.0	39	44	76	24	1.96	−45	oily	1000	9	2	1
30.6	69.4	MeCN	130	160	8	55	43	24.0	9	31	89	12	1.92		wax	3200	36	4	4
29.0	71.0	MeCN	130	550	8	80	30	13.5	24	38	82	18	1.90		wax	1700	16	3	3
29.2	70.8	MeCN	130	550	8	90	43	27.3	39	46	76	24	1.95	−55	oily	900	4	2	1
29.2	70.8	MeCN	110	550	8	85	140	54.4	33	44	73	27	1.97	−50	oily	1600	12	4	3
32.9	67.1	MeCN	110	450	8	80	43	10.3	33	37	71	29	1.95	−54	oily	1700	12	5	2
66.6	33.4	MeCN	110	450	8	90	48	15.5	36	39	50	50	1.94	−77	liquid	800	2	3	1
66.6	33.4	MeCN	110	450	5	50	50	15.0	36	23	50	50	1.85	−75	liquid	800	3	3	0
0	100	MeCN	110	550	8	25	31	14.3	31	10	100	0	1.90				25	0	0
100	0	MeCN	110	550	8	23	10	1.4	37	8	0	100	2.00				0	*a*	0

[a] *m* ranging between 1 and 2; *n*, *m*, and *r* refer to Scheme 5.

−110 to +100 °C at a rate of 20 °C/min. to record the curves. The temperature of the half-height of the corresponding heat capacity jump was defined as the T_g.

Results and Discussion

The synthesis of fluorinated telechelic copolymers was achieved by the radical copolymerization of vinylidene fluoride (VDF) and hexafluoropropene (HFP), initiated by hydrogen peroxide under the conditions of dead-end polymerization, as shown in Scheme 1.

In a first step, this reaction was optimized while in a second step the synthesis of telechelic fluorodiols was studied.

(I) Radical Copolymerization of VDF and HFP Initiated by H_2O_2. Several parameters of this reaction have been investigated to improve the yield of the telechelic copolymer: the polymerization process, the nature and the amount of the solvent used, the initial molar ratio, C_i, $[H_2O_2]_i/[\text{fluoroolefin}]_i$, the initial molar ratio $[VDF]_i/[HFP]_i$, the temperature, and the reaction time. The influence of these experimental parameters is discussed below.

(A) Polymerization in Emulsion. Two different kinds of polymerization processes have been studied: the emulsion and the solution polymerizations.

As seen in Table 1, various companies produce fluorinated elastomers containing VDF and HFP [Viton (E. I. du Pont de Nemours), Tecnoflon (Ausimont), Fluorel (3M-Dyneon), or Daiel (Daikin)]. Most reactions are performed in an emulsion process, involving potas-

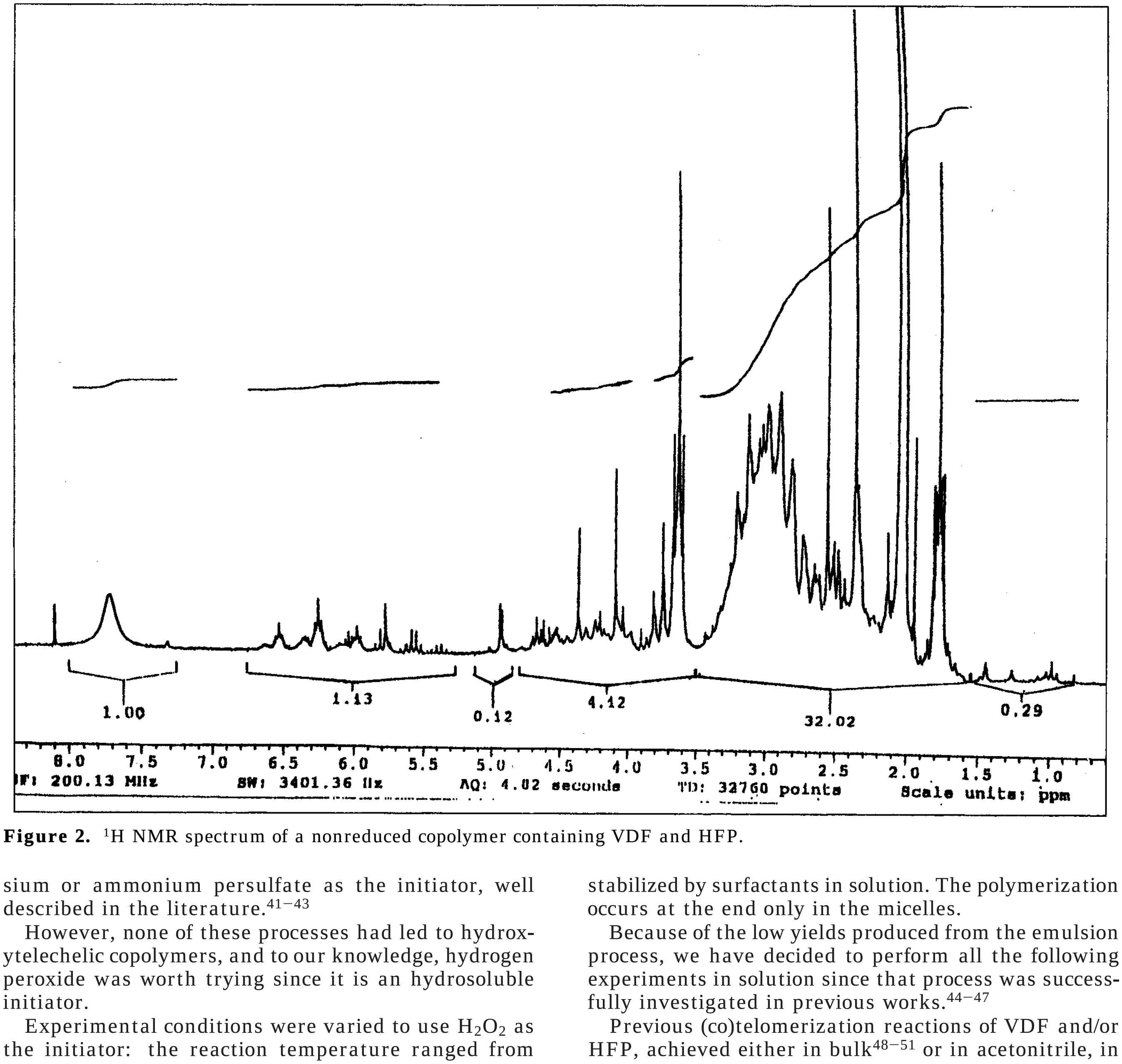


Figure 2. ^{1}H NMR spectrum of a nonreduced copolymer containing VDF and HFP.

sium or ammonium persulfate as the initiator, well described in the literature.[41−43]

However, none of these processes had led to hydroxytelechelic copolymers, and to our knowledge, hydrogen peroxide was worth trying since it is an hydrosoluble initiator.

Experimental conditions were varied to use H_2O_2 as the initiator: the reaction temperature ranged from room temperature to 90 °C, and the emulsifying agent was Forafac 1199 (an acrylamide telomer, $C_nF_{2n+1}[CH_2\text{-}CH(CONH_2)]_pX$, where $n = 6, 8, 10$, or 12, $p = 20{-}35$, and X stands for I or H, commercialized by Atofina). As the gaseous fluorinated monomers are poorly soluble in water, acetonitrile was used as the cosolvent since it is regarded as a good solvent for fluorinated monomers.

The emulsion polymerization led to a poor mass conversion rate (ca. 10%). The mass conversion rate was defined as the ratio of the weight of the gases that reacted in the polymerization to the total weight of the gases introduced in the autoclave. Even the use of hollow blades for the mechanical anchor of the autoclave did not allow an improvement in the yield of the reaction.

Several hypotheses could be proposed to explain this phenomenon: hydrogen peroxide is soluble in water and fluorinated monomers are soluble in acetonitrile.

If we consider a system of emulsion polymerization, the polymerization proceeds in the solvent: a monomer reacts with a free radical, and then the propagation leads to a small amount of polymeric chain that is stabilized by surfactants in solution. The polymerization occurs at the end only in the micelles.

Because of the low yields produced from the emulsion process, we have decided to perform all the following experiments in solution since that process was successfully investigated in previous works.[44−47]

Previous (co)telomerization reactions of VDF and/or HFP, achieved either in bulk[48−51] or in acetonitrile, in 1,1,2-trifluorotrichloroethane (F-113), or in methyl acetate as the solvents,[52,53] led us to use such a solvent in the copolymerization. Interestingly, according to Russo,[54] these solvents are rather inert and do not act as transfer agents.

(B) Polymerization in Solution. The results of these experiments have been gathered in Table 2. The first part below concerns the influence of various experimental parameters while the second part reports the characterization of the products. The structure of the fluoroelastomer is given by the assessment of n, m, and r values given in Table 2 that refers to Scheme 5.

(B-1) Influence of Experimental Parameters onto the Conversion of Fluoroolefins. (a) Influence of the Nature of the Solvent and Its Amount. First, the mixture F-113/acetonitrile in 28/72 molar ratio was used. Although the gas mass conversion rate of the gaseous monomers was slightly improved, compared to that obtained from the emulsion process, it was however still low (30%).

Methyl acetate was then used, leading to few improvements (38%).

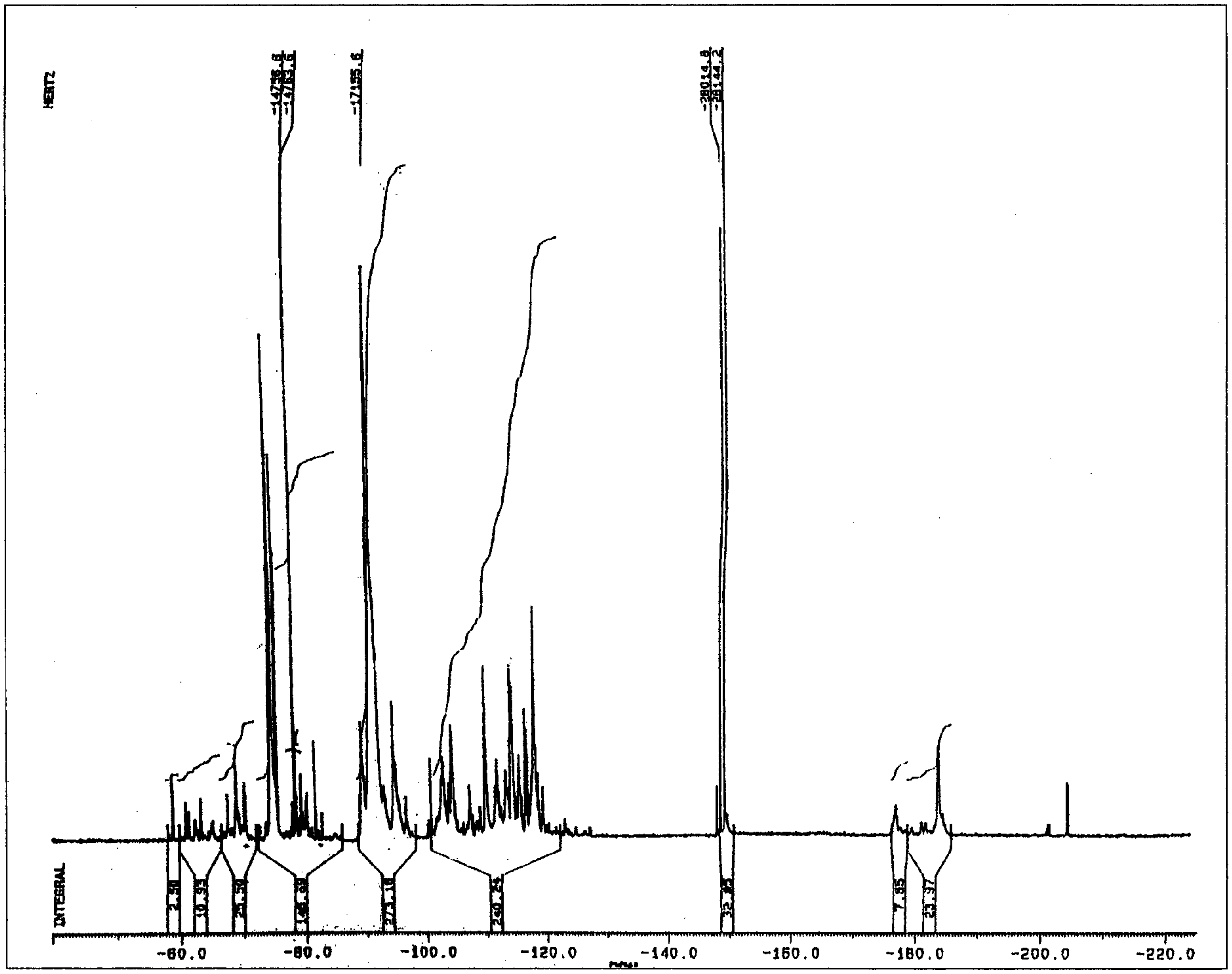


Figure 3. ^{19}F NMR spectrum of a nonreduced copolymer containing VDF and HFP.

As a matter of fact, the best results were obtained in the presence of acetonitrile without any cosolvent. The conversion rate varied from 35 to 90% (Table 2). These variations of yields could be linked to the amount of solvent introduced into the autoclave.

Indeed, this parameter influences the pressure of gaseous monomers: it can be assumed that the higher the quantity of introduced solvent in the autoclave, the lower the free volume left to gaseous reactants and hence the higher the pressure in the autoclave. This leads to an improved rate of solubilization of gaseous monomers. This phenomenon was observed by comparison between the influence of the amount of solvent on the reaction conversion rate: the former varied between 250 and 500 g of acetonitrile leading to 35% to almost quantitative conversion rate, respectively, for similar conditions carried out in a 1-L autoclave (Table 2).

Beside this parameter that plays a crucial role in the copolymerization reaction, the influence of the reactant initial molar ratio was also studied.

(b) Influence of the Reactant Molar Ratio. The initial $[H_2O_2]_i$/[sum of concentrations of $[\text{fluoroalkenes}]_i$] molar ratio, C_i, was considered to investigate the influence of C_i onto the average degree of polymerization $\overline{DP_n}$ of the product. Therefore, the dead-end polymerization of monomers requires to be carried out with an elevated C_i value: the higher the C_i value, the higher the conversion rate and the lower the $\overline{M_n}$ value.

(c) Influence of the Temperature. It is known that the temperature has a drastic effect in the initiation step of the reaction, but it also has an influence on the liquid or gaseous state of the solvent during the reaction and above all on the pressure in the autoclave.

From several studies involving the dead-end polymerization of butadiene initiated by hydrogen peroxide,[55] we have been able to establish that the thermal initiation by H_2O_2 starts from 80 °C and is suitable for polymerization reactions with a temperature close to 90 °C, although no half-lives of that initiator were determinated at these different temperatures.

The comparison of the results obtained at various reaction temperatures (90, 110, and 130 °C) shows that the copolymerizations are required to be performed between 110 and 130 °C to yield a satisfactory conversion rate (Table 2). In this temperature range, the conversion rate was high, and experimentally this was evidenced by a sharp decrease of the pressure when the reaction proceeded.

(d) Influence of the Reaction Time. Most experiments were carried out with a reaction time ranging from the stop of the pressure decrease to 8 h after the decrease, to reach a maximal conversion rate. It ap-

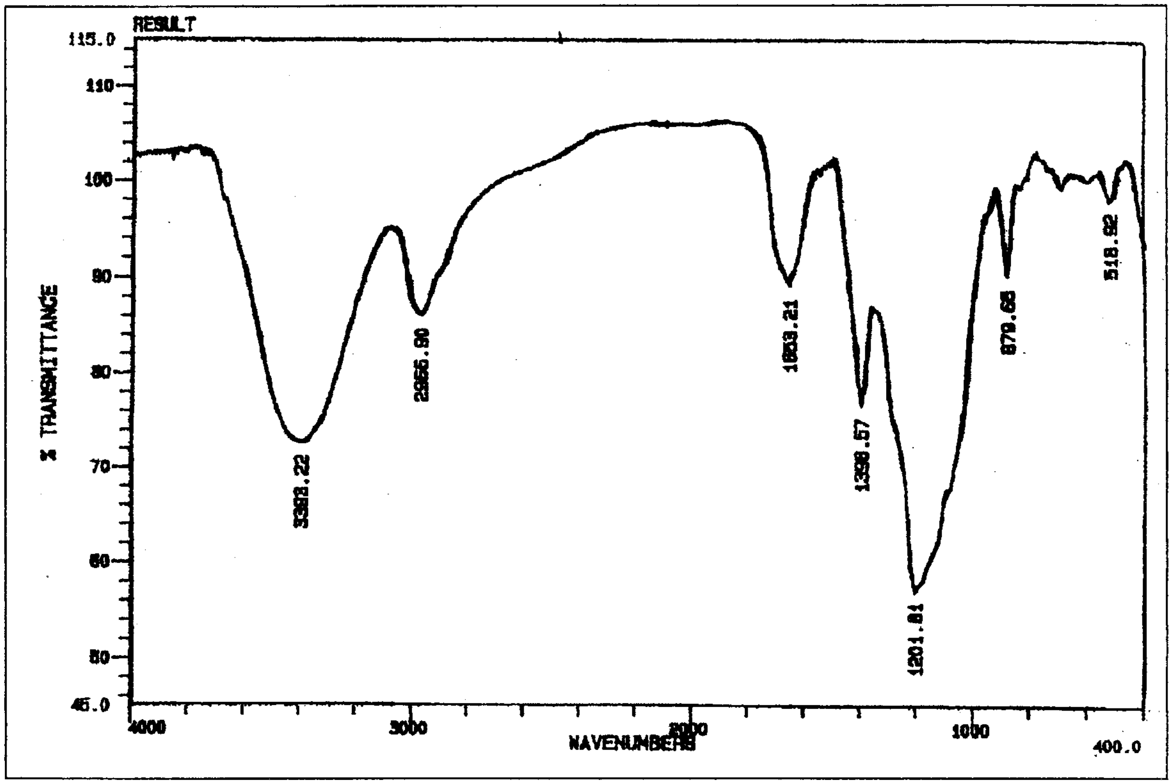
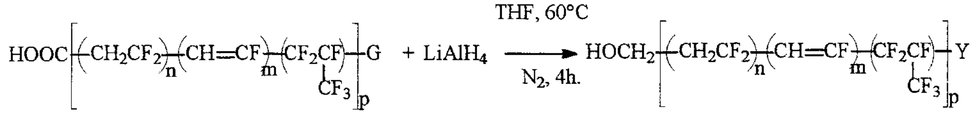


Figure 4. IR spectrum of a hydroxytelechelic copolymer containing VDF and HFP.

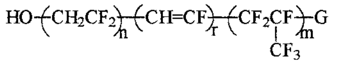
Scheme 4. Reduction of Carboxylic Functions of Copolymers Containing VDF and HFP Using $LiAlH_4$



$$HOOC\left[(CH_2CF_2)_n(CH{=}CF)_m(CF_2\underset{CF_3}{CF})\right]_p G + LiAlH_4 \xrightarrow[N_2,\ 4h.]{THF,\ 60°C} HOCH_2\left[(CH_2CF_2)_n(CH{=}CF)_m(CF_2\underset{CF_3}{CF})\right]_p Y$$

where G represents hydroxyl, hydroxymethyl or carboxylic function and Y represents hydroxyl or hydroxymethyl function.

Scheme 5. General Formula of Hydroxytelechelic Copolymers Containing VDF and HFP



$$HO(CH_2CF_2)_n(CH{=}CF)_r(CF_2\underset{CF_3}{CF})_m G$$

where G represents hydroxyl or hydroxymethyl function.

peared that the product aspect evolves then from a colorless to a brown compound. It was noticed that the proportion on each fluoroolefin unit has an important effect on the nature of the products.

(B-2) Characterization of the Products. Several methods were used to characterize the microstructure, the functionality, and the molecular weights of these fluorinated oligomers by means of IR, ^1H NMR, and ^{19}F NMR spectroscopies, size exclusion chromatography, and titration of carboxyl functions, and finally, their thermal properties were assessed.

(a) IR Spectroscopy. The oligomers produced from that reaction were characterized by IR spectroscopy. The IR spectra (Figure 1) show various absorption bands assigned to characteristic fluorinated groups containing C−F bond: 1400, 1200, and 1100 cm^{-1}. The large band of OH vibrations in carboxylic functions was noted at $\nu_{COOH} = 3400\ cm^{-1}$. The presence of carboxylic functions was confirmed by an absorption band at 1730 cm^{-1}, characteristic of the carbonyl frequency. The products contain fluorinated bonds and carboxylic functions. However, at 1670 cm^{-1} was noted a sharp band assigned to −CH=CF− bonds. In addition, the bands characteristic of hydroxyl groups (ν_{OH} = 3300 and 2960 cm^{-1}) were also observed in the IR spectra.

(b) Size Exclusion Chromatography. The synthesis of fluorinated standards has never been described in the literature, and no commercially available products can be used to perform size exclusion chromatography with fluorinated products. Previous works performed in our laboratory led to possible fluorostandards produced by telomerization of VDF[48,49] or HFP[50,51,56] or by cotelomerizations of VDF and HFP[57] in the presence of $C_nF_{2n+1}I$ (n = 4, 6, 8) or $IC_pF_{2p}I$ (p = 2, 4, 6). Hence, a wide range (from 430 to 2500) of highly fluorinated telomers were obtained, and they have been used as standards for calibration of size exclusion chromatography $C_nF_{2n+1}[(VDF)_m(HFP)]_pX$ and $X[(VDF)_q(HFP)]_r$-$C_pF_{2p}[(VDF)_s(HFP)]_tX$ where n = 4, 6, and 8,[48] m, q, and s = 1−8, p = 2, 4, and 6, r and t =1−10, and X = H or I. This calibration has been correlated with the retention times of polystyrene standards to allow one correct extrapolation for products having molecular weights ranging between 2000 and 6000. Starting from C_i of 24, 35, 40, and 46%, $\overline{M_n}$ of the products were about 830, 700, 500, and 380, respectively. As expected, the lower the initial H_2O_2 concentration, the higher the average $\overline{M_n}$. However, these measurements were not quite accurate because of the lack of standards for VDF/HFP copolymers.

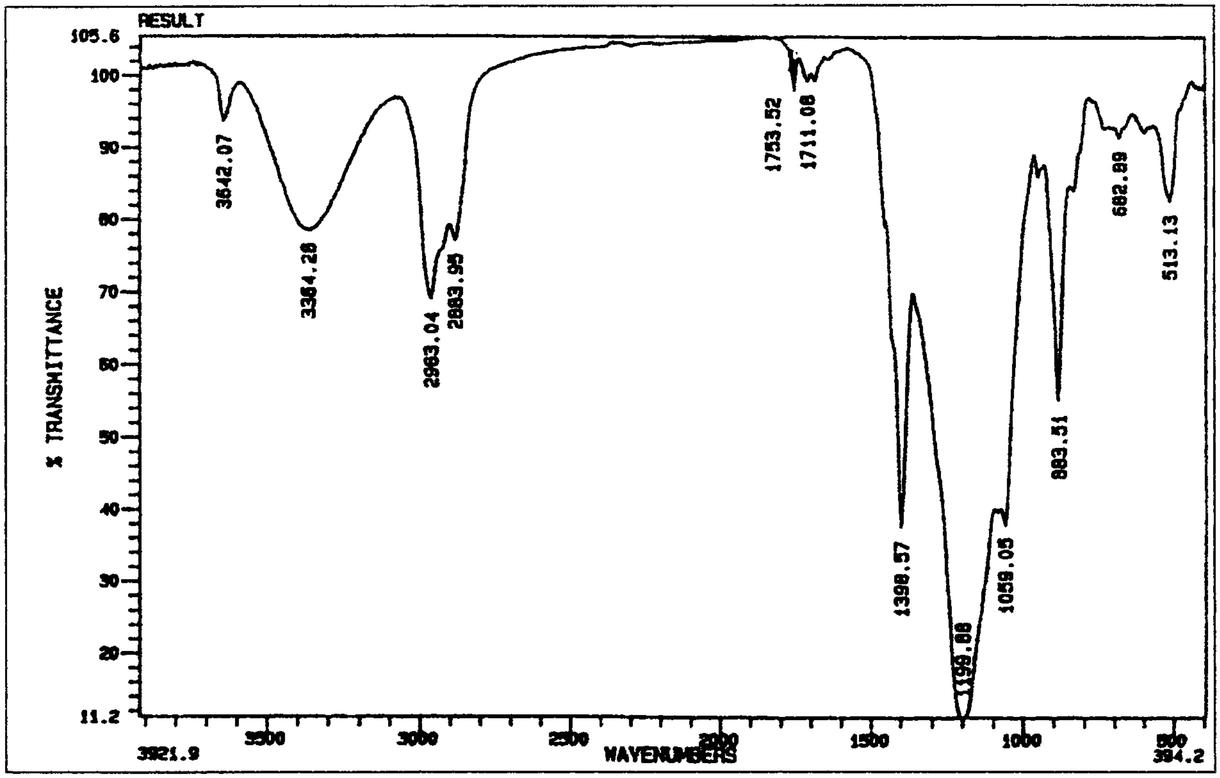


Figure 5. IR spectrum of a hydroxytelechelic copolymer containing VDF and HFP without any CF=CH bond.

c) Assessments of the microstructure by NMR spectroscopy. Both ^{1}H and ^{19}F NMR spectroscopies (Figures 2 and 3) enabled us to characterize the microstructure of these amorphous copolymers.

To increase the pertinence of analyses, we first studied the spectra of the polymers prepared by the homopolymerizations of VDF and HFP. In the former homopolymerization, the ^{1}H NMR spectrum shows the following peaks:

•First, a triplet at 3.7 ppm, assigned to the methylene group of $CH_2-CF_2-C\mathbf{H_2}-OH$ ($^3J_{H-F}$ = 13.0 Hz) is observed. This attribution was confirmed by adding a drop of CCl_3NCO in the NMR tube and it was noted a low field shift[58] of the signal to 4.5 ppm.

•Second, a multiplet between 2.8 and 3.0 ppm, corresponding to $C\mathbf{H_2}$ of the $(C\mathbf{H_2}-CF_2)$ units, which are characteristic of the normal head-to-tail addition of VDF units in the poly(vinylidene fluoride) blocks is observed. The tail-to-tail reversed adducts $-CF_2-C\mathbf{H_2}-C\mathbf{H_2}-CF_2-$ were identified by a multiplet centered at 2.5 ppm. The normal sequence/reverse sequence ratio was estimated at about 95%, as observed in commercially available PVDF.

•Finally, a low intensity triplet ($^2J_{H-F}$ = 54.8 Hz) of triplets ($^3J_{H-H}$ = 6.6 Hz) centered at 6.4 ppm, assigned to $-CH_2-CF_2-\mathbf{H}$, coming from transfer reactions (Scheme 2), was observed.

The ^{19}F NMR spectrum of the telechelic PVDF shows the presence of characteristic head-to-tail signals $(CH_2-C\mathbf{F_2})_n$ ("normal" additions in the VDF blocks) at −92 ppm, and that of several expected signals ranging between −113 and −116 ppm assigned to the "reversed" head-to-head additions. The main feature of this spectrum comes from the signal at −108 ppm assigned to $-C\mathbf{F_2}-CH_2-OH$. The presence of CF_2 group adjacent to carboxylic acid groups appears on the spectrum as a signal centered at −150 ppm.[59]

The ^{1}H NMR spectrum of the product obtained from the "oligomerization" of HFP in the presence of H_2O_2 shows a complex system centered on 5.5 ppm assigned to $CF(CF_3)\mathbf{H}$. This system corresponds to the coupling of the transferred proton with the gemined fluorine ($^3J_{H-F}$ = 48 Hz) and then doubled by the fluorine in β position and quartered by the lateral CF_3 group of the HFP unit.

The ^{1}H NMR spectra of the copolymers show the following spectral features:

•A multiplet ranging between 2.4 and 3.6 ppm assigned to $-C\mathbf{H_2}-COOH$.

•The signals between 3.6 and 4.7 ppm corresponding to $C\mathbf{H_2}-OH$.

•The complex systems between 5.5 and 6.5 ppm attributed to transfer on the polymer, assigned to $-CH_2-CF_2-\mathbf{H}$ and $-CF(CF_3)\mathbf{H}$, where this proton transfer may arise from the eventual proton radical coming from the decomposition of H_2O_2 (in a minor way, Scheme 2).

•A broad peak between 9 and 15 ppm attributed to $COO\mathbf{H}$.

Its ^{19}F NMR spectroscopy exhibits some signals between −73 and −80 ppm corresponding to $C\mathbf{F_3}$ from head-to-tail, head-to-head, and tail-to-tail additions. A signal centered at −210 ppm is assigned to $CF_3-C\mathbf{F}H$ coming from the transfer to polymer and close to −100 ppm: $-CF(C\mathbf{F_3})H$. The presence of the CF_2 groups adjacent to the acid end group is evidenced by the signal at −150 ppm.

Five neat zones of signals can be noted in the ^{19}F NMR VDF/HFP copolymers spectra:

Zone 1, ranging from −70 to −80 ppm, corresponds to $C\mathbf{F_3}$ side groups of HFP base units.

In Zone 2, the signals ranging in the −88 to −95 ppm area concern $-CH_2C\mathbf{F_2}-CH_2C\mathbf{F_2}-$ sequences assigned to "normal" additions of VDF units.

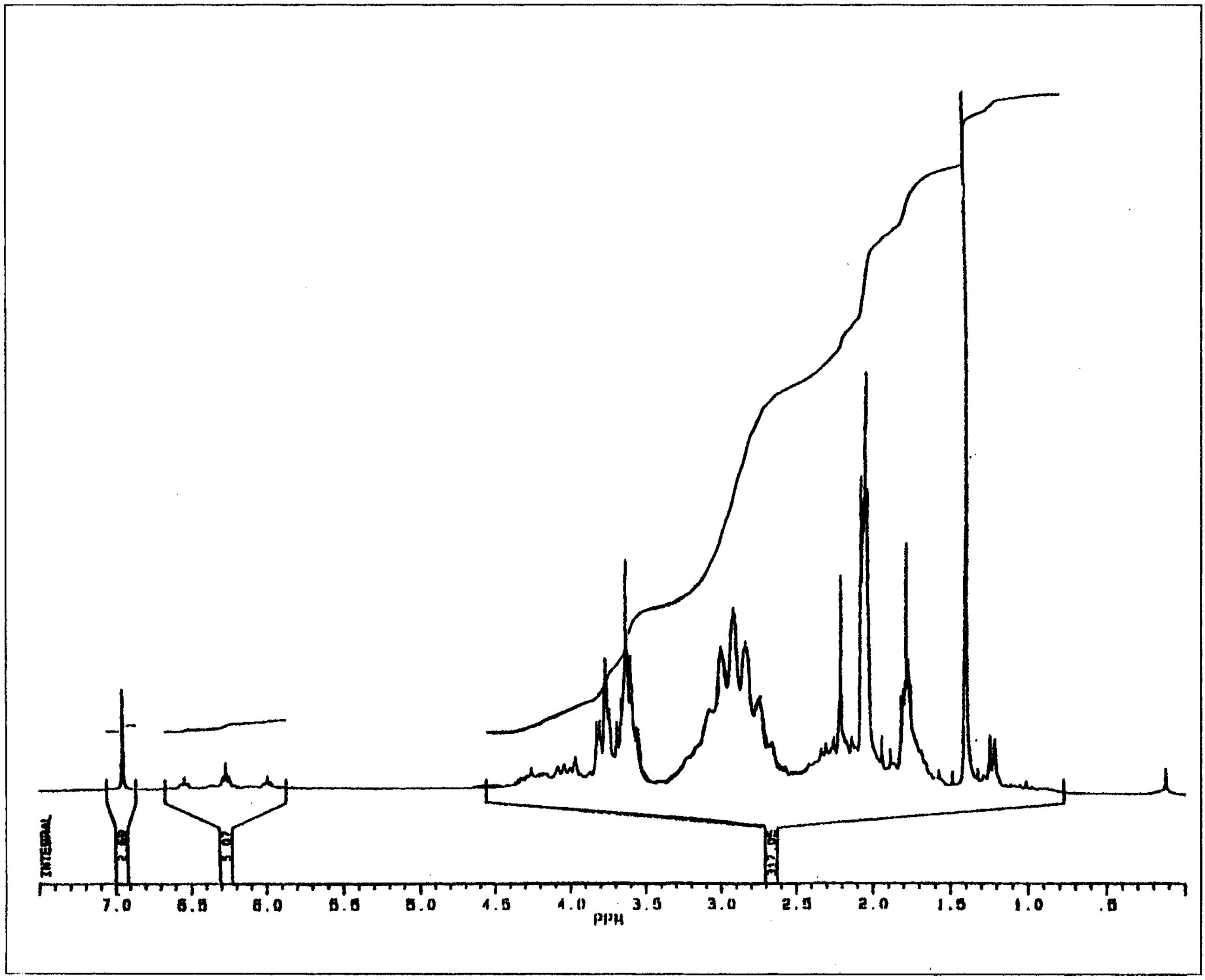


Figure 6. ^{1}H NMR spectrum of a hydroxytelechelic copolymer containing VDF and HFP.

Zone 3 indicates a peak centered at −110 ppm attributed to the difluoroethylene group in the $CH_2\mathbf{CF_2}{-}CF_2CF(CF_3){-}$ sequence from the additions of growing chains $-VDF^{\bullet}$ onto HFP units.

The fourth zone of peaks centered between −113 and −116 ppm corresponds to the $-CH_2\mathbf{CF_2}{-}\mathbf{CF_2}CH_2{-}$ sequence arising from the head-to-head additions of VDF units.

Finally, in zone 5, ranging between −179 and −185 ppm, the signals are assigned to "tertiary" fluorine (i.e., $C\mathbf{F}(CF_3)CF_2$ of HFP), and the peak centered at −210 ppm corresponds to $C\mathbf{F}{-}H$ group owing to the transfer of a proton on the macroradical terminated by a HFP unit.

Some signals ranging from −120 to −130 ppm are detected in the ^{19}F spectrum, showing the presence of $CF{=}CH$ bonds. These signals will be assessed further in this study.

Hence, the molar percentages of VDF in the copolymers can be assessed from the following equation:

$$\text{mol. \% of VDF} = \frac{[I_{-92} + I_{-95} + I_{-110} + I_{-113} + I_{-116}]/2}{[I_{-92} + I_{-95} + I_{-110} + I_{-113} + I_{-116}]/2 + [I_{-70\text{ to }-80}]/3}$$

where I_{-n} represents the integral of the signal centered at $-n$ ppm noted on the ^{19}F NMR spectrum. Table 2 indicates these molar percentages, and as expected, it is noted that in all cases, the molar percentage of VDF in the copolymer is higher than that in the feed. This shows that the copolymerization of VDF with HFP is not modified in the presence of H_2O_2 or $HO^{\bullet}$ radicals.

(d) Titration of Carboxyl End Groups. As mentioned above, the radical copolymerization of VDF and HFP initiated by hydrogen peroxide led to fluoroelastomers bearing carbonyl functions. The titration of carboxyl end group in the telechelic VDF/HFP elastomers was performed in the presence of potassium hydroxide with phenolphthalein as color indicator. The results were gathered in Table 2. The carboxyl functionality was assessed to 1.85 ± 0.15. This means that the addition of hydroxyl free radical occurs mainly onto the fluorinated carbon atoms, leading to acid fluoride intermediates that were chemically changed into carboxylic acid functions.

(e) Assessment of Thermal Properties by the Determination of the Glass Transition Temperature. Differential scanning calorimetry (DSC) was used to determine the glass transition temperature, and the results are listed in Table 2. Except the oligomers produced from the homopolymerization of VDF in the presence of H_2O_2 (they were semicrystalline), the copolymers were amorphous and their T_g ranged between

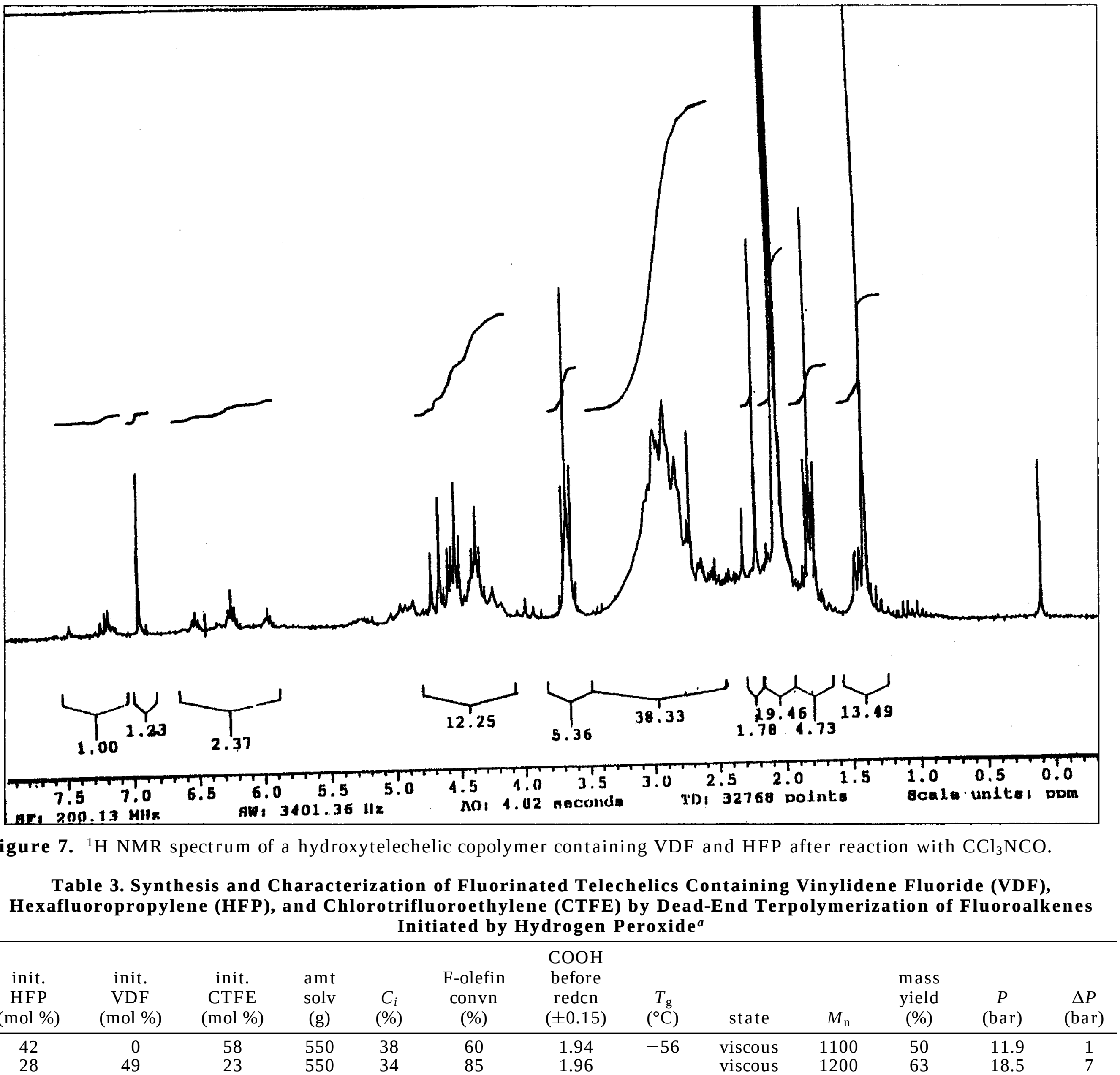


Figure 7. ^{1}H NMR spectrum of a hydroxytelechelic copolymer containing VDF and HFP after reaction with CCl_3NCO.

Table 3. Synthesis and Characterization of Fluorinated Telechelics Containing Vinylidene Fluoride (VDF), Hexafluoropropylene (HFP), and Chlorotrifluoroethylene (CTFE) by Dead-End Terpolymerization of Fluoroalkenes Initiated by Hydrogen Peroxide[a]

init. HFP (mol %)	init. VDF (mol %)	init. CTFE (mol %)	amt solv (g)	C_i (%)	F-olefin convn (%)	COOH before redcn (±0.15)	T_g (°C)	state	M_n	mass yield (%)	P (bar)	ΔP (bar)
42	0	58	550	38	60	1.94	−56	viscous	1100	50	11.9	1
28	49	23	550	34	85	1.96		viscous	1200	63	18.5	7
28	44	28	570	41	78	1.97	−64	viscous	980	67	18.9	6
31	30	39	590	35	90	1.94	−64	viscous	1200	84	109	90

[a] All reactions have been performed with acetonitrile as solvent at 110 °C for 8 h.

−77 and −41 °C. Besides, as reported in the literature,[42] it is known that fluoroelastomers containing VDF and HFP base units only, exhibit T_g higher than −26 °C. As a consequence, these low T_g clearly evidence low molecular weight copolymers. This statement is in good agreement with the above results of average molecular weights of those fluoroelastomers assessed by SEC. Although these values are higher than those of perfluoropolyethers,[60] they are relevant competitors of fluorosilicones for which the T_g are not lower than −65 °C.[61]

(B-3) Interpretation of These Results. The study of these results shows some more information about our products. The NMR and the IR spectroscopies prove that the copolymers are fluorinated compounds containing VDF and HFP units. Before reduction, all characterization methods display the main presence of carbonyl end groups and a few hydroxyl end groups. These remarks can be explained by the radical mechanism of the reaction, as shown in Scheme 2.

As known, the decomposition of hydrogen peroxide mainly produces $OH^\bullet$ radicals.[38,39] Their electrophilicity should make them reactive onto the CH_2 site of VDF (since the CF_2 site group is quite electrophilic). In addition, it is noted that the copolymerization of VDF and HFP led to higher yields than those obtained in the cases of the homopolymerizations of both fluoroolefins. This confirms previous works on the (co)telomerization of HFP and/or VDF with methanol that displays good yields when HFP was used, but medium yields only were noted from the telomerization of VDF.[53] That shows that HFP reacts more easily with hydroxymethyl radicals than VDF does. Such behaviors can be explained by the high reactivity of hydroxyl radicals with the electrophilic HFP.

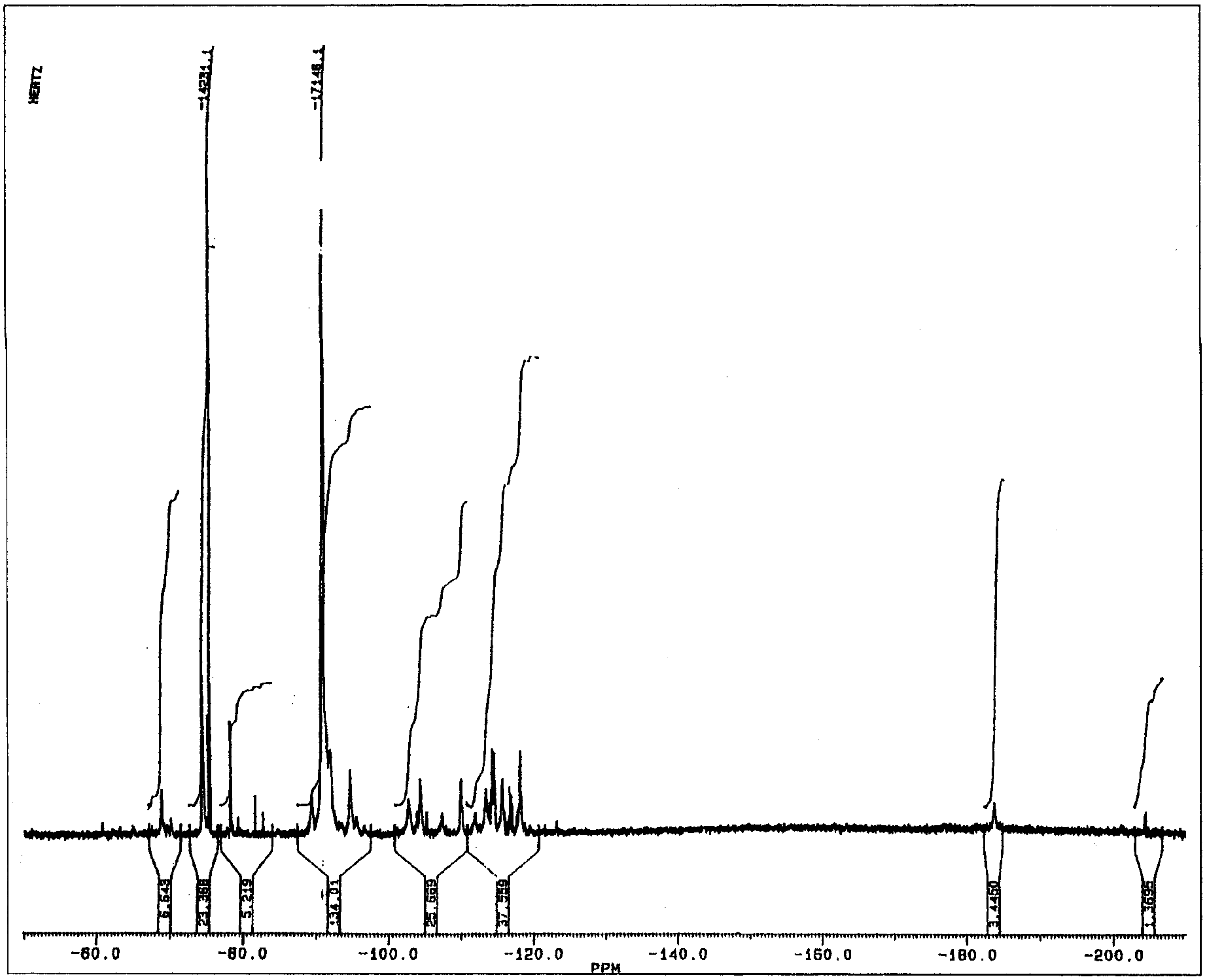


Figure 8. ^{19}F NMR spectrum of a hydroxytelechelic copolymer containing VDF and HFP.

The presence of an inner unsaturation was revealed by IR spectroscopy (absorption at 1660 cm^{-1} assigned to the vibration of the CH=CF bond) and allowed us to suggest the formula described in Scheme 3, where the copolymer has a random structure. The unsaturation should induce a colored product.[62]

The explanation of the presence of CH=CF bonds in the copolymer comes from the reaction conditions: it appears that the longer the reaction time, the higher the intensity of CH=CF bonds, and this is increased for higher temperatures. The reaction lasting only 5 h did not give any colored products and interestingly, the IR spectrum of the reduced elastomer did not show any absorption at 1660 cm^{-1}. This is in good agreement with the observations reported by Schmiegel and Logothetis[62] who showed that under tough conditions, $CF_2CF(CF_3)-CH_2CF_2-$ sequence can undergo an HF elimination leading to a $CF_2C(CF_3)=CHCF_2-$ group. This unsaturated group can be detected in the ^{19}F spectrum of the cooligomer ranging between −120 and −130 ppm. This double bond was responsible of a coloration of the products. In addition, when the molar percentages of VDF and HFP base units incorporated into the copolymer were the same (i.e., 50 mol %), it can be concluded that the copolymer exhibits an alternated structure. Indeed, this was confirmed by the absence of the signal centered at −91 ppm usually assigned to the VDF unit in the PVDF block adjacent to HFP unit. This is in good agreement with Pianca et al.[63] or with a recent work[45] who showed that HFP does not propagate in the VDF/HFP copolymer[64] and that confirms Schmiegel's investigation[65] who did not observe two consecutive HFP units in VDF/HFP copolymers. This last study confirms the chemical shifts of the CF=CH group.

(B-4) Reduction of Acid VDF/HFP Copolymers into Fluorotelechelic Diols. Several ways are known to allow the reduction of carboxylic groups into hydroxyl functions. We have chosen reduction in the presence of $LiAlH_4$, which is used as described in Scheme 4.

This reaction occurred at 70 °C for 2 h in the presence of a four-time molar excess of $LiAlH_4$ about the VDF/HFP copolymer. After reaction and treatment, telechelic diols were obtained in 95% yield. The loss of product can be explained by the difficult separation of the product and the hydrolysis residues of $LiAlH_4$.

(a) Characterization of Macrodiols by IR Spectroscopy. After the reduction of the carboxylic functions, IR spectra indicate the absence of the bands at 1730 cm^{-1}, characteristic of the carbonyl frequency, showing that the reduction of the carboxylic end groups was complete (Figure 4). The other absorption bands were not modified by the reduction of carboxylic end group except the bands at 3500 cm^{-1}, which are characteristic of the presence of hydroxyl function

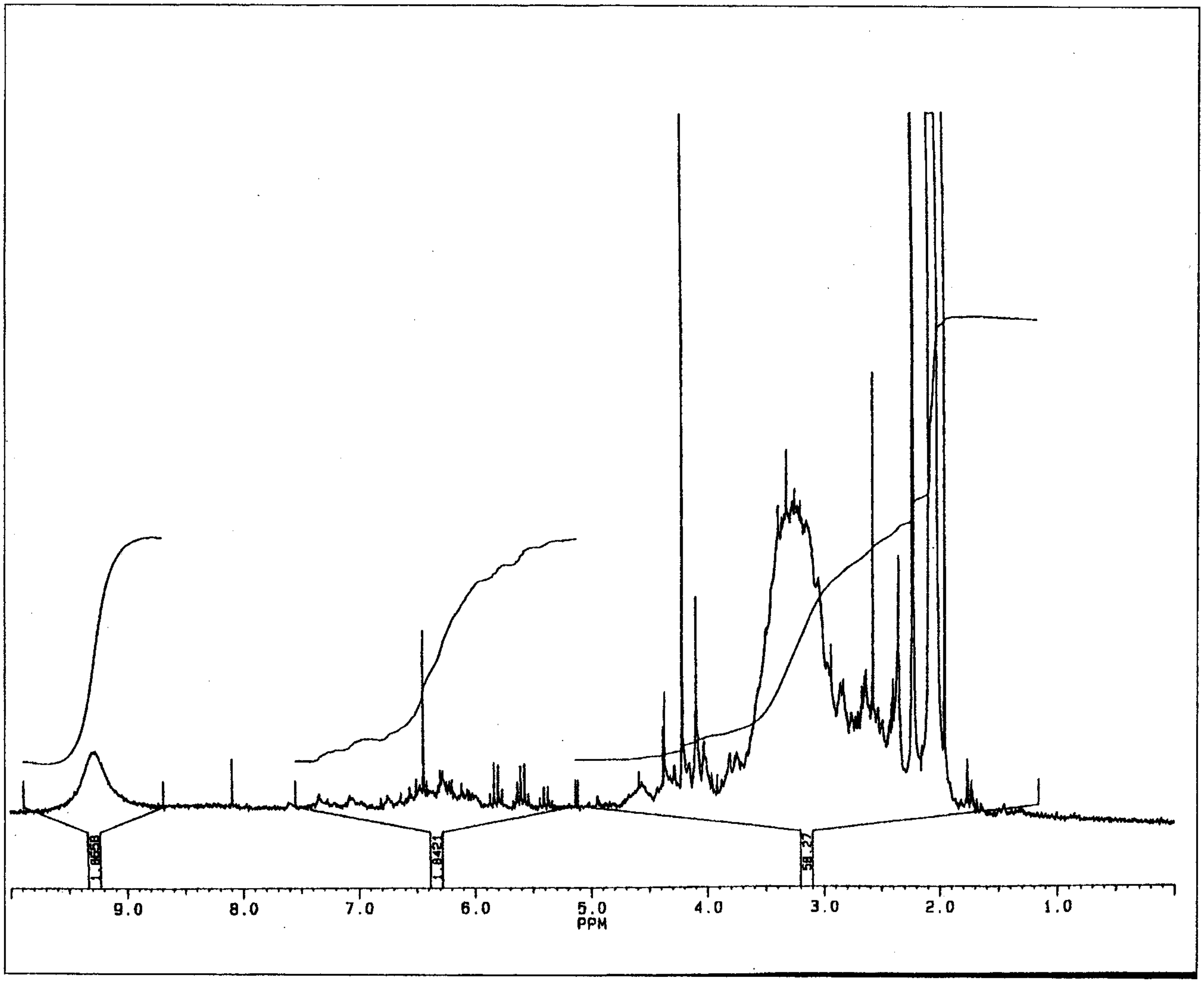


Figure 9. ^{1}H NMR spectrum of a carboxyhydroxy telechelic copolymer containing VDF, HFP, and CTFE.

vibration. However, after this quantitative reduction evidenced by means of IR spectroscopy, it appears that the amount of CH═CF was higher.[66]

The IR spectrum of the reduced noncolored product (Figure 5), which was not supposed to contain CF═CH functions, did not exhibit any absorption bands at 1660 cm^{-1}. This result confirms that using softer reaction conditions led to a product, which has not undergone dehydrofluorination reaction.

(b) Characterization of Telechelic Fluoroelastomeric Diols by NMR Spectroscopy. The ^{1}H NMR spectra of the reduced copolymers exhibit on one hand the absences of the broad peak ranging between 9 and 15 ppm and of the multiplet between 2.4 and 2.6 ppm, assigned to $CO_2\mathbf{H}$ and to $-C\mathbf{H}_2-COOH$, respectively (Figure 6). On the other hand, they also show the presence of a signal centered at 3.6 ppm attributed to $CH_2C\mathbf{H}_2OH$. The addition of CCl_3NCO to the product shows the low fields shift from 3.6 ($CH_2C\mathbf{H}_2OH$) and 4.7 ppm ($CF_2C\mathbf{H}_2OH$) to 4.2 and 4.9 ppm (Figure 7), as an expected behavior characteristic of protons adjacent to a hydroxyl group.[58]

In addition, the ^{19}F NMR spectra of these fluoromacrodiols (Figure 8) display the absence of the peak centered at −150 ppm, assigned to $-C\mathbf{F}_2COOH$. The complete consumption of this peak confirms the quantitative reduction of these functions. The molar percentages of VDF in the diols were similar to those of the nonreduced precursors even for low molecular weight oligomers, as evidenced by the characteristic chemical shifts (and their integrals) assigned to expected polyfluorinated groups.

(c) Other Analyses. The size exclusion chromatography shows that the average molecular weights in number of the copolymers are not modified by that reduction. They ranged from 800 to 3200.

After reduction of the products, the carboxyl end group contents were lower than 3×10^{-5} mol g^{-1} confirming the good reactivity of these functions. The titration of hydroxyl end groups was carried out by using acetylation method. The titration showed the complete reduction of carboxylic end groups since the hydroxyl functionality ranges between 1.98 and 2.00.

These hydroxyl fluorinated products present the general structure displayed in Scheme 5. Differential scanning calorimetry showed that the reduction of carboxylic end groups did not produce any drastic modifications on the T_g values of the copolymers: the T_g only decreases of 1 or 2 °C.

(II) Terpolymerization of VDF with HFP and CTFE Initiated by H_2O_2. The same investigations were performed for the radical terpolymerization of vinylidene fluoride, hexafluoropropene and chlorotrifluoroethylene initiated by hydrogen peroxide. The

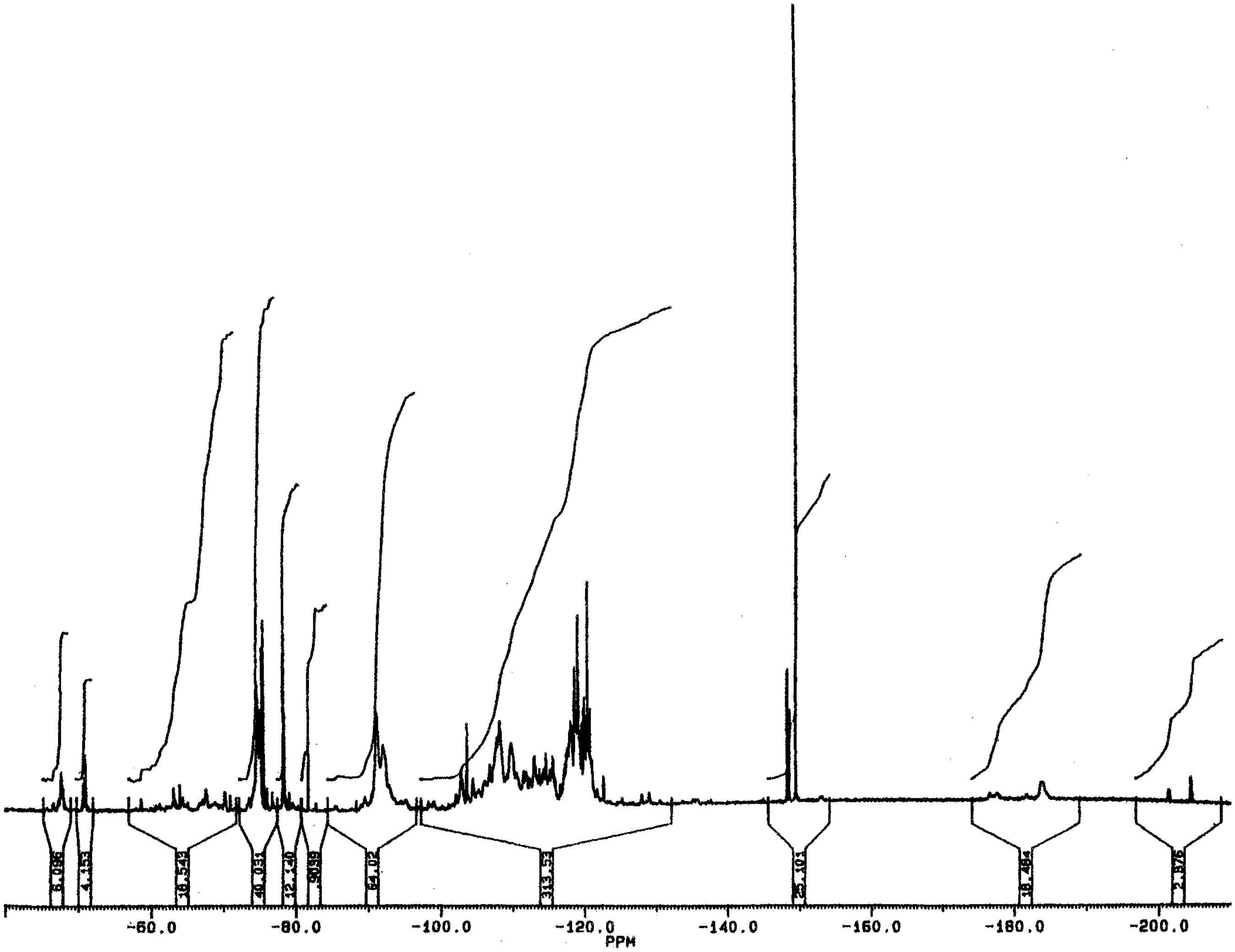


Figure 10. ^{19}F NMR spectrum of a carboxyhydroxy telechelic copolymer containing VDF, HFP, and CTFE.

polymerization process, the amount of solvent and the ratio of fluoroolefins were varied to achieve the best yields (Table 3).

It appears that as for the radical copolymerization of VDF/HFP initiated by H_2O_2, the emulsion process cannot lead to an interesting monomer conversion estimated under 5% about initial fluoroolefins. The reaction was realized at 90 °C for 8 h. The total amount of water and cosolvent (acetonitrile) was about 635 g and the total gas introduced represented 117 g, with 53 mol % of VDF, 25 mol % of HFP, and 22 mol % of CTFE initiated by a C_i of 31%.

As a matter of fact, other experiments were carried out in solution with acetonitrile as the solvent and the reaction conditions are gathered in Table 3. Interestingly, the presence of CTFE enables the alkene conversions and the yield of the terpolymerization to be higher than those arising from the copolymerization.

As in previous cases, the IR spectra show the presence of carboxyl end groups, and traces of dehydrofluorinated product. The other absorption bands of the IR spectra were not significant enough of the presence of CTFE: the absorption bands were similar to those observed in the IR spectra of the copolymers.

The ^1H NMR spectra (Figure 9) did not show any difference when compared with those of copolymers while the ^{19}F NMR spectroscopy shows the insertion of CTFE, VDF and HFP base units in the copolymers (Figure 10).

The titration of carbonyl end groups led to a general carboxylic functionality of about 1.85 ± 0.15. SEC analysis shows that for a C_i of 35%, the molecular weight of the terpolymer was about 800.

After reduction, the IR analysis showed the same modifications that those noted after the reduction of copolymers: the complete reduction is proved by the absence of the bands at 1730 cm^{-1}.

The glass transition temperatures of those products were about −64 °C. Those products were much viscous than the copolymers described above.

Conclusions

It has been shown that hydrogen peroxide is an efficient initiator that enables to react onto fluoroalkenes different from TFE. While the generated $OH^\bullet$ radicals react onto CH_2 group of VDF, they might also react toward CF_2 leading to a carboxylic acid end group. The parameters of dead-end polymerization have been studied and the best conditions were the amount of acetonitrile ranging between 45 and 55% of the total volume of the autoclave, an initial $[H_2O_2]_i/([VDF]_i + [HFP]_i)$ molar ratio ranging between 10 and 50% and a reaction performed at 110 °C for 5 h, leading to 90% conversion rate of fluoroalkenes. Interestingly, it was shown that the presence of H_2O_2 and hence $HO^\bullet$ radicals does not modify the reactivity of both alkenes, showing that VDF incorporates better the copolymer than HFP does. Although fluorinated cotelomers were used as standards for these telechelic fluoroelastomers, indicating that average molecular weights were ranging between 800 and 3200, the assessment of true average molecular weights still requires further investigations. The reduction of carboxylic acid into hydroxyl end groups was achieved in the presence of an excess of $LiAlH_4$ leading to good yields of telechelic diol fluoroelastomers. Interestingly, low glass transition temperatures (ranging between −77 and −41 °C) were achieved. These amorphous products are useful monomers and intermediates for polycondensation or polyaddition, under investigation.

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