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# Synthesis and copolymerisation of fluorinated monomers bearing a reactive lateral group. Part 21<sup>\*</sup>. Radical copolymerisation of vinylidene fluoride with 2-hydroperfluorooct-1-ene<sup>†</sup>.

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## ABSTRACT

The synthesis and the radical copolymerisation of 2-hydroperfluorooct-1-ene (HPO) with vinylidene fluoride (VDF), initiated by *tertio*-butyl peroxyvalate (TBPPI) at 75°C are presented. That fluorinated alkene (HPO) was synthesised in two steps starting from the thermal or redox telomerisation of VDF with C<sub>6</sub>F<sub>13</sub>I (after purification of the monoadduct compound by rectification) followed by a dehydroiodination in the presence of various alkalis. Their influences are discussed toward the yield of the reaction. The compositions of the resulting random-type copolymers were calculated by means of <sup>19</sup>F NMR spectroscopy and allowed one to quantify the respective amounts of each monomeric unit in the copolymer. From the Tidwell and Mortimer method, the reactivity ratios ( $r_i$ ) of both comonomers for this copolymerisation were determined showing a higher incorporation of VDF :  $r_{\text{VDF}} = 12.0 \pm 3.0$  and  $r_{\text{F}_2\text{C}=\text{CHC}_6\text{F}_{13}} = 0.9 \pm 0.4$  at 74°C.

## KEY WORDS

Vinylidene fluoride, 2-hydroperfluorooct-1-ene, radical copolymerisation, NMR spectroscopy, reactivity ratio

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\* Part 20, see ref. [38]

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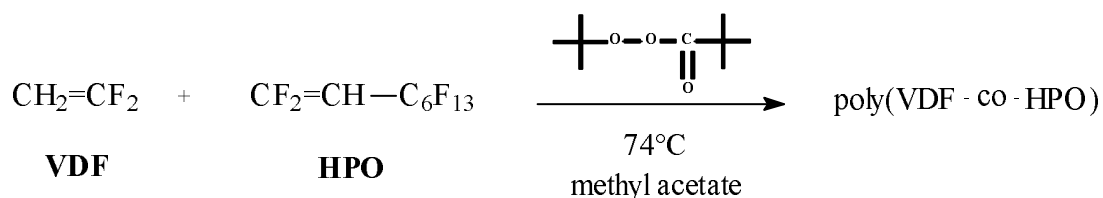
# GRAPHICAL ABSTRACT

## Synthesis and copolymerisation of fluorinated monomers bearing a reactive lateral group. Part 21. Radical copolymerisation of vinylidene fluoride with 2-hydroperfluorooct-1-ene.

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The synthesis of 2-hydroperfluorooct-1-ene (HPO) monomer and its radical copolymerisation with vinylidene fluoride (VDF) was achieved :



The kinetics of copolymerisation of VDF with  $\text{F}_2\text{C}=\text{CHC}_6\text{F}_{13}$  (HPO) led to the determination of the reactivity ratios :  $r_{\text{VDF}} = 12.0 \pm 3.0$  and  $r_{\text{F}_2\text{C}=\text{CHC}_6\text{F}_{13}} = 0.9 \pm 0.4$  at 74°C.

## Introduction

Fluorinated copolymers [1-3] are attractive for their exceptional properties and, in spite of their high price, show a lower crystallinity-rate than that of the fluorohomopolymers [4]. As a matter of fact, the appropriate choice of the comonomer enables one to bring complementary properties [3] : cyclohexyl group for the solubility, hydroxy and epoxy functions for curability, carboxylic group for adhesion, amido bridge for mechanical properties and perfluorinated group for enhanced surface properties.

We have found interesting to investigate that last property and especially that of poly(vinylidene fluoride), PVDF. Although many copolymerisations of VDF with a wide variety of hydrogenated [5, 6] or fluorinated comonomers [3] have already been successfully achieved, that of VDF with 2H-perfluoroalkenes have been scarcely investigated. To our knowledge, the only survey concerns the use of 2-hydroxypentafluoropropylene (PFP) yielding original fluorinated copolymers studied by the 3M [7] and the Montedison [8] companies to circumvent VDF / hexafluoropropylene elastomers (called Daei<sup>®</sup>, Tecnoflon<sup>®</sup>, Viton<sup>®</sup> or Fluorel<sup>®</sup>) [1, 9-12]. However, these former ones did not find the same fate as that of the latter ones.

In an academic point of view, Usmanov *et al.* [13] studied the kinetics of copolymerisation of VDF and PFP initiated by  $\gamma$  rays at various temperatures and showed that VDF was more incorporated in the copolymer than PFP. It was thus worth increasing the fluorinated chain length to enable the resulting copolymers to show improved surface characteristics. To our knowledge, such an opportunity has never been reported in the literature. Hence, the objective of this article deals with the synthesis of 2-hydroperfluorooct-1-ene (HPO) and its radical copolymerisation with VDF.

## Results and discussion

The radical copolymerisation of vinylidene fluoride (VDF) with 2-hydroperfluorooct-1-ene (HPO) was carried out in methyl acetate solution, initiated by *tertio*-butyl peroxyvalate as follows :

### Insert Scheme 1

Before investigating the kinetics of that copolymerisation the synthesis of HPO was optimised.

#### 1. Synthesis of 2-hydroperfluorooct-1-ene (HPO).

The preparation of this fluoroalkene was achieved in a two-step procedure starting from a telomerisation reaction [3] of VDF with 1-iodo-perfluoro-n-hexane followed by the dehydroiodination of the monoadduct ( $C_6F_{13}CH_2CF_2I$ ), as shown in Scheme 2.

### Insert Scheme 2

The first step [14, 15] can be initiated either thermally (from 180°C) leading to a telomeric distribution that can be made narrower with a higher temperature and with a slight excess of n- $C_6F_{13}I$ , or in the presence of a redox catalyst ( $FeCl_3/Ni$  or  $CuCl$ ) yielding monoadduct selectively ( $C_6F_{13}CH_2CF_2I$ ). From both these initiating systems, the n- $C_6F_{13}I$  conversions were quantitative or 65%, respectively.

The second step was already reported by different teams : pioneered by Fields and Haszeldine [16] in 1964, it was also studied by Apsley *et al.* [17], by Saloutina *et al.* [18], and then by Hung and Schmiegel [19]. However, these authors did not describe the influence of various bases onto the conversion of the iodinated product and the amount of HPO. It was thus worth revisiting this second step to optimise this reaction.

Table 1 summarises the obtained results when various alkalies ( $KF/Al_2O_3$ ,  $K_2CO_3/BuCN$ , triethylamine, tributylamine and pyridine) were used in almost similar conditions. These dehydroiodination reactions were monitored by gas chromatography and confirmed by  $^1H$  and  $^{19}F$  NMR (Figure 1). Indeed, in the  $^1H$  NMR spectrum, the signal assigned to the methylene

group, located in the  $\beta$  position about the iodide atom for the telomer precursor, centered at 3.5 ppm, underwent a low field shift to 4.8 ppm with a modification of its multiplicity when the dehydroiodination occurred. Beside gas chromatography, the conversion rate of the reaction could thus be assessed from the  $^1\text{H}$  NMR spectra via the ratio of the integrals of both these signals.

**Insert Table 1**

**Insert Figure 1**

The  $^1\text{H}$  NMR spectrum shows the quantitative conversion of  $\text{C}_6\text{F}_{13}\text{CH}_2\text{CF}_2\text{I}$  by the absence of the  $-\text{CH}_2\text{CF}_2\text{I}$  signal at 3.5 ppm and the presence at 4.7 ppm of the  $-\text{CH}=\text{CF}_2$  signal. The  $^{19}\text{F}$  NMR spectrum (Figure 1) shows the absence of signal at -38.2 assigned to the difluoromethylene groups in the  $\alpha$  position about the iodide in the precursor. It also exhibits the complex signals centered at -61.2 ppm and -72.4 ppm, assigned to both fluorine atoms of  $-\text{CH}=\text{CF}_2$  end group.

The  $^{13}\text{C}$  NMR spectrum (Figure 2) exhibits the characteristic signals of the expected product : at 73.4 ppm the doublet of doublets of doublets corresponding to  $\text{C}_6\text{F}_{13}\text{CH}=\text{CF}_2$  ( $^2J_{\text{CF}} = 35.9$  Hz,  $^2J_{\text{CF}} = 27.6$  Hz and  $^2J_{\text{CF}} = 12.1$  Hz) ; the 105 to 130 ppm zone is assigned to the  $\text{CF}_2$  of the perfluorinated chain and the triplet of triplets located at 160.2 ppm is attributed to the  $-\text{CH}=\text{CF}_2$  end group ( $^1J_{\text{CF}} = 294.2$  Hz and  $^3J_{\text{CF}} = 7.0$  Hz).

**Insert Figure 2**

## 2. Copolymerisation of VDF with 2-hydroperfluorooct-1-ene (HPO)

### 2.2 Copolymerisation of VDF with the 2-hydroperfluorooct-1-ene

The radical copolymerisations of VDF with the 2-hydroperfluorooct-1-ene ( $\text{C}_6\text{F}_{13}\text{CH}=\text{CF}_2$ ) were carried out in Carius tube with *tert*iobutyl peroxyvalate as the initiator ( $[\text{tBu-OO-CO-tBu}]_0 / ([\text{VDF}]_0 + [\text{C}_6\text{F}_{13}\text{CH}=\text{CF}_2]_0) = 1$  mol. %) in methyl acetate as the solvent.

After reaction, the copolymers were precipitated in cold pentane and analysed by  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectroscopy. The physical properties of the materials depend on the proportions between VDF and  $\text{C}_6\text{F}_{13}\text{CH}=\text{CF}_2$  and varied from wax to powder. They were usually soluble in acetone and in dimethylformamide (DMF) or dimethylacetamide (DMAc) for high proportions in VDF.

### 2.2.a Copolymerisation kinetics

Seven copolymerisations were performed (Table 2) for 3 hours at 74°C from initial  $[\text{VDF}]_0/[\text{HPO}]_0$  molar ratios ranging between 11.8/88.2 and 87.1/12.9.

#### **Insert Table 2**

Due to the very wide field of the  $^{19}\text{F}$  versus the  $^1\text{H}$  field and because of the overlapping of the signals of methylene groups of VDF and proton of HPO in the copolymers, the amounts of both comonomeric units in the copolymers were determined by  $^{19}\text{F}$  NMR only. Figure 3 represents the  $^{19}\text{F}$  NMR spectrum of the dried poly(VDF-co-HPO) produced from an initial  $[\text{VDF}]_0/[\text{HPO}]_0$  molar ratio of 87.1/12.9.

#### **Insert Figure 3**

This spectrum can be divided into four distinct zones corresponding to the characteristic signals of each comonomer : first, at -81 ppm a triplet attributed to the trifluoromethyl end group in the HPO olefin ; from -91 to -115.7 ppm, the peaks assigned to the  $\text{CF}_2$  that belong to the VDF ; then, the -121 to -127 ppm zone attributed to the perfluorinated chain of HPO olefin. As previously, the signals of each monomer are presented in the spectrum of the copolymer. The assignments of the different signals are listed in Table 3.

#### **Insert Table 3**

From the integrals of the characteristic signals in the  $^{19}\text{F}$  NMR spectra, the assessment of the amounts of both comonomeric units in the copolymers is given by the following equation :

$$\text{mol \% VDF in the copolymer} = \frac{\frac{(I_{-91.0} + I_{-94.8} + I_{-111.2} + I_{-113.7} + I_{-115.7})}{2}}{\frac{(I_{-91.0} + I_{-94.8} + I_{-111.2} + I_{-113.7} + I_{-115.7})}{2} + \frac{I_{-81.0}}{3}} * 100 \quad (\text{equation 1})$$

The results are presented in Table 2 and the composition curve (i.e., the mol. % of VDF in the copolymer versus that in feed) is shown in Figure 4.

#### **Insert Figure 4**

For each composition in feed ( $f_1$ ), the value of the respective composition in the copolymer ( $F_1$ ) is placed up to the bisector (where  $F_1=f_1$ ), that means that VDF is more reactive than  $C_6F_{13}CH=CF_2$  and its incorporation is easier than the longer olefin. From these values and by using the Tidwell and Mortimer method [20], the monomer reactivity ratios were determined. It was found that  $r_{VDF} = 12.0 \pm 3.0$  and  $r_{F_2C=CHC_6F_{13}} = 0.9 \pm 0.4$  at  $74^\circ C$ . These values can be compared to those of other fluoromonomers able to copolymerise with VDF (Table 4). The traditional method for the determination of relative reactivity of a macroradical to several monomers was used. Indeed, it is common to compare the values  $1/r_A = k_{AB}/k_{AA}$  as the ratio of rate constants of crossed propagation to that of propagation ( $k_{AA}$ ). Thus, the higher the  $1/r_A$  value, the more able the radical is to react with the second monomer B. Table 4 [13, 21-43] allows one to suggest the following increasing series of relative reactivities of monomers to  $\dots VDF^\bullet$  radicals :  $F_2C=CHC_6F_{13} < F_2C=CHCF_3 < HFP < PMVE < PPVE < VDF < TrFE < CTFE$  (recent value)  $\approx BrTFE < H_2C=CFCF_2OR_F < TFE < F_2C=CFC_3H_6SCOCH_3 < F_2C=CFC_3H_6OAc < H_2C=CHF \approx CTFE$  (old value)  $< ethylene$ , although numerous kinetics still deserve to be investigated. Since all these radical copolymerisations were not carried out in the same experimental conditions (choice of initiator, solvent, time and temperature), the reactivity ratios were not assessed from the same law of kinetics. So, HPO fluoroolefin has a very low reactivity compared to that of VDF and the copolymers of both these monomers show a better incorporation of VDF.

#### **Insert Table 4**



## Conclusion

$C_6F_{13}CH=CF_2$  (HPO) was synthesised from a two step-reaction starting from the radical or redox telomerisation of the vinylidene fluoride (VDF) with  $C_6F_{13}I$ . Several bases were used to enable the dehydroiodination of  $C_6F_{13}CH_2CF_2I$  and sodium chloride gave the best yield of HFO after a total conversion of this VDF monoadduct. The kinetics of radical copolymerisation of VDF with HPO initiated by TBPPI led to the following reactivity ratios :  $r_{VDF} = 12.0 \pm 3.0$  and  $r_{F_2C=CHC_6F_{13}} = 0.9 \pm 0.4$  at  $74^\circ C$  showing that i) VDF was more reactive than HPO, and ii) the microstructure of the resulting copolymers was composed of PVDF microblocks separated by one HPO unit. Indeed, by comparing the values of reactivity ratios of a wide range of different fluoromonomers, HPO was the least reactive onto macroradical terminated by a VDF extremity. Hence, original PVDFs bearing  $C_6F_{13}$  side-group were produced, with improved surface properties, under investigation.

## EXPERIMENTAL PART

### 1. Materials

Vinylidene fluoride (VDF) was kindly offered by Solvay S.A.. *Tertiobutyl* peroxyvalate (TBPPI) and C<sub>6</sub>F<sub>13</sub>I were generously offered by “La Chalonaise des Peroxydes” (Châlon sur Marne, France) and Atofina (now Arkema, at Pierre Bénite, France). Tributylamine, triethylamine, pyridine and acetonitrile were provided by Aldrich and were used as received. C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>CF<sub>2</sub>I was obtained either by thermal or redox telomerisation of VDF with C<sub>6</sub>F<sub>13</sub>I and purified by rectification as described in previous studies [14, 15].

### 2. NMR Spectroscopy

The <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR were recorded at ambient temperature on Bruker AC 200 and AC 250 instruments, using deuterated chloroform or acetone as the solvents and TMS (resp. CFC<sub>13</sub>) as the references for <sup>1</sup>H, <sup>13</sup>C (resp. <sup>19</sup>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 <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra were the following : flip angle 90 °, 30 ° and 30 ° ; acquisition time : 4.5 sec, 2.9 sec and 0.7 sec ; pulse delay : 2 sec, 2 sec and 5 sec ; number of scans : 16, 12000 and 64, and a pulse width of 5 μsec for <sup>19</sup>F NMR.

### 3. GC analysis

Gas chromatography (GC) was carried out on Delsi apparatus (330), fitted with an OV1 column, 2m x 1/4 inch under nitrogen pressure. The injector was maintained at 255°C and the detector at 260°C. The heating program was regulated from 35°C to 250°C, with a heating rate of 10°C.min<sup>-1</sup>. The GC apparatus was connected to a Hewlett Packard (3390) integrator that led to an automatic peak area calculation system.

### 4. Synthesis of C<sub>6</sub>F<sub>13</sub>CH=CF<sub>2</sub>

Dehydroiodination reactions were carried out in a two necked round bottom flask equipped with a condenser using K<sub>2</sub>CO<sub>3</sub>/BuCN, triethylamine, tributylamine and pyridine in almost similar conditions (two mole excess of base about C<sub>6</sub>F<sub>13</sub>C<sub>2</sub>H<sub>4</sub>I were used with triethylamine, tributylamine and pyridine while stoichiometric amount when K<sub>2</sub>CO<sub>3</sub>/BuCN was used).

### With NEt<sub>3</sub>

In a two necked round bottom flask equipped with a condenser containing 16.0 g ( $1.58 \cdot 10^{-1}$  mol.) of NEt<sub>3</sub>, were dropwise added at room temperature and under stirring, 40.04 g ( $7.85 \cdot 10^{-2}$  mol.) of C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>CF<sub>2</sub>I. In the course of the addition of C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>CF<sub>2</sub>I into the base, a discoloration of the pink solution and the formation of a yellow solid could be observed. Then, the solution was heated up to 90°C for five hours. Hydrochloric acid (0.5098 N) was added to the medium and the olefin was extracted with chloroform. The solution was dried with Na<sub>2</sub>SO<sub>4</sub> and the solvent removed by distillation. HPO was purified by distillation (B.p. = 108°C) as a colorless liquid.

<sup>19</sup>F NMR (acetone d<sub>6</sub>, ppm) (Figure 1)  $\delta$  : -72.2 (ddt, <sup>2</sup>J<sub>FF</sub> = 12.5 Hz, <sup>3</sup>J<sub>FH</sub> = 26.7 Hz, <sup>4</sup>J<sub>FF</sub> = 5.0 Hz, 1F) ; -73.4 (dd, <sup>2</sup>J<sub>FF</sub> = 15.2 Hz, <sup>3</sup>J<sub>FH</sub> = 7.7 Hz, 1F) ; -82.3 (m, CF<sub>3</sub>-Rf-CH=CF<sub>2</sub>, 3F) ; -108.7 (m, RfCF<sub>2</sub>CH=CF<sub>2</sub>, 2F) ; -122.4 (m, RfCF<sub>2</sub>CF<sub>2</sub>CH=CF<sub>2</sub>, 2F); -123.6 (m, C<sub>3</sub>F<sub>7</sub>CF<sub>2</sub>, 2F); -124.5 (m, C<sub>2</sub>F<sub>5</sub>CF<sub>2</sub>, 2F) ; -127.3 (m, CF<sub>3</sub>CF<sub>2</sub>, 2F).

<sup>1</sup>H NMR (acetone d<sub>6</sub>, ppm)  $\delta$  : 4.7 (ddt, Rf-CHH=CF<sub>2</sub>, 1H, <sup>3</sup>J<sub>H<sub>F</sub>trans</sub> = 21.7 Hz, <sup>3</sup>J<sub>H<sub>F</sub>cis</sub> = 12.4 Hz, <sup>3</sup>J<sub>HF</sub> ≈ 12.4 Hz, <sup>4</sup>J<sub>HF</sub> ≈ 2.2 Hz).

<sup>13</sup>C NMR (acetone d<sub>6</sub>, ppm) (Figure 2)  $\delta$  : 77.0 (ddd, Rf-CH=CF<sub>2</sub>, <sup>2</sup>J<sub>CF1'</sub> = 35.9 Hz, <sup>2</sup>J<sub>CF1''</sub> = 27.6 Hz, <sup>2</sup>J<sub>CF3</sub> = 12.1 Hz) ; 105 to 130 (series of triplets, assigned to the different CF<sub>2</sub> of the perfluorinated chain) ; 160.2 (tt, Rf-CH=CF<sub>2</sub>, <sup>1</sup>J<sub>CF</sub> = 294.2 Hz, <sup>3</sup>J<sub>CF</sub> = 7.0 Hz).

### With NBu<sub>3</sub>

In a two necked round bottom flask equipped with a distillation device were introduced 75.9g ( $4.1 \cdot 10^{-1}$  mol) of NBu<sub>3</sub>. Under stirring, 110.66g ( $2.2 \cdot 10^{-1}$  mol.) of C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>CF<sub>2</sub>I were dropwise added at room temperature. As above, the consumption of C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>CF<sub>2</sub>I was checked by the discoloration of the pink solution and the formation of a yellow solid (about 7 hrs). The fluoroolefin was distilled under atmospheric pressure (B.p. = 107°C) as soon as formed.

## **5. Copolymerisation of VDF with C<sub>6</sub>F<sub>13</sub>CH=CF<sub>2</sub>**

The copolymerisation reactions of VDF with C<sub>6</sub>F<sub>13</sub>CH=CF<sub>2</sub> were performed in borosilicate Carius tubes (length 130 mm, inner diameter 10 mm, thickness 2.5 mm; for a total volume of 8 cm<sup>3</sup>). After introducing the liquid and solid reactants (initiator, monomer and methylacetate), the tube was tightly connected to a manifold. After five freeze – thaw cycles,

the adequate VDF amount was trapped in the tube which was cooled with liquid nitrogen under vacuum.

The expected VDF quantity transferred in the tube was introduced from a beforehand calibration curve linking the VDF pressure (bars) versus the trapped weight (grams) of VDF (for example a difference of pressure of 0.66 bar corresponds to 1.000 gram of VDF). The tube was sealed while immersed in liquid nitrogen and left stirred at the chosen temperature for 3 hours. Then, the copolymers were precipitated from cold pentane and analysed by  $^{19}\text{F}$  NMR and  $^1\text{H}$  NMR spectroscopy.

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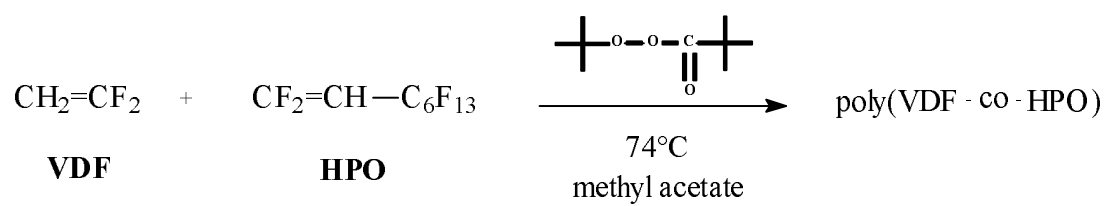
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## **Scheme Captions**

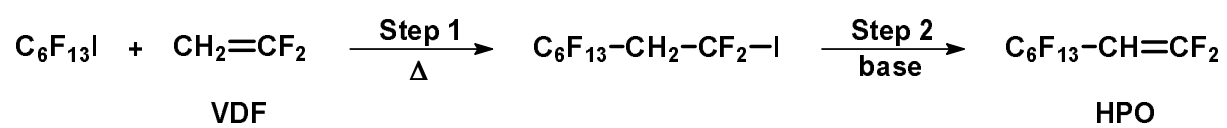
***Scheme 1*** : Copolymerisation of VDF with HFO at 74°C in methyl acetate initiated with tertio-butyl peroxyvalate.

***Scheme 2*** : Synthesis of 2-hydroperfluorooct-1-ene(HFO).



**Scheme 1:** Copolymerisation of VDF with HPO at 74°C in methyl acetate initiated with tertio-butyl peroxyvalate.





*Scheme 2 : Synthesis of 2-hydroperfluorooct-1-ene(HPO)*

## **Table Captions**

**Table 1:** *Experimental conditions and results of the dehydroiodination of  $C_6F_{13}CH_2CF_2I$  in presence of various bases.*

**Table 2 :** *Monomer/copolymer compositions from the kinetics of radical copolymerisation of VDF with HPO determined by  $^{19}F$  NMR spectroscopy. Copolymerisation conditions :  $[tBu-OO-CO-tBu]_0 / ([VDF]_0 + [HPO]_0) = 1$  mol. %,  $74^\circ C$ , 3 hrs.*

**Table 3 :**  *$^{19}F$  NMR assignments of poly(VDF-co-HPO) copolymers.*

**Table 4 :** *Monomer reactivity ratios for the copolymerisation of VDF (A) with other fluoroalkenes (B) (ethylene and vinyl acetate).*

Base	Temperature (°C)	Reaction time (hours)	Conversion (%) of $C_6F_{13}CH_2CF_2I$	Mol. % of $C_6F_{13}CH=CF_2$	Mol. % of by product
KF/Al <sub>2</sub> O <sub>3</sub> /CH <sub>3</sub> CN	80	5	60	72	28
NEt <sub>3</sub>	90	5	80	75	25
Pyridine	110	5	10	77	23
K <sub>2</sub> CO <sub>3</sub> /BuCN	125	8	75	33	67
NBu <sub>3</sub>	120	7	100	86	14
NaCl	120	5	100	98	2

**Table 1:** Experimental conditions and results of the dehydroiodination of  $C_6F_{13}CH_2CF_2I$  in presence of various bases.

Experiment n <sup>o</sup>	(mol. %) VDF in feed	(mol. %) VDF in the copolymer
1	11.8	26.2
2	15.2	37.8
3	31.5	69.8
4	47.9	89.5
5	62.0	96.5
6	75.2	97.4
7	87.1	99.0

**Table 2** : Monomer/copolymer compositions from the kinetics of radical copolymerisation of VDF with HPO determined by <sup>19</sup>F NMR spectroscopy. Copolymerisation conditions : [tBu-OO-CO-tBu]<sub>0</sub>/([VDF]<sub>0</sub> + [HPO]<sub>0</sub>) = 1 mol. %, 74°C, 3 hrs.

Chemical shift (ppm)	structure
-81.0	$-(\text{CH}_2\text{-CF}_2)\text{-}[\text{CF}_2\text{-CH}(\text{CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_3)]\text{-}$
-91.0	$-\text{CF}_2\text{-CH}_2\text{-CF}_2\text{-CH}_2\text{-CF}_2\text{-}$
-94.8	$(\text{CH}_2\text{-CF}_2)\text{-}(\text{CF}_2\text{-CH}_2)\text{-}(\text{CH}_2\text{-CF}_2)\text{-}(\text{CH}_2\text{-CF}_2)$
-95.8	$-(\text{CH}_2\text{-CF}_2)\text{-}(\text{CH}_2\text{-CF}_2)\text{-}[\text{CF}_2\text{-CH}(\text{CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_3)]\text{-}$
-111.2	$-(\text{CH}_2\text{-CF}_2)\text{-}[\text{CF}_2\text{-CH}(\text{CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_3)]\text{-}$
-113.7	$(\text{CH}_2\text{-CF}_2)\text{-}(\text{CF}_2\text{-CH}_2)\text{-}(\text{CH}_2\text{-CF}_2)\text{-}$
-114.5	$\text{HCF}_2\text{-CH}_2\text{-CF}_2\text{-CH}_2\text{-}$
-115.0	$-(\text{CH}_2\text{-CF}_2)\text{-}[\text{CF}_2\text{-CH}(\text{CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_3)]\text{-}$
-115.7	$(\text{CH}_2\text{-CF}_2)\text{-}(\text{CF}_2\text{-CH}_2)\text{-}(\text{CH}_2\text{-CF}_2)\text{-}$
-122.1	$-(\text{CH}_2\text{-CF}_2)\text{-}[\text{CF}_2\text{-CH}(\text{CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_3)]\text{-}$
-123.6	$-(\text{CH}_2\text{-CF}_2)\text{-}[\text{CF}_2\text{-CH}(\text{CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_3)]\text{-}$
-124.5	$-(\text{CH}_2\text{-CF}_2)\text{-}[\text{CF}_2\text{-CH}(\text{CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_3)]\text{-}$
-127.3	$-(\text{CH}_2\text{-CF}_2)\text{-}[\text{CF}_2\text{-CH}(\text{CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_3)]\text{-}$

**Table 3 :**  $^{19}\text{F}$  NMR assignments of poly(VDF-co-HPO) copolymers.

Monomer B	$r_A$	$r_B$	$r_A r_B$	$1/r_A$	Ref.
H <sub>2</sub> C=CH <sub>2</sub>	0.05	8.5	0.42	20.00	[21]
H <sub>2</sub> C=CHOCOCH <sub>3</sub>	-0.40	1.67	-0.67	-2.5	[22]
	0.50	2.0	1.00	2.0	[23]
H <sub>2</sub> C=C(CF <sub>3</sub> )CO <sub>2</sub> H	0.33	0	0	3.03	[24]
FCH=CH <sub>2</sub>	0.17	4.2 – 5.5	0.71 – 0.94	5.88	[25]
	0.20 – 0.43	3.8 – 4.9	0.76 – 2.11	2.33 – 5.00	[26]
H <sub>2</sub> C=CFCF <sub>2</sub> OR <sub>F</sub>	0.38	2.41	0.92	2.63	[27]
F <sub>2</sub> C=CFH	0.70	0.50	0.35	1.43	[28]
F <sub>2</sub> C=CHCF <sub>3</sub>	9.0	0.06	0.54	0.11	[13]
F <sub>2</sub> C=CHC <sub>6</sub> F <sub>13</sub>	12.0	0.90	10.80	0.08	Our work
CFCl=CF <sub>2</sub>	0.73	0.75	0.55	1.37	[29]
	0.17	0.52	0.09	5.88	[30]
CFBr=CF <sub>2</sub>	0.43	1.46	0.63	2.33	[29]
CF <sub>2</sub> =CF <sub>2</sub>	0.23	3.73	0.86	4.35	[29, 31]
	0.32	0.28	0.09	3.13	[32]
CF <sub>3</sub> -CF=CF <sub>2</sub>	6.70	0	0	0.15	[33]
	2.45	0	0	0.40	[31]
	2.90	0.12	0.35	0.34	[34]
F <sub>2</sub> C=CFOCF <sub>3</sub>	3.40	0	0	0.29	[35]
F <sub>2</sub> C=CFOC <sub>3</sub> F <sub>7</sub>	1.15	0	0	0.86	[35]
F <sub>2</sub> C=CFO(HFP)OC <sub>2</sub> F <sub>4</sub> SO <sub>2</sub> F	0.57	0.07	0.04	1.75	[36]
CF <sub>2</sub> =CFCH <sub>2</sub> OH	0.83	0.11	0.09	1.02	[37]
CF <sub>2</sub> =CF(CH <sub>2</sub> ) <sub>2</sub> Br	0.96	0.09	0.09	1.00	[38]
CF <sub>2</sub> =CF(CH <sub>2</sub> ) <sub>3</sub> OAc	0.17	3.26	0.59	5.56	[39]
F <sub>2</sub> C=CF(CH <sub>2</sub> ) <sub>3</sub> SAc	0.60	0.41	0.25	4.07	[40]
CF <sub>2</sub> =CFCO <sub>2</sub> CH <sub>3</sub>	0.30	0	0	3.33	[41]
F <sub>2</sub> C=C(CF <sub>3</sub> )COF	7.60	0.02	0.15	0.13	[42]
F <sub>2</sub> C=C(CF <sub>3</sub> )OCOC <sub>6</sub> H <sub>5</sub>	0.77	0.11	0.08	1.30	[43]

**Table 4 :** Monomer reactivity ratios for the copolymerisation of VDF (A) with other fluoroalkenes (B) (ethylene and vinyl acetate).

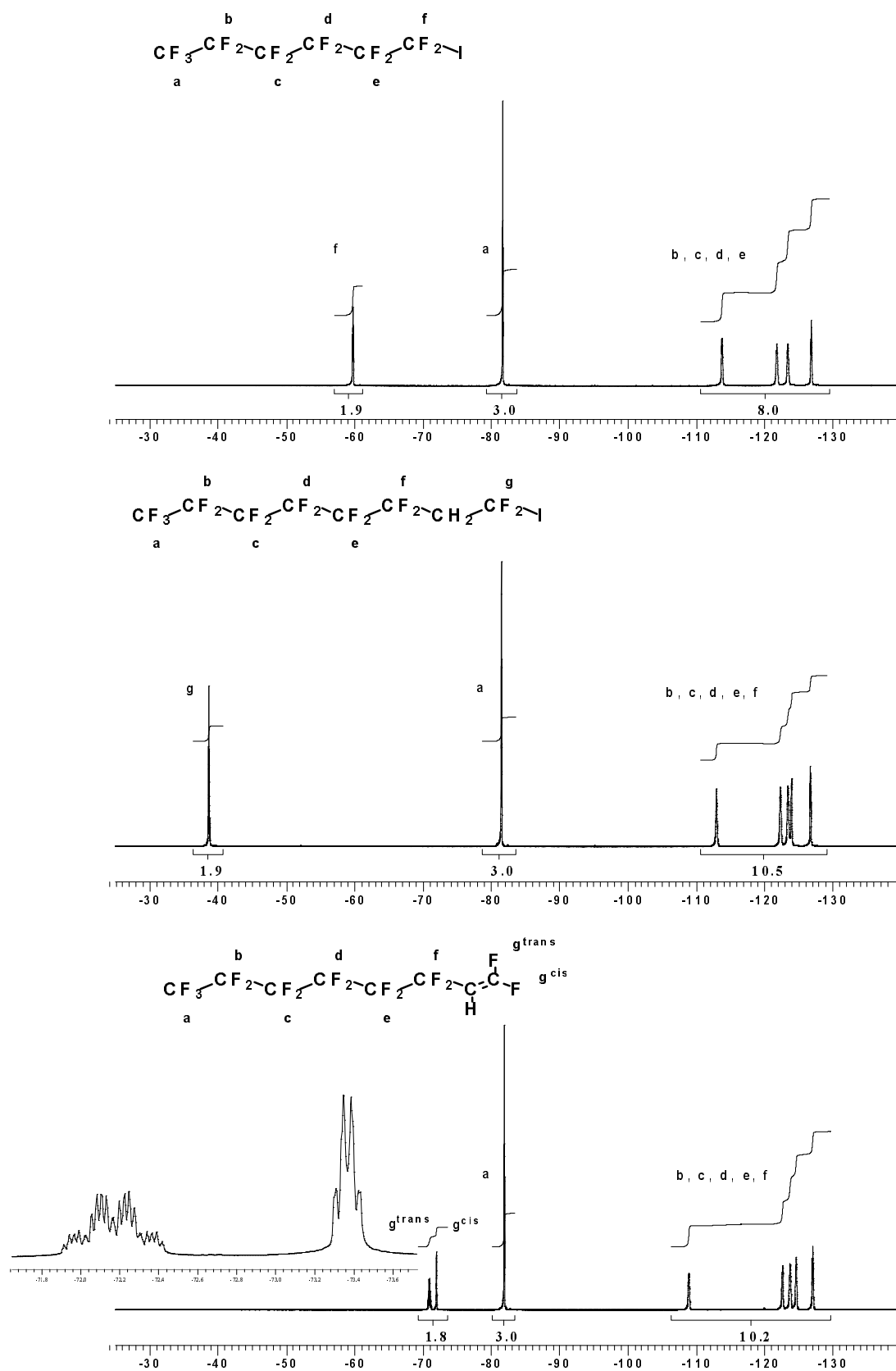
## Figures Captions

**Figure 1 :**  $^{19}\text{F}$  NMR spectra (recorded in  $\text{CDCl}_3$ ) of 1-iodoperfluorohexane (uppest figure), 1-iodo-2,2-dihydroperfluorooctane and 2-hydroperfluorooct-1-ene(HPO) (lowest figure) with expansion of the  $-71.6$  to  $-73.8$  ppm zone.

**Figure 2 :**  $^{13}\text{C}$  NMR spectrum of 2-hydroperfluorooct-1-ene(recorded acetone  $d^6$ ) with expansion of the  $76.3$  to  $79.0$  ppm zone (the signal centred at  $151$  ppm is assigned to the backfolding of the signal of carbonyl of acetone)

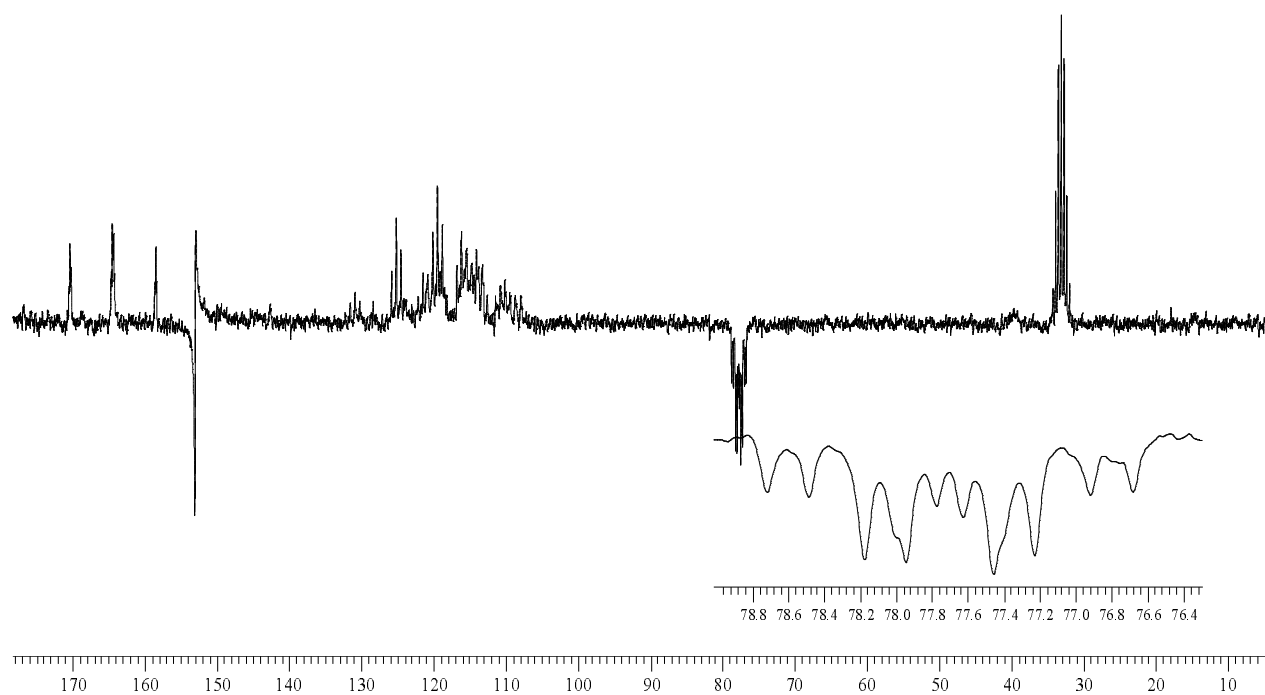
**Figure 3 :**  $^{19}\text{F}$  NMR spectrum of poly(VDF-co-HPO) copolymer (recorded in acetone  $d^6$ ). Copolymerisation conditions :  $[\text{tBu-OO-CO-tBu}]_0/([\text{VDF}]_0 + [\text{HPO}]_0) = 1$  mol. %,  $74^\circ\text{C}$ , 3 hrs and VDF/HPO initial molar ratio in the feed =  $87.1/12.9$ .

**Figure 4 :** Monomer-polymer composition curve from radical copolymerisation of VDF with HPO, calculated from  $^{19}\text{F}$  NMR. The full line represents the theoretical curve.

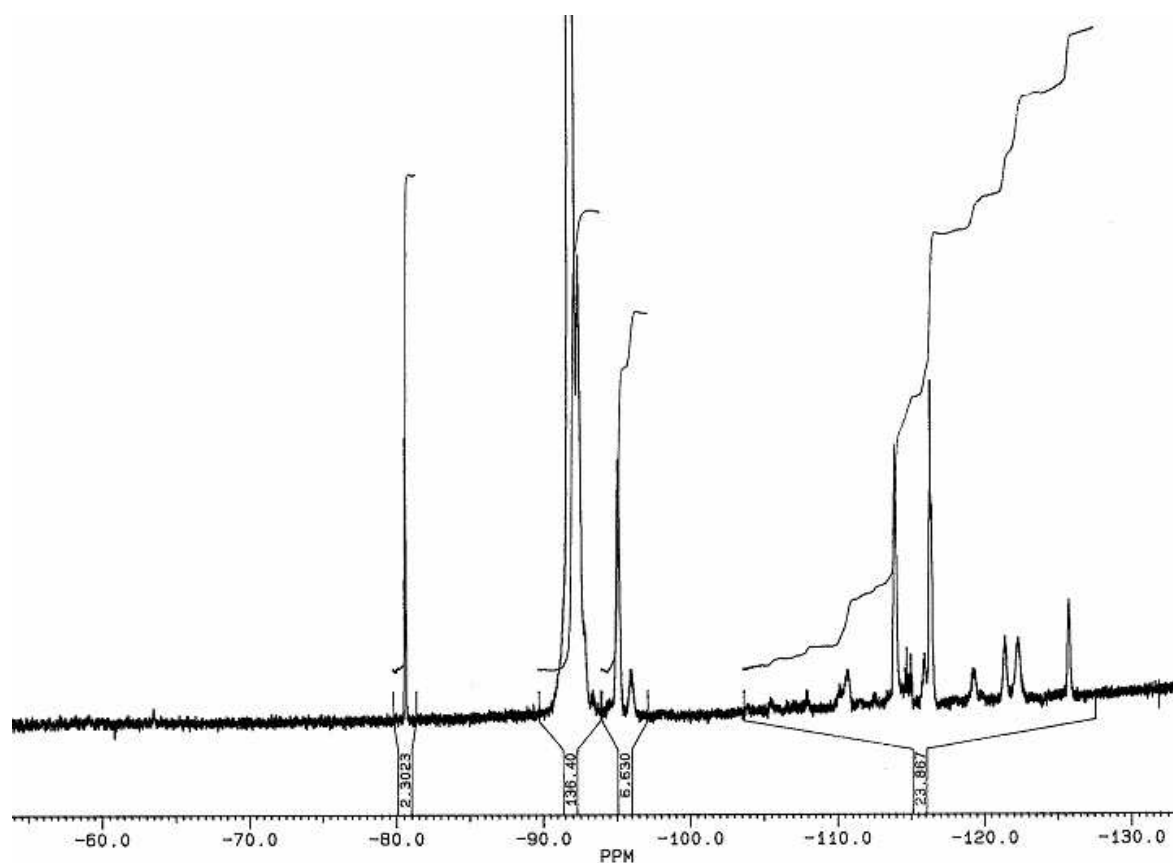


**Figure 1 :**  $^{19}\text{F}$  NMR spectra (recorded in  $\text{CDCl}_3$ ) of 1-iodoperfluorohexane (upper figure), 1-iodo-2,2-dihydroperfluorooctane and 2-hydroperfluorooct-1-ene(HPO) (lowest figure) with expansion of the -71.6 to -73.8 ppm zone.

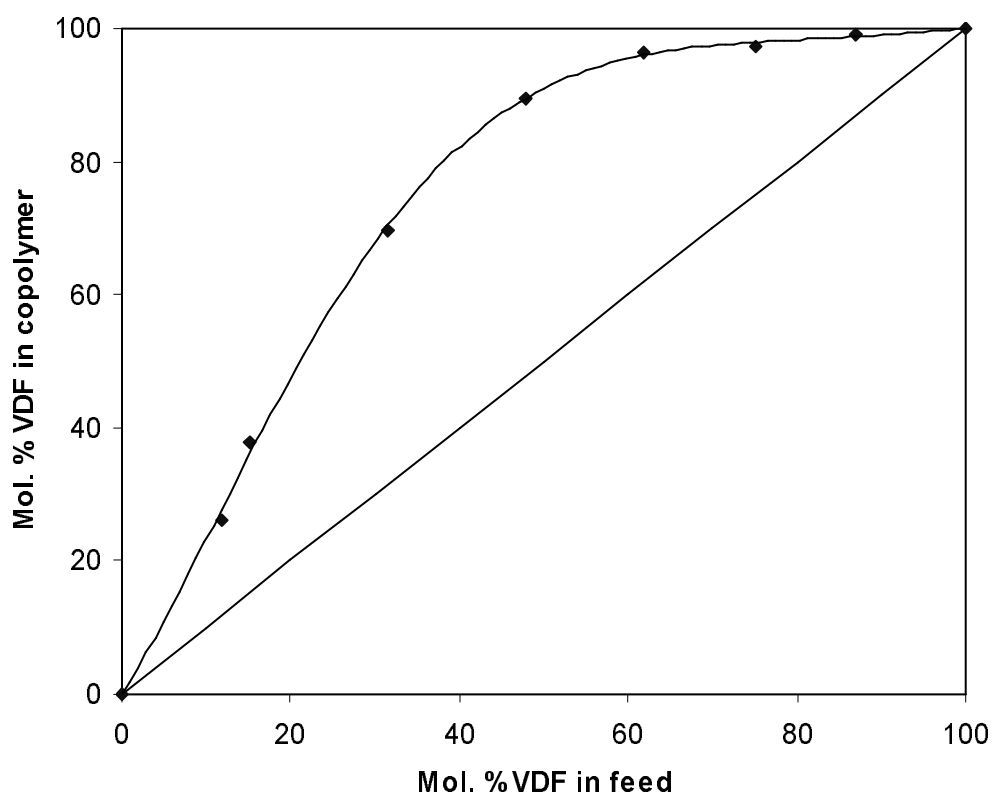




**Figure 2 :**  $^{13}\text{C}$  NMR spectrum of 2-hydroperfluorooct-1-ene (recorded acetone  $d^6$ ) with expansion of the 76.3 to 79.0 ppm zone (the signal centred at 151 ppm is assigned to the backfolding of the signal of carbonyl of acetone)



**Figure 3 :**  $^{19}\text{F}$  NMR spectrum of poly(VDF-co-HPO) copolymer (recorded acetone  $d_6$ ). Copolymerisation conditions :  $[\text{tBu-OO-CO-tBu}]_0 / ([\text{VDF}]_0 + [\text{HPO}]_0) = 1 \text{ mol. \%}$ ,  $74^\circ\text{C}$ , 3 hrs and VDF/HPO initial molar ratio in the feed = 87.1/12.9.



**Figure 4** : Monomer-polymer composition curve from radical copolymerisation of VDF with HPO, calculated from  $^{19}\text{F}$  NMR. The full line represents the theoretical curve.