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Fluorinated cotelomers based on vinylidene fluoride (VDF) and hexafluoropropene (HFP): Synthesis, dehydrofluorination and grafting by amine containing an aromatic ring

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Abstract

The synthesis of $C_6F_{13}CH_2C(CF{=}CFCF_3){=}N{-}C_2H_4{-}C_6H_5$ (**11**) from the addition of $H_2N{-}C_2H_4{-}C_6H_5$ onto $C_6F_{13}CH_2CF_2CF_2CFHCF_3$ (**3**) is presented. $C_6F_{13}CH_2CF_2CF_2CFHCF_3$ (**3**) and $C_6F_{13}CH_2CF_2CF(CF_3)CF_2H$ (**3′**) isomers were obtained from the thermal stepwise cotelomerization of vinylidene fluoride and hexafluoropropene with $C_6F_{13}I$, followed by the selective reduction of the iodine end atom. At 200 °C, the **3/3′** molar ratio reached 9.0. In contrast to selective reduction, dehydrofluorination led to various derivatives, which were characterized by ^{1}H NMR and ^{19}F NMR spectroscopy, and hence a reaction pathway could be suggested. The grafting of an amine containing an aromatic ring onto the cotelomers based on VDF and HFP occurred selectively on VDF/HFP diad and, in some instances a further step involving the formation of an imine was observed. The addition of 2-phenylethylamine onto the dehydrofluorinated intermediates was found to be quantitative.

Keywords: Vinylidene fluoride (VDF); Hexafluoropropene (HFP); Radical telomerization; Grafting by amine; ^{19}F NMR characterization

1. Introduction

It is well known that diamines enable the crosslinking of fluorinated copolymers based on vinylidene fluoride (or 1,1-difluoroethylene, VDF) [1–3]. In the case of fluoropolymers containing VDF/HFP diads (where HFP stands for hexafluoropropene), it has been proposed that the reaction pathway is composed of four steps: (i) dehydrofluorination of the VDF/HFP diad, (ii) regeneration of the diamine, (iii) Michael addition of the diamine onto unsaturated bonds, and (iv) reorganization leading to an imine group [3,4]. Further investigation is required to allow a better understanding of the nature of the dehydrofluorination and the addition of the amine onto the double bond, as when the copolymer is crosslinked the characterization is difficult to carry out. Hence it is of interest to study the grafting of a monoamine onto short model molecules containing VDF and HFP units.

The telomerization of vinylidene fluoride has been extensively investigated [5–19]. Perfluoroalkyl iodides or α,ω-diiodoperfluoroalkanes act as efficient chain transfer agents (CTA), since they easily undergo CF_2–I bond cleavage [5,6,9,11,12,14,15,20–22] leading to low molecular weight molecules. Most studies on the direction of addition of the telogen onto the asymmetric monomer (VDF) have shown that the addition mainly occurs onto the methylene groups of VDF [11,15,20–27], and that it is regioselective. The stepwise telomerizations of VDF and HFP with perfluoroalkyl iodides or α,ω-diiodoperfluoroalkanes acting as CTAs have been investigated [15,21,28].

Fluorinated oligomers containing a CF_2CH_2 group can be readily dehydrofluorinated, leading to a CF=CH group [29–31] identified by ^{19}F NMR spectroscopy [15,32]. Condensation of an amine leads to unsaturated enamine compounds [33,34]. Fluorinated compounds have been synthesized and the reaction pathway of their crosslinking with amine studied by FTIR [35], however the grafting (or crosslinking) of amines onto fluorinated (model) molecules has not at this stage been studied by ^{19}F and ^{1}H NMR spectroscopy.

The main purpose of this article is to investigate the dehydrofluorination of a $R_FCH_2CF_2CF_2CFHCF_3$ (**3**) model

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molecule for poly(VDF-*co*-HFP) commercially available copolymers followed by the grafting of amines containing an aromatic ring onto the resulting dehydrofluorinated products, to allow a better understanding of the mechanism for grafting amines onto poly(VDF-*co*-HFP) copolymers. Model molecules (mainly telomers) containing vinylidene fluoride/hexafluoropropene (VDF/HFP) diad(s) were synthesized and the different steps that permitted grafting 2-phenylethylamine onto cotelomers were investigated.

First, iodo fluoroalkane was prepared by stepwise (or sequential) thermal cotelomerization containing VDF/HFP diad model molecule, then reduced into hydrogeno fluoroalkane homologue. This model molecule was dehydrofluorinated and characterized by spectroscopy. Finally, 2-phenylethylamine was grafted onto the model molecule. Each step was monitored by ^{1}H and ^{19}F NMR spectroscopy. Such highly fluorinated organic compounds are models of choice to understand what occurs in the grafting of amine onto commercially available poly(VDF-*co*-HFP) copolymers or the crosslinking of such macromolecules in the presence of bisamines.

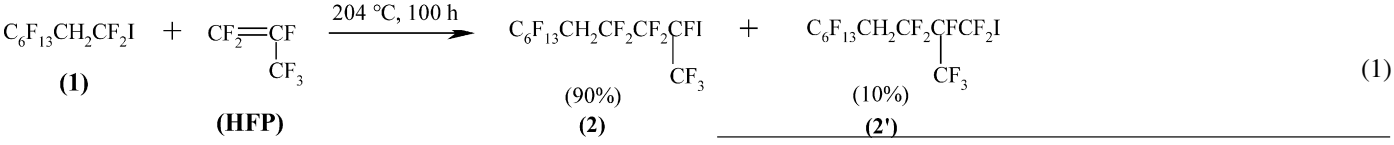
2. Results and discussion

2.1. Synthesis of $C_6F_{13}CH_2CF_2CF_2CFICF_3$ (2) and reduction into $C_6F_{13}CH_2CF_2CF_2CFHCF_3$ (3)

2.1.1. Cotelomers based on vinylidene fluoride and hexafluoropropene

The telomerizations of vinylidene fluoride (VDF) [21,22,24], trifluoroethylene (TrFE) [36], and hexafluoropropene (HFP) [25,28,37] with perfluoroalkyl iodides [20,22,24,36,37] or α,ω-diiodoperfluoroalkanes [28] have been previously investigated. Such reactions were successfully achieved using thermal initiation due to the low dissociation energy of CF_2–I bond (ca. 45 kJ mol^{-1}). $C_6F_{13}CH_2CF_2I$ (**1**) was obtained by distillation of the product mixture generated from the thermal reaction of VDF with $C_6F_{13}I$ at 180 °C [21,24].

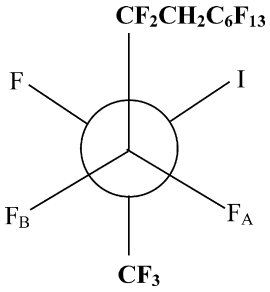
The model molecule for the addition of amines was synthesized by thermal telomerization of HFP with $C_6F_{13}CH_2CF_2I$ [15,21], illustrated by the following equation:



(1)

The telomerization reaction was carried out at 204 °C for 100 h. As expected, only the monoadduct was obtained since HFP does not homopolymerise [19,38]; it was composed of 88.9 mol% of normal **2** adduct and 11.1 mol% of reverse **2′** isomers. This result is readily confirmed in the literature [25,39,40]. The formation of both isomers was shown by ^{19}F NMR spectroscopy with two clear observations:

(i) ^{19}F NMR spectrum of **2** exhibits the presence of an AB system centered at −107.6 ppm, attributed to both anisochronous fluorine atoms of the difluoromethylene group in the $–CF_2C^*FICF_3$ sequence, due to the presence of the adjacent asymmetric carbon atom bearing a bulky iodine atom. The coupling constant is $^{2}J_{F_aF_b} = 298$ Hz. The most stable conformation is the following one:

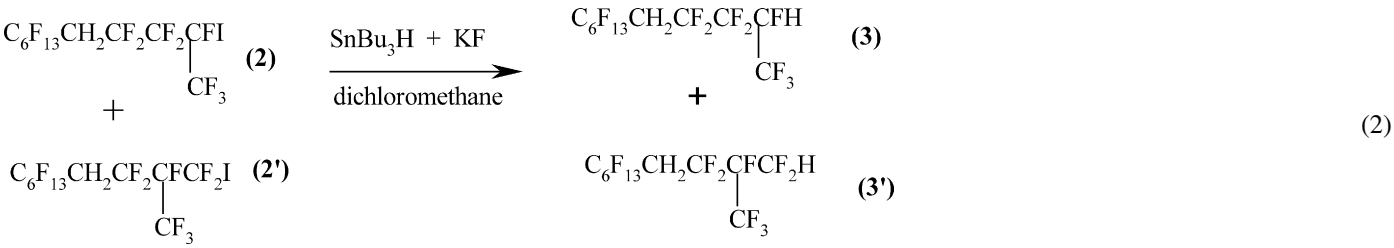


where F_A and F_B are the non-equivalent fluorine atoms (since F_A and F_B fluorine atoms do not have the same chemical environments) assigned to difluoromethylene group of HFP unit. This orientation minimizes the energy of conformation, thus the F_B coupled more with the fluorine atom than did F_A.

(ii) The presence of the signal located at −39.6 ppm assigned to the difluoromethylene groups in the α position about the iodide in the precursor (**1**), enables the yield of the reaction of telomerization to be determined; it was found to be 56%.

2.1.2. Selective reduction of the iodine end-atom

The reduction of $C_6F_{13}CH_2CF_2CF_2CFICF_3$ normal (**2**) and $C_6F_{13}CH_2CF_2CF(CF_3)CF_2I$ reverse (**2′**) isomers leading to $C_6F_{13}CH_2CF_2CF_2CFHCF_3$ (**3**) and $C_6F_{13}CH_2CF_2CF(CF_3)CF_2H$ reverse (**3′**) isomers were carried out at room temperature, as follows [15,21]:



(2)

The presence of KF improved the reduction because the $SnBu_3I$ produced reacted with KF yielding $SnBu_3F$, which was easier to eliminate from the mixture. In these conditions, the reduction was quantitative, and normal **3** and reverse **3′** isomers were characterized by ^{19}F and ^{1}H NMR spectroscopy. The ^{19}F NMR spectrum exhibits the high field shift from −148.4 to −214.0 ppm assigned to the chemical reduction of $–CF_2CFICF_3$ of **2** into $–CF_2CFHCF_3$ of **3**, respectively; it also shows the selective conversion of **2′** into **3′** by the high field shift of the signal assigned to $–CF_2I$ in **2′** to $–CF_2H$ in **3′** from −51.3 to −133.1 ppm.

The ^{1}H NMR spectrum (Fig. 1, spectrum a) exhibits the doublet ($^{2}J_{FH}$ = 42 Hz) of doublets ($^{3}J_{FH}$ = 18 Hz) of quartets ($^{3}J_{FH}$ = 5 Hz) of doublets ($^{3}J_{F_dH}$ = 2 Hz) centered at 5.96 ppm, characteristic of the proton end-group of **3**. This spectrum also shows the presence of a triplet ($^{2}J_{FH}$ = 51 Hz) of doublets ($^{3}J_{FH}$ = 6 Hz) centered at 6.75 ppm assigned to the $–CF_2H$ end-group of molecule **3′** (Fig. 1, spectrum a). The integral of $–CF_2H$ in the ^{1}H NMR spectrum indicates a **3/3′** molar ratio of 8/1 as for that of **2/2′**. The methylene groups in both isomers **3** and **3′** gave two different quintets, due to the influence of electro withdrawing CF_3 side groups located in δ or γ positions, respectively. This is in good agreement with previous investigations [25,37].

2.2. Dehydrofluorination of $C_6F_{13}CH_2CF_2CF_2CFHCF_3$ (3) and $C_6F_{13}CH_2CF_2CF(CF_3)CF_2H$ (3′)

Poly(VDF-*co*-HFP) copolymers can be grafted or cross-linked by several agents, such as bisphenates or diamines [1–3]. The grafting of amine onto poly(VDF-*co*-HFP) copolymer has been extensively studied by many authors [3,4,35,41–43], and it has been shown that amines graft onto VDF/HFP diads of poly(VDF-*co*-HFP) copolymers by a reaction pathway consisting of four different steps [1,3,4,44–46]. Scheme 1 represents those different steps.

To identify the sites of grafting of amines onto poly(VDF-*co*-HFP) copolymers, it was deemed necessary to synthesize a model molecule that exhibits a VDF/HFP diad, such as the **3** and **3′** isomers. Initially, it is important to define which of the fluorines is the active site for dehydrofluorination, and as such both the isomers **3** and **3′** were investigated.

Such model molecules are limited in their supply, and to the best of our knowledge, only Apsey et al. [15] carried out the dehydrofluorination of $(CF_3)_2CFCH_2CF_2CH_2CF_2CH_2CF_3$ with 1,8-diazabicyclo[5,4,0]-undec-7-ene (DBU) in dimethylacetamide (DMAc) at room temperature. As these authors obtained dehydrofluorination of $CFCH_2$ group, leading to $(CF_3)_2C{=}CHCF_2CH_2CF_2CH_2CF_3$, they concluded that preferential elimination of HF occurred from positions involving the "*tertiary*" fluorine [41,47]. The identification of the dehydrofluorination of **3** and **3′** cotelomers was achieved by ^{19}F and ^{1}H NMR spectroscopy, and is reported below.

2.2.1. ^{19}F NMR characterization of intermediates and products

The total product mixture resulting from the dehydrofluorination of the isomers **3** and **3′** in the presence of sodium hydroxide was a mixture composed of the unreacted isomers and products **4–9** (Scheme 2), as identified by ^{19}F NMR

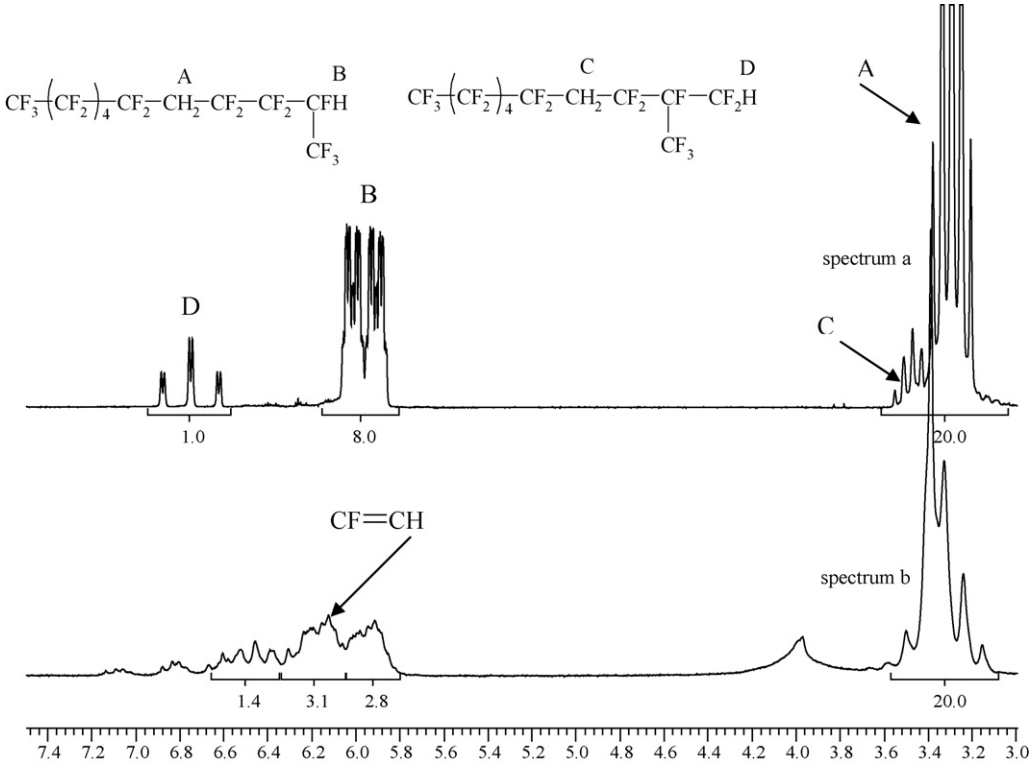
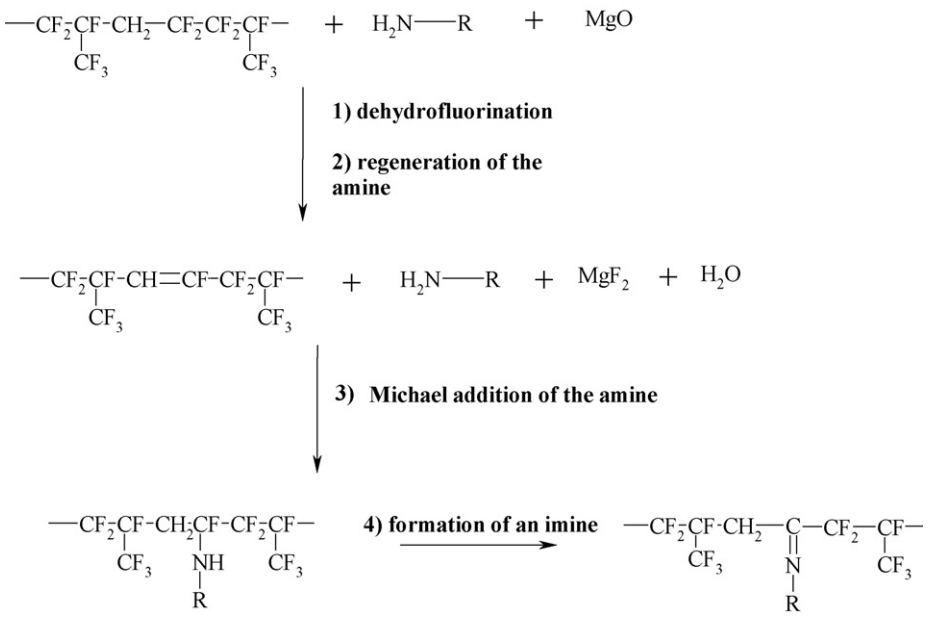


Fig. 1. ^{1}H NMR spectra of the mixture of $C_6F_{13}CH_2CF_2CF_2CFHCF_3$ (**3**) and $C_6F_{13}CH_2CF_2CF(CF_3)CF_2H$ (**3′**) isomers (spectrum a) and of the mixture of **4–9** molecules (dehydrofluorination of **3** and **3′** molecules in the presence of NaOH) (spectrum b) (recorded in acetone d^6 on 400 MHz Bruker).



Scheme 1. Reaction pathway of grafting of amines onto poly(VDF-*co*-HFP) copolymers in four main steps [3]; where VDF and HFP are vinylidene fluoride and hexafluoropropene, respectively.

spectroscopy. Unreacted **3** and **3′** could not be eliminated. The assigned signals are listed in Table 1 [48–55]. To develop Table 1, the chemical shifts of published molecules were taken into account, such as

CF_3–CF=CH–CF_2–CF_3 *-74.1, -115.3, -113.5, -85.9 ppm* [30,31,54]

CF_3–CH=CF–CF_2–CF_3 *-59.7, -113.6, -122.8, -83.9 ppm* [30,31,54]

CF_3–CF_2–CF_2–CF=CF–CF_2–CF_3 (trans) *-81.2, -128.4, -119.5, -155.2, -154.4, -121.8, -84.8 ppm* [48,50,54]

CF_3–CF_2–CF_2–CF=CF–CF_2–CF_3 (cis) *-81.1, -126.8, -116.2, -134.2, -134.8, -118.1, -84.1 ppm* [48,50,54]

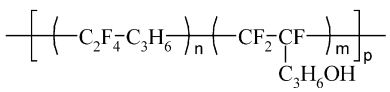
CF_3–CF=CF–CF_2–CF_2–CF_2–CF_3 (trans) *-64.3, -157.6, -156.4, -118.8, -124.7, -126.7, -81.5 ppm* [48,50,54]

(3)

CF_2=CF–CnF_{2n+1} *-93 and -109, -191 ppm* [48,50]

CF_2=CF–CnH_{2n+1} *-103.4, -120.7, -181.4 ppm* [52,53]

CF_2=CH–CF_2–CnF_{2n+1} *-61.2, -72.4, -126.9 ppm* [54,55]

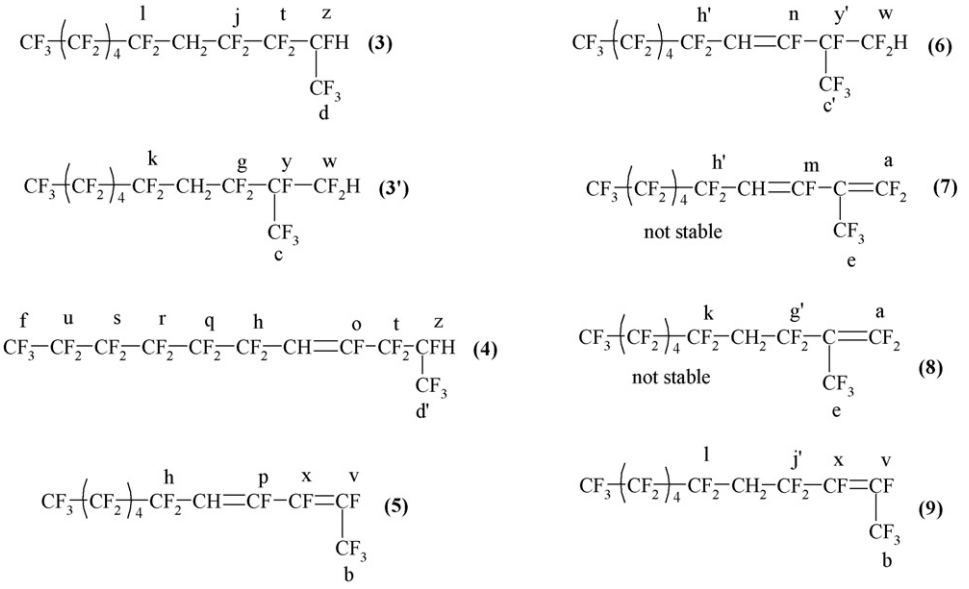

[51]

The signals given in Table 1 are assigned to the fluorine atoms of products **4** and **9**, besides unreacted isomers **3** and **3′**, as given in Scheme 2.

The integrals of signals assigned to the difluoromethylene groups of VDF adjacent to HFP enable the calculation of the proportion of each molecule (from **3** to **9**); the values are summarized in Table 2.

Table 2 shows that the dehydrofluorination of isomers **3** and **3′** by NaOH is not quantitative. Molecules **7** and **8** are returned in low amounts (0.3% and 0.2% respectively), as the end-group of isomer **3′** (i.e., –CF(CF_3)–CF_2H) is considered to be inert to deprotonation by common bases. If isomer **3′** did undergo dehydrofluorination leading to molecule **8**, the terminal unsaturation would be expected to react rapidly with more hydroxide, and hydrolysis to form an internal olefin structure close to that of molecule **8** but containing an –OH link.

The absence of signals centered at −105, −125 and −175 ppm, which are attributed to the three fluorine atoms in a



Scheme 2. Possible structures of molecules **4–9** produced after dehydrofluorination of isomers **3** and **3′** with sodium hydroxide. Letters a–z are assigned to fluorine atoms of the characteristic signals in ^{19}F NMR spectra of molecules **3** and **3′** and **4–9**.

Table 1
Assignments of ^{19}F NMR peaks (according to Scheme 2), type of signals, coupling constants, and number of fluorine atoms after dehydrofluorination of **3**, **3′** into **4–9** molecules (Scheme 2)

Chemical shift in ^{19}F NMR (ppm)	Assigned fluorine atom in Scheme 2	Signal, coupling constant (Hz)	Number of fluorine atoms
−65.4; −66.2 (low intensity)	a, non-equivalent		2F
−68.9; −69.5	b, *cis* and *trans*	d.d., $^3J_{FF} = 9$, $^4J_{CFC=CF} = 23$	3F
−72.5; −72.8	c, c′	m	3F
−74.6; −75.0	d, d′	d.d.t.	3F
−76.2 (low intensity)	e	t.t., $^4J_{CFC=CF} = 8$	3F
−81.5	f	m	3F
−98.2 (low intensity)	g′	m	2F
−99.9	g	m, $^3J_{FH} = 13$	2F
−108.3	h′	m, $^3J_{FH} = 12$	2F
−108.9; −109.3	h, non-equivalent	d.d.t. = s, $^3J_{FH} = 13$, $^4J_{CFC=CF} = 13$, $^3J_{FF} = 12$	2F
−110.9	j′	m	2F
−111.5	j	m	2F
−112.3	k	m	2F
−113.0	l	m	2F
−113.4 (low intensity)	m (*cis* and *trans*)	m	1F
−114.4; −114.9	n, *cis* and *trans*	d.t.d.	1F
−118.3; −118.6	o, *cis* and *trans*	d.t.t., $^3J_{CF=CH(trans)} = 13$, $^3J_{CF=CH(cis)} = 11$	1F
−119.8	p, only *trans*	d.t.d.	1F
−121.7	q	m	2F
−122.8	r	m	2F
−123.2	s	m	2F
−124.4	AB system of t	AB system $J = 290$	2F
−126.3	u	m	2F
−127.8	AB system of t		2F
−129.4	AB system of t		2F
−131.5; −131.8	v *cis*	d.d.q., $^3J_{CF=CF} = 48$	1F
−133.1	w	d.d.q., $^2J_{FH} = 49$, $^3J_{FF} = 8$, $^4J_{FF} = 4$	2F
−134.6; −134.9	x *cis*	d.q.d., $^3J_{CF=CF} = 51$, $^4J_{CF=CCF} = 9$, $^3J_{FF} = 3$	1F
−155.2; −156.0	v *trans*	d.d.q., $^3J_{CF=CF} = 138$, $^4J_{CF=CCF} = 20$, $^3J_{FF} = 9$	1F
−162.6; −163.4	x *trans*	d.q.d., $^3J_{CF=CF} = 138$, $^4J_{CF=CCF} = 20$, $^3J_{FF} = 9$	1F
−188.4; −188.7	y and y′	m	1F
−214.7	z	d.q.t, $^2J_{FH} = 35$, $^3J_{FF(1)} = 11$, $^3J_{FF(1)} = 5$	1F

d, t, q and m stand for doublet, triplet, quartet and multiplet, respectively.

Table 2
Proportion of each molecule (from **3** to **9**) calculated from the ^{19}F NMR spectrum of the dehydrofuorination of **3** and **3′** isomers

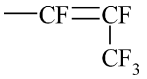
Molecules	Assigned fluorine atom	Chemical shift (ppm, ^{19}F NMR)	Integrals	Percentage (%)
3	j	−111.5	150.0	59.0
3′	g	−99.9	7.2	2.8
4	o	−118.3; −118.6	7.6	3.0
5	p	−119.8	15.4	6.1
6	n	−114.4; −114.9	12.4	4.9
7	m	−113.4	0.8	0.3
8	g′	−98.2	0.6	0.2
9	j′	−110.9	60.4	23.7

Structure of the species are given in Scheme 2.

trifluorovinyl end-group [56] as noted in $F_2C{=}CFC_3H_6OH$ [57], $F_2C{=}CFC_3H_6{-}SCOCH_3$ [58] or $F_2C{=}CFOAr{-}Br$ [59], indicates the absence of the dehydrofluorinated $F_2C{=}CFCF_2CF_2CH_2C_6F_{13}$ molecule which could be produced from the dehydrofluorination of **3** precursor.

Different ^{19}F NMR signals have shown that dehydrofluorination of isomer **3**, by a strong base, induced the elimination of HF from positions involving the "*tertiary*" fluorine (from HFP end-group) such as in the reaction of Scheme 3 [15,49–53,55].

The double bonds introduced from the dehydrofluorination of isomer **3** (Scheme 3) should lead to the isomeric structure (α), as shown below:



(α)

The presence of isomer **9** bearing (α) unsaturation was evident from the assignments of ^{19}F NMR signals and the coupling constants (in Table 1), as follows:

- two doublets of multiplets centered at −134.6 and −134.9 ppm (for fluorine atom "x" in *cis* configuration of molecules **5** and **9**) and −162.6 and −163.4 ppm (for fluorine atom "x" in *trans* configuration of molecules **5** and **9**) [31,54,60];
- two doublets of multiplets located at −131.5 and −131.8 ppm (for fluorine atom "v" in *cis* configuration of molecules **5** and **9**) and at −155.2 and −156.0 ppm (for fluorine atom "v" in *trans* configuration of molecules **5** and **9**) [31,54,60];
- two doublets of doublets ($^4J_{CFC=CF}$ = 23 Hz) centered at −68.9 and −69.5 ppm assigned to the three fluorine atoms of CF_3 group (signal "b") in *cis* and *trans* configurations, respectively [54].

In addition to this reaction, dehydrofluorination is also known to occur on the CH_2–CF_2 bond of the VDF unit adjacent to one normal, or reverse, HFP unit [1,3,61]. Scheme 4 represents the dehydrofluorination of CF_2–CH_2 group of the VDF unit adjacent to one normal HFP of molecule **9**.

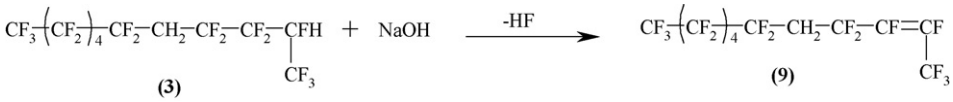
The evidence for such a reaction was obtained by ^{19}F NMR spectroscopy (Table 1) due to the presence of several signals assigned to the fluorine atom in CH=CF groups in molecules **4**–**6** [54], as follows:

- at −118.3 and −118.6 ppm, assigned to fluorine atom "o" of molecule **4** in *cis* and *trans* configurations, respectively [31,35,54];
- at −119.8 ppm, attributed to fluorine atom "p" of molecule **5** only in *trans* configuration because of steric hindrance [31,35,54];
- at −114.4 and −114.9 ppm, assigned to fluorine atom "n" of molecule **6** in *cis* and *trans* configuration, respectively [15,62].

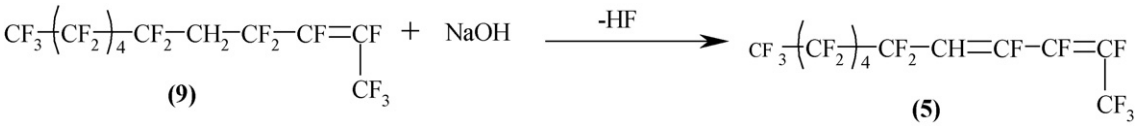
The dehydrofluorination of the VDF units is also evident by the ^{19}F NMR due to the shift of signal of the fluorine atom of CF_2 adjacent to VDF unit ($C_5F_{11}CF_2$–CH_2CF_2–HFP) from −113.0 to −108.9 and −109.3 ppm for normal HFP chaining, and from −112.3 to −108.3 ppm for reverse HFP chaining.

2.2.2. Characterization by ^1H NMR spectroscopy

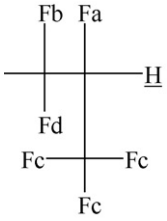
The ^1H NMR spectra of isomers **3** and **3′** and their respective products after dehydrofluorination in Fig. 1 confirm these results.



Scheme 3. Dehydrofluorination of "*tertiary*" fluorine of isomer **3** in the presence of sodium hydroxide, leading to molecule **9**.



Scheme 4. Reaction of molecule **9** with sodium hydroxide, leading to the dehydrofluorination of the CH_2–CF_2 group of VDF unit adjacent to HFP unit.



$^2J_{FaH}$ =42 Hz
$^3J_{FbH}$ =18 Hz
$^3J_{FcH}$ =5 Hz
$^3J_{FdH}$ =2 Hz

Scheme 5. Coupling constants between the proton and fluorine atoms F_a, F_b, F_c and F_d in **3** cotelomer.

The proton in the CFH group of $C_6F_{13}CH_2CF_2CF_2CFHCF_3$ molecule **3** (Fig. 1, spectrum a) couples with both adjacent and β-position fluorine atoms, with different coupling constants, as shown in Scheme 5.

The quintet centered at 3.47 ppm (protons C in Fig. 1, spectrum a) is assigned to CH_2 protons of VDF unit of isomer **3′**. In addition, the quintet centered at 3.29 ppm is assigned to CH_2 protons of isomer **3** (named A for spectrum a in Fig. 1).

Spectrum b in Fig. 1 shows the decrease of the signal of all protons, while a new complex signal centered at 6.20 ppm, assigned to CF=C*H*, is complicated and difficult to analyse. This confirms the dehydrofluorination of the CH_2–CF_2 unit in isomers **3** and **3′**. Thus, dehydrofluorination of isomers **3** and **3′** in the presence of a strong base induced the elimination of HF from hydrofluorinated groups containing a $CFHCF_3$, leading to unsaturated end-group α (–CF=CF(CF_3)) in isomer **3**. The CH_2–CF_2 group in the VDF unit adjacent to one normal or reverse HFP unit is also dehydrofluorinated, leading to a CF=CH group identified by ^{19}F and ^1H NMR spectroscopy. Although the telomer containing VDF and HFP was totally converted from the iodo perfluoroundecane compound to the reduced one, the yield of the reaction of dehydrofluorination of VDF unit was difficult to assess (14%). ^1H NMR spectroscopy only allowed to conclude that dehydrofluorination was not quantitative. Moreover, –CF(CF_3)–CF_2H of isomer **3′** underwent dehydrofluorination leading to molecule **8**, however the unsaturated terminal bond underwent rapid nucleophilic reaction with hydroxide, yielding an internal olefinic structure isomer of **8**.

2.3. Addition of 2-phenylethylamine onto $C_6F_{13}CH_2CF_2CF_2CFHCF_3$ (3) and $C_6F_{13}CH_2CF_2CF(CF_3)CF_2H$ (3′) isomers

After dehydrofluorination, the next step was to investigate the grafting of amines (Scheme 1), using Michael addition of the regenerated amine. The addition of 2-phenyl ethylamine onto model molecules **3** and **3′** was monitored by ^{19}F NMR spectroscopy to identify the site of grafting. Table 3 summarizes the main change between the chemical shifts in the ^{19}F NMR spectrum of dehydrofluorinated molecules **4–9** (given in Table 1), and ^{19}F NMR spectrum of the same molecules after reacting with 2-phenylethylamine.

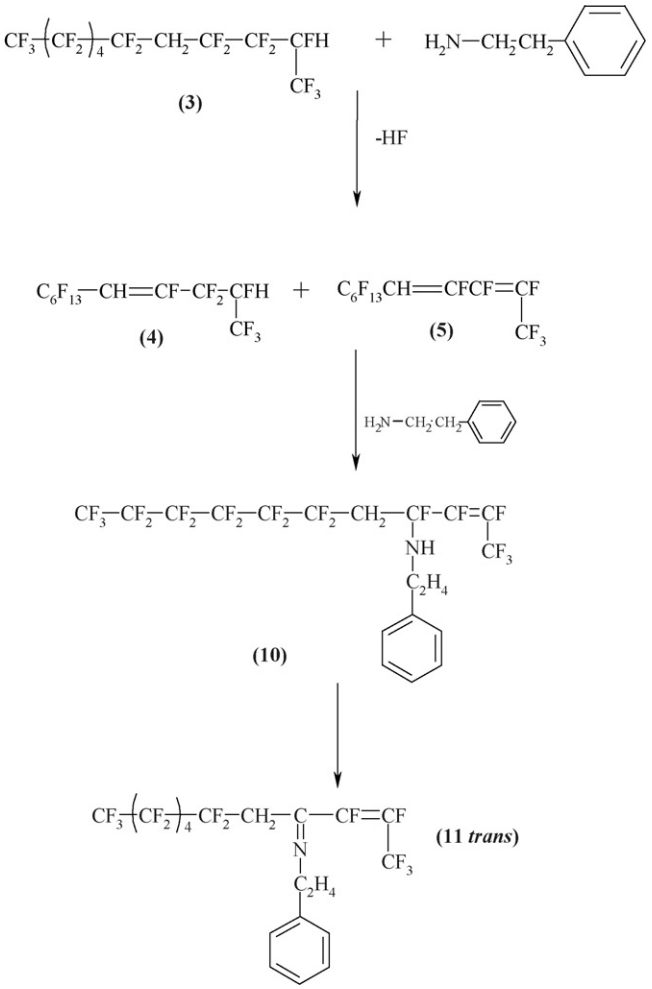
First, it is noted that the ^{19}F NMR spectrum of the total product mixture arising from the addition of 2-phenylethylamine to isomers **3** and **3′** is very similar to that of the total product mixture after dehydrofluorination of the same isomers with NaOH, except for the changes mentioned in Table 3. Table 3 shows that only molecules **4–6** underwent such an addition, because there appears to be a low amount of molecule **7**. Moreover, no modification can occur on molecule **7**, as the fluorine atom "m" is too hindered to undergo any addition of amine.

Table 3
Main modifications in the signals assigned to **4–9** molecules after addition of 2-phenylethylamine onto $C_6F_{13}CH_2CF_2CF_2CFHCF_3$ (**3**) and $C_6F_{13}CH_2CF_2CF(CF_3)CF_2H$ (**3′**) isomers

Absent	Present	Decreased	Assignments of peaks
−68.9	−73.2		b *cis* of **5**
−119.8			p of **5**
		−155.2; −156.0 and 162.6; −163.4	v and x *trans* of **5**
	−109.6	−109.3	h of **4** and **5**
	−117.5	−118.3	o *cis* of **4**
	−115.5	−114.9	n *trans* of **6**

The letters b, h, n, o, p, v and x correspond to the assignments of the fluorinated groups in Scheme 2.

The pathway of the grafting reaction is divided in two main steps (Scheme 1): when submitted to the 2-phenylethylamine, isomer **3** is first dehydrofluorinated, leading to molecules **4** and **5**. Then molecules **4** and **5** are submitted to the addition of the amine, leading to molecule (**11** *trans*), mentioned below.



Scheme 6. Dehydrofluorination and addition of 2-phenylethylamine onto molecule **3**.

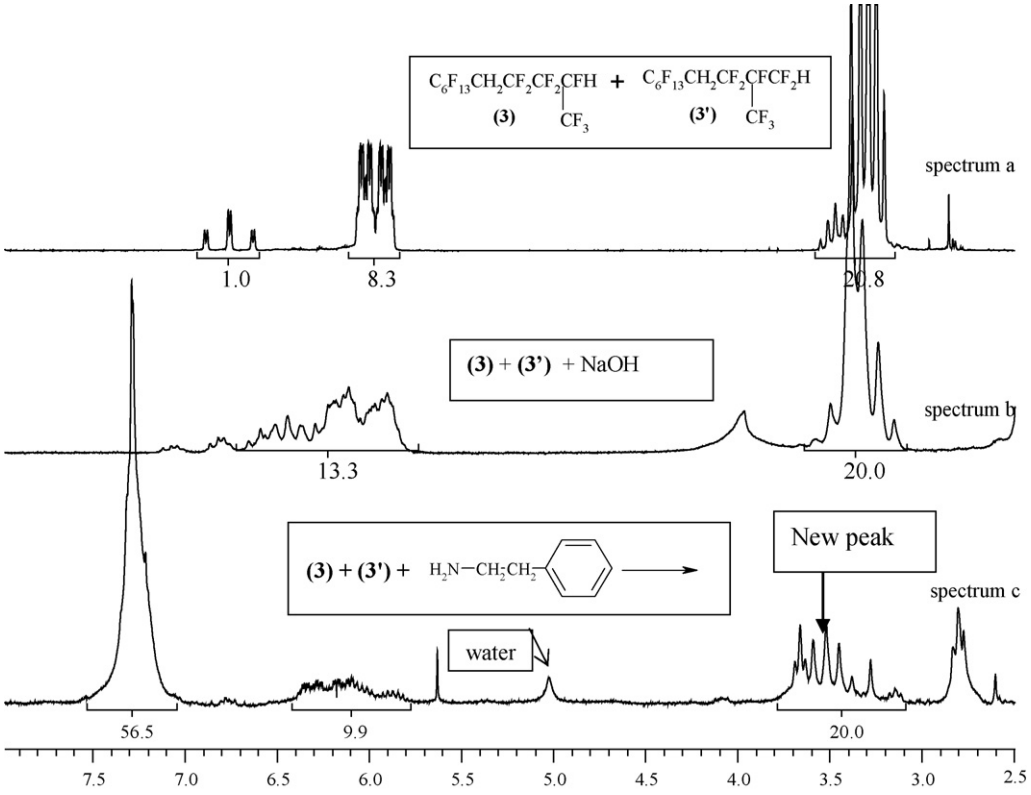


Fig. 2. ^{1}H NMR spectra of **3** and **3′** isomers (spectrum a); of **3** and **3′** isomers after dehydrofluorination with NaOH (spectrum b); and of **3** and **3′** isomers after addition of 2-phenylethylamine (spectrum c) (recorded in acetone d^6).

Indeed, for **4** two changes occurred: the integral of the signal of fluorine atoms ''h'' and ''o *cis*'' decreased. The decreasing of these peaks concomitant to the presence of two other signals located at −109.6 and −117.5 ppm, lead to the conclusion that molecule **3** was chemically changed into molecule **10**, after addition reaction of amine, as mentioned in Scheme 6. However, the addition of amine only occurred on the *cis* form of molecule **5**, probably due to steric hindrance.

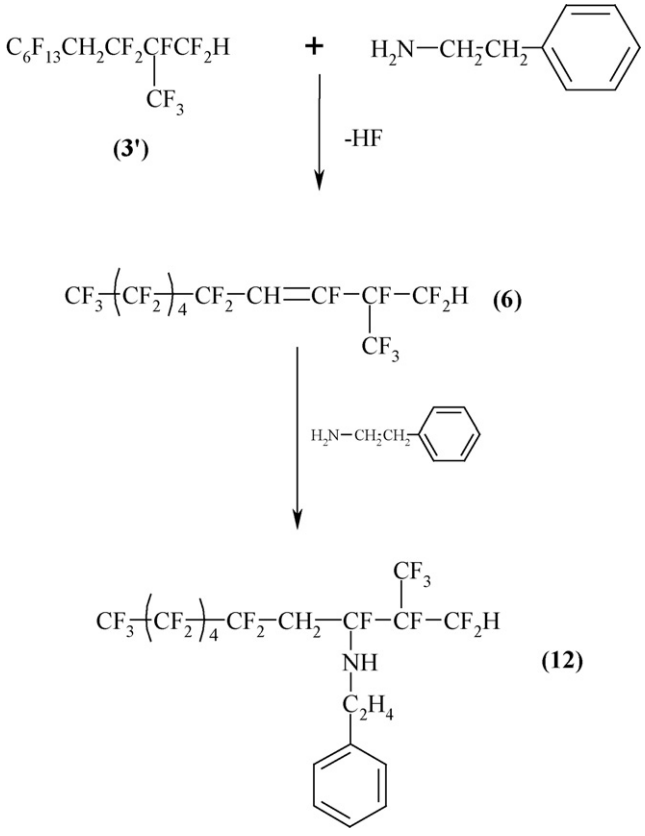
Molecule **5** underwent chemical modification, as indicated by the NMR signals. Those assigned to fluorine atoms ''h'' and ''p'' decreased and disappeared, respectively. In addition, the signals of fluorine atoms ''v and x in *trans* configuration'' only decreased. As for assignments of molecule **4**, the signal attributed to fluorine atom ''h'' was shifted upfield from −108.9 and −109.3 to −109.6 ppm. Because molecule **5** exists in its unique *trans* configuration for CF=CH group (''p'' *trans* configuration), the *trans* configuration molecule only underwent addition, leading to molecule **11** in *trans* configuration, as mentioned in Scheme 6.

Scheme 6 summarizes the addition reaction on both molecules **4** and **5**.

This result was confirmed by ^{1}H NMR spectroscopy, and is explained in Fig. 2.

Finally, molecule **6** underwent a significant change, as evidenced by the signal centered at −114.9 ppm, assigned to fluorine atom ''n *trans* configuration'' which decreased, while the presence of a few signal centered at −115.5 ppm was noted.

Hence, molecule **3′** reacted with amine to produce molecule **6** after partial dehydrofluorination. Then, the addition of amine yielded molecule **12**, as shown in Scheme 7.

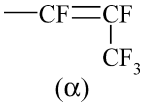


Scheme 7. Dehydrofluorination and addition of 2-phenylethylamine onto molecule **3′**.

However, molecule **12** is not stable and can undergo further dehydrofluorination to produce an imine.

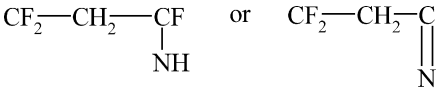
Fig. 2 represents the ^{1}H NMR spectra of molecules **3** and **3′** after dehydrofluorination in the presence of NaOH and after addition of 2-phenylethylamine.

An extraction with concentrated HCl permitted removal of all unreacted 2-phenylethylamine. The presence of the signal centered at 7.28 ppm, assigned to the aromatic protons of 2-phenylethylamine, provides evidence that the grafting of this amine onto isomers **3** and **3′** was successful. Moreover, the drastic decrease (from spectrum a to spectrum c of Fig. 2) of the multiplet centered at 5.95 ppm, assigned to end-group protons in isomer **3**, showed that these groups underwent a dehydrofluorination returning the following perfluorinated groups:

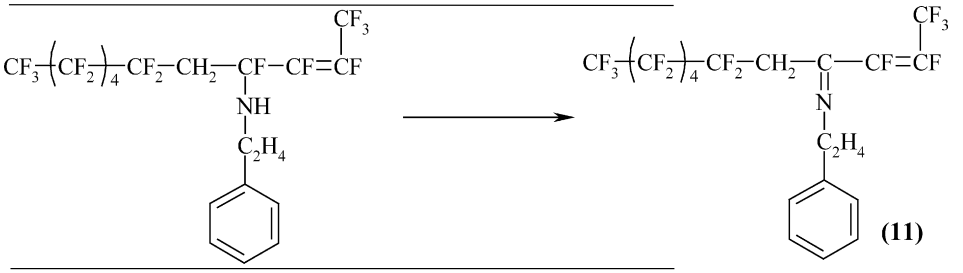


(α)

The decrease of the multiplet centered at 6.75 ppm and assigned to end-group protons of isomer **3′** was also noted, suggesting partial dehydrofluorination. As this signal is very close to that of the aromatic protons of the amine in spectrum c, it is difficult to provide a quantitative conclusion. The absence of a broad signal close to 5.10 ppm in spectrum c proves that there is no CF_2–CH=C–N bonds [34]. Moreover, the absence of any signal in spectrum c of Fig. 2 at 4.00 ppm highlights an absence of CF_2–C*H*–N groups [34]. Finally, taking the results from ^{1}H and ^{19}F NMR into account, the grafting of amine can lead to the following (β) and (χ) structures:



(β) (χ)



(11)

Spectrum c in Fig. 2 shows the presence of a new signal centered in 3.51 ppm which is assigned to the protons of the CH_2 group of the (χ) group [29]. Hence, the final step of the reaction pathway for grafting of amine can be confirmed by ^{1}H NMR spectroscopy.

Integrals of characteristic signals in spectrum c (Fig. 2) enable us to assess the yield of the addition of amine onto isomers **3** and **3′**, as given in the following equation:

$$\text{yield}\,(\%) = \frac{\int \text{peak centered at } 7.28\ \text{ppm}/5}{\int \text{signal ranging between } 3.30 \text{ and } 3.80\ \text{ppm}/2} \quad (4)$$

where the signals ranging between 3.30 and 3.80 ppm are assigned to CH_2 of VDF units of β and χ groups, and the signal centered at 7.28 ppm is assigned to the aromatic protons of the 2-phenylethylamine, which is added onto isomers **3** and **3′**. From the integrals of the signals in Fig. 2, Eq. (3) gives a yield of ca. 100%, which shows that each CF_2 of VDF units of isomers **3** and **3′** underwent addition of an amine.

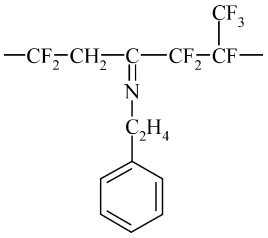
Thus, the ^{1}H NMR identification of isomers **3** and **3′** confirms that dehydrofluorination occurs mainly at "*tertiary*" fluorine and then on the CH_2–CF_2 bond [15,29,34] and that, importantly, dehydrofluorination is not quantitative. The ^{1}H NMR characterization also confirms the site for grafting of amines, and provides some explanation as to the reaction pathway that leads to an imine (Scheme 1). The addition of amine onto isomers **3** and **3′** is quantitative.

3. Conclusion

This research has provided some insight to the reaction pathway for the crosslinking (or grafting) of amines onto poly(VDF-*co*-HFP) copolymers. A new fluorinated model molecule containing a VDF/HFP diad was synthesized and was dehydrofluorinated and subsequently grafted to an amine. This was successfully carried out by thermal telomerization of HFP with $C_6F_{13}CH_2CF_2I$ leading mainly to $C_6F_{13}CH_2CF_2CF_2CFICF_3$. Second, its reduction selectively yielded $C_6F_{13}CH_2CF_2CF_2CFHCF_3$. The dehydrofluorination of that compound led to an unsaturated $C_6F_{13}CH{=}CFCF{=}CF(CF_3)$ molecule. The overall yield was 6%.

The addition of 2-phenylethylamine onto $C_6F_{13}CH_2CF_2CF_2$ $CFHCF_3$ model molecule led to the following molecule, with a quantitative conversion of the VDF/HFP cotelomer.

The addition of an amine supports the reaction of dehydrofluorination leading to the formation of the double bond. From the information gathered, it may be deduced that the dehydrofluorination of a poly(VDF-*co*-HFP) copolymer from sodium hydroxide leads to –CH=CF–$CF_2CF(CF_3)$– group. Unfortunately, the dehydrofuorination of the HFP units on model molecule **3** does not allow the same conclusion to be extrapolated for the dehydrofluorination of HFP units on a poly(VDF-*co*-HFP) molecule. The grafting of an amine onto a poly(VDF-*co*-HFP) copolymer returns the following structure:



Hence, it is expected that the grafting of amine onto poly(VDF-*co*-HFP) copolymers should selectively occur onto VDF units adjacent to HFP units in the configuration mentioned above. The methodology and suggested reaction pathway of grafting are currently under investigation for commercially available poly(VDF-*co*-HFP) copolymers.

4. Experimental

4.1. Materials

8-Iodo-7*H*,7*H*-perfluorooctane was synthesized either by thermal or redox telomerization of vinylidene fluoride (VDF) with perfluorohexyl iodide and purified by rectification as described in previous studies [11,15,24].

Hexafluoropropene (HFP) and 1,1,1,3,3-pentafluorobutane were kindly offered by Solvay S.A. 2-Phenylethylamine, sodium thiosulfate, tributylstannane, acetone, dichloromethane, potassium fluoride and sodium hydroxide were purchased from Aldrich (Saint Quentin Fallavier, France) and used as received.

4.2. NMR spectroscopy

The ^{1}H and ^{19}F NMR spectra were recorded at room temperature on Bruker AC 200, AC 250 and AC 400 instruments, using deuterated acetone as the solvent, and trimethylsilane, TMS (or CCl_3F) as the references for ^{1}H (or ^{19}F) nuclei. The letters s, d, t, q, qi and m stand for singlet, doublet, triplet, quartet, quintet and multiplet, respectively. Coupling constants and chemical shifts are given in Hz and ppm, respectively. The experimental conditions for ^{1}H (or ^{19}F) NMR spectra were as follows: flip angle 90° (or 30°), acquisition time 4.5 s (or 0.7 s), pulse delay 2 s (or 5 s), number of scans 16 (or 32) and a pulse width of 5 μs for ^{19}F NMR.

4.3. GC analysis

Gas chromatography (GC) was carried out on Delsi apparatus (model 330), fitted with a SE 30 column, 3 m × 1/8 in. (i.d.) under nitrogen pressure maintained at 0.6 bar at the entrance to the column. The injector and the detector were maintained at 255 and 260 °C, respectively. The heating program was regulated from 50 to 250 °C, with a heating rate of 15 °C min^{-1}. The GC apparatus was connected to a Hewlett Packard integrator (model 3390) that provided an automatic peak area calculation.

4.4. Telomerization of hexafluoropropene with 8-iodo-7H,7H-perfluorooctane

The end-capping reaction of $C_6F_{13}CH_2CF_2I$ by HFP was performed in a Parr 160 mL Hastelloy autoclave, equipped with a manometer, a rupture disk, inlet and outlet valves. It was equipped with a magnetic stirrer. The autoclave was left closed for 20 min and purged at 30 bar of nitrogen pressure to prevent any leakage, degassed and put under vacuum. Then, 40.12 g (7.9×10^{-2} mol) of pure $C_6F_{13}CH_2CF_2I$ (**1**), 14.21 g (9.5×10^{-2} mol) of hexafluoropropene and 10.53 g of 1,1,1,3,3-pentafluorobutane were introduced under nitrogen atmosphere. The temperature was maintained at 204 °C for 100 h. Post reaction, the autoclave was cooled in ice and unreacted monomer removed. After work up with sodium thiosulfate, the total product mixture was purified by distillation (bp: 93–97 °C/23 mmHg; yield 56%; $C_6F_{13}CH_2CF_2CF_2CFICF_3$ (90%) and $C_6F_{13}CH_2CF_2CF(CF_3)CF_2I$ (10%)) as a colorless liquid that turned pink with light. Then, these precursors were analysed by gas chromatography (GC) and characterized by ^{1}H and ^{19}F NMR spectroscopy.

4.4.1. 8-Iodo-7H,7H-perfluorooctane, $C_6F_{13}CH_2CF_2I$ (1) [24]

^{19}F NMR (acetone d^6, ppm) δ: −39.9 (–CF_2I, 2F); −80.8 (CF_3–, 3F); −111.9 ($CF_2CF_2CH_2$–, 2F); −121.7 (–$CF_2CF_2CH_2$, 2F); −122.7 ($CF_3C_2F_4CF_2$, 2F); −123.1 ($CF_3CF_2CF_2$, 2F); −126.2 (CF_3CF_2, 2F).

^{1}H NMR (acetone d^6, ppm) δ: 3.5 ($CF_2CH_2CF_2I$, $^{3}J_{HF}$ = 16.0 Hz, 2H).

4.4.2. 10-Iodo-7H,7H-perfluoroundecane, $C_6F_{13}CH_2CF_2CF_2CFICF_3$ (2) [21]

^{19}F NMR (acetone d^6, ppm) δ: −73.0 (–CF_2CFICF_3, 3F); −81.4 (CF_3CF_2, 3F); −107.6 ($CF_2CF_2CFICF_3$, AB system, 2F); −108.9 ($CH_2CF_2CF_2$, 2F); −112.0 ($CF_2CF_2CH_2$, 2F); −121.7 ($CF_2CF_2CH_2$, 2F); −122.8 ($CF_3C_2F_4CF_2$, 2F); −123.2 ($CF_3CF_2CF_2$, 2F); −126.3 (CF_3CF_2, 2F); −148.4 (CF_2CFICF_3, 1F).

^{1}H NMR (acetone d^6, ppm) δ: 2.9 ($CH_2CF_2CF_2CFICF_3$, $^{3}J_{HF}$ = 17.0 Hz, 2H).

4.4.3. 10-Iodo-7H,7H-perfluoro-9-methyldecane, $C_6F_{13}CH_2CF_2CF(CF_3)CF_2I$ (2′)

^{19}F NMR (acetone d^6, ppm) δ: −51.3 (–$CF(CF_3)CF_2I$, 2F); −70.3 (–$CF(CF_3)CF_2I$, 3F); −81.4 (CF_3CF_2–, 3F); −101.8 (CH_2CF_2CF, 2F); −112.0 ($CF_2CF_2CH_2$, 2F); −121.7 ($CF_2CF_2CH_2$, 2F); −122.8 ($CF_3C_2F_4CF_2$, 2F); −123.2 ($CF_3CF_2CF_2$, 2F); −126.3 (CF_3CF_2, 2F); −160.6 ($CF_2CF(CF_3)$, 1F).

^{1}H NMR [21] (acetone d^6, ppm) δ: 2.9 (CH_2CF_2, $^{3}J_{HF}$ = 17.0 Hz, 2H).

4.5. Reduction of $C_6F_{13}CH_2CF_2CF_2CFICF_3$ (2) and $C_6F_{13}CH_2CF_2CF(CF_3)CF_2I$ (2′) precursors

To 39.60 g of a mixture composed of $C_6F_{13}CH_2CF_2CF_2CFICF_3$ (3.36×10^{-2} mol) and $C_6F_{13}CH_2CF_2I$

(3.41×10^{-2} mol), 19.61 g of tributylstannane ($SnBu_3H$) (6.77×10^{-2} mol) was added dropwise in dichloromethane with stirring, at room temperature and under nitrogen for just over 10 min. It was observed to be exothermic and lead to decoloration of solution. Fifty weight percentage of potassium fluoride (KF) was added and after decantation and filtration of $SnBu_3F$, the fluorinated lower phase was characterized by GC and then by ^{19}F and ^{1}H NMR corresponding to a mixture containing $C_6F_{13}CH_2CF_2H$, $C_6F_{13}CH_2CF_2CF_2CFHCF_3$ and $C_6F_{13}CH_2CF_2CF(CF_3)CF_2H$. The reduction was quantitative.

Dichloromethane was evaporated and the products were distilled under vacuum to separate $C_6F_{13}CH_2CF_2H$ from $C_6F_{13}CH_2CF_2$–HFP–H (bp: 37–39 °C/43.2×10^{-3} mbar, colorless liquid).

4.5.1. 7H,7H,10H-perfluoroundecane, $C_6F_{13}CH_2CF_2CF_2CFHCF_3$ (3)

^{19}F NMR (acetone d^6, ppm) δ: −74.9 (–$CF_2CF(CF_3)H$, 3F); −81.8 (CF_3CF_2–, 3F); −112.0 ($CH_2CF_2CF_2$, 2F); −113.4 ($CF_2CF_2CH_2$, 2F); −121.9 ($CF_2CF_2CH_2$, 2F); −123.1 ($CF_3C_2F_4CF_2$, 2F); −123.4 ($CF_3CF_2CF_2$, 2F); −126.6 (CF_3CF_2–, 2F); −127.4 (CF_2CF_2CF, AB system, J = 320 Hz, 2F); −214.0 ($CF_2CF(CF_3)$, 1F).

^{1}H NMR (acetone d^6, ppm) (Fig. 1, Scheme 5): 3.29 (qi, $CF_2CH_2CF_2CF_2$, $^{3}J_{FH}$ = 17 Hz, 2H); 5.96 (ddqd, $CF_bF_dCF_aH(CF_{c3})$, $^{2}J_{F_aH}$ = 42 Hz, $^{3}J_{F_bH}$ = 18 Hz, $^{3}J_{F_cH}$ = 5 Hz, $^{3}J_{F_dH}$ = 2 Hz, 1H).

4.5.2. 7H,7H,10H-perfluoro-9-methyldecane, $C_6F_{13}CH_2CF_2CF(CF_3)CF_2H$ (3′)

^{19}F NMR (acetone d^6, ppm) δ: −72.8 ($CF(CF_3)CF_2H$, 3F); −81.8 (CF_3CF_2–, 3F); −99.9 (CH_2CF_2CF, 2F); −113.4 ($CF_2CF_2CH_2$, 2F); −121.9 ($CF_2CF_2CH_2$, 2F); −123.1 ($CF_3C_2F_4CF_2$, 2F); −123.4 ($CF_3CF_2CF_2$, 2F); −126.6 (CF_3CF_2–, 2F); −133.1 ($CF(CF_3)CF_2H$, 2F); −188.8 (CF_2CF(CF3), 1F).

^{1}H NMR (acetone d^6, ppm) (Fig. 1) δ: 3.3 (qi, $CF_2CH_2CF_2$, $^{3}J_{FH}$ = 17 Hz, 2H); 6.8 (td, –$CF(CF_3)CF_2H$, $^{2}J_{FH}$ = 51 Hz, $^{3}J_{FH}$ = 6 Hz, 1H).

4.6. Dehydrofluorination of $C_6F_{13}CH_2CF_2CF_2CFHCF_3$ (3) and $C_6F_{13}CH_2CF_2CF(CF_3)CF_2H$ (3′)

To 5.01 g (9.0×10^{-3} mol) of a mixture of **3** and **3′**, 0.56 g of NaOH (1.5 equiv.) was added at room temperature in acetone and the mixture stirred for 4 h. Without further treatment, the product was analyzed by ^{19}F and ^{1}H NMR spectroscopy. The total product mixture was composed of several compounds (from **4** to **9**) characterized by ^{19}F and ^{1}H NMR spectroscopy and reported in Table 1. The dehydrofluorination of isomers **3** and **3′** was not quantitative:

1. the mol% of dehydrofluorinated VDF units was 14.2%,
2. the mol% of dehydrofluorinated HFP units was 30.4%.

4.7. Addition of 2-phenylethylamine

To 2.54 g (5.0×10^{-3} mol) of a mixture of **3** and **3′** in acetone, 0.86 g (8.0×10^{-3} mol) of 2-phenylethylamine (1.5 equiv.) was added and stirred at 50 °C for 4 h. The mixture was washed with concentrated HCl (35%). All 2-phenylethylamine that did not react was dissolved in HCl, whereas the organic phase was extracted with methylene chloride. The extracted phase was analyzed by ^{1}H and ^{19}F NMR spectroscopy. Addition of the aromatic containing amine onto isomers **3** and **3′** was quantitative.

Acknowledgments

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