

Synthesis and copolymerization of fluorinated monomers bearing a reactive lateral group.

Part 20*. Copolymerization of vinylidene fluoride with 4-bromo-1,1,2-trifluoroethylene

J. Guiot^a, M.-A. Néouze^b, L. Sauguet^a, B. Améduri^a, B. Boutevin^a

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

^bLaboratoire de Chimie Moléculaire et Organisation du Solide, Université Montpellier II, Place Eugène Bataillon, 34095 Montpellier, France

ABSTRACT

The radical copolymerization of vinylidene fluoride (VDF) with 4-bromo-1,1,2-trifluorobut-1-ene (C₄Br) is presented. That bromofluorinated alkene was synthesized in three steps starting from the addition of bromine onto chlorotrifluoroethylene (CTFE). In contrast to the ethylenation of 1,1-difluoro-1,2-dibromochloroethane that failed, that of 2-chloro-1,1,2-trifluoro-1,2-dibromoethane was optimized leading to 2-chloro-1,1,2-trifluoro-1,4-dibromobutane. Then kinetics of copolymerization of VDF with this brominated monomer led to the determination of the reactivity ratios : $r_{\text{VDF}} = 0.96 \pm 0.67$ and $r_{\text{C}_4\text{Br}} = 0.09 \pm 0.63$ at 50°C. The suspension copolymerization was also carried out, and the chemical changes of the resulting bromo-containing PVDFs were attempted and consisted in elimination or nucleophilic substitution of the bromine mainly.

KEY WORDS

vinylidene fluoride ; radical copolymerization ; reactivity ratio ; 4-bromo-1,1,2-trifluorobut-1-ene ; NMR spectroscopy

* [Part 19 : see reference 60]

GRAPHICAL ABSTRACT

Synthesis and copolymerization of fluorinated monomers bearing a reactive lateral group. Part 20.

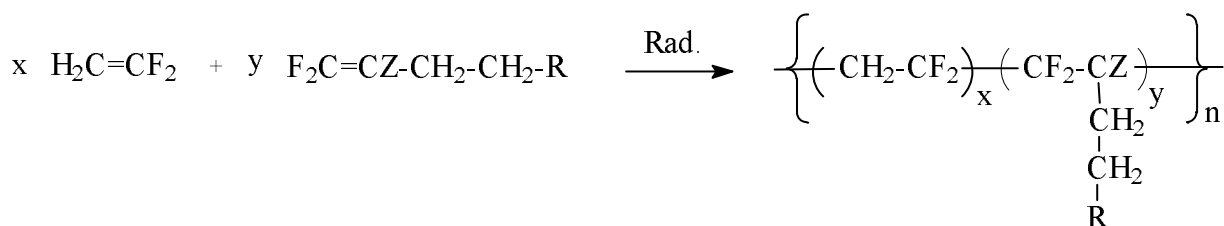
Copolymerization of vinylidene fluoride with 4-bromo-1,1,2-trifluoroethylene

J. Guiot^a, M.-A. Néouze^b, L. Sauguet^a, B. Améduri^a, B. Boutevin^a

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

^bLaboratoire de Chimie Moléculaire et Organisation du Solide, Université Montpellier II, Place Eugène Bataillon, 34095 Montpellier, France

The synthesis of bromine-containing monomers and their radical copolymerization with vinylidene fluoride (VDF) was achieved:



R = Br, N⁺R₃Br⁻ or other group; Z=F or H

The kinetics of copolymerization of VDF with F₂C=CFC₂H₄Br (C4Br) led to the determination of the reactivity ratios : r_{VDF} = 0.96 ± 0.67 and r_{C4Br} = 0.09 ± 0.63 at 50°C. The suspension copolymerization was also carried out.

INTRODUCTION

Polyvinylidene fluoride¹ (PVDF) exhibits very interesting piezo and pyroelectrical properties and other characteristics (such as chemical inertness to acids and solvents except DMF, DMSO, trifluorotoluene and dimethyl acetamide, low permeability, resistance to nuclear radiations) that enable it to be used in many applications (loud speakers, piano keys, IR detectors, paints and coatings and in various fields of mine, food, biomedical and engineering industries). However, its high crystallinity content, low solubility and base sensitivity are limitations. To try to overcome such drawbacks, hexafluoropropene (HFP) or chlorotrifluoroethylene (CTFE) were successfully copolymerized with VDF or terpolymerized with functional fluorinated vinyl ethers or other cure site monomers.

The copolymerization of vinylidene fluoride (or 1,1-difluoroethylene, VDF) was studied by numerous authors. Most chemical industries involved in the synthesis of VDF produced copolymers of VDF that have already been produced in industrial scales. Functional fluoro-olefin based-copolymers can be prepared by reaction with a comonomer, either bearing the expected functional group or a group able to bring the appropriate function by chemical modification²⁻⁷. The subsequent lateral functional group of the polymer provides specific and complementary properties : adhesion for carbonyl groups⁸, solubility for a cyclohexyl group⁹, crosslinking ability from hydroxydes or epoxides^{3,7,10-14}, surface properties for a perfluoro-group¹⁵ and good hydrophilic properties combined with resistance to heat and chemicals for phosphonated functions¹⁶⁻¹⁸.

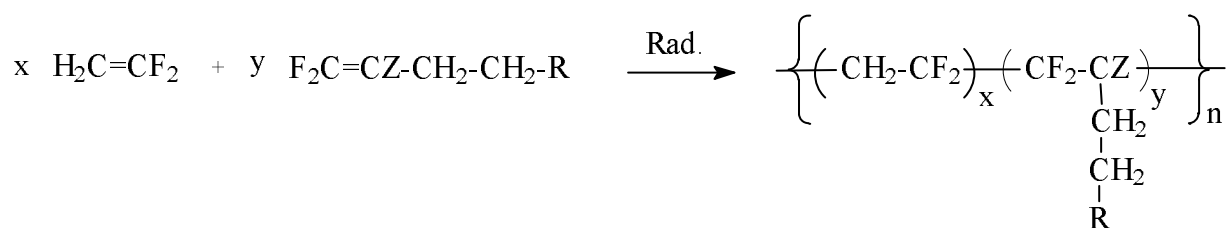
In order to enhance the properties of these fluorinated copolymers (increase of molecular weight, insolubility, thermal and mechanical properties), their crosslinking is recommended. It can be achieved either from crosslinkable agents (such as polyamines¹⁹⁻²⁵, polyphenols^{24,26-29}, or peroxide/triallyl isocyanurate systems^{30,31}) or from the use of cure site monomers (CSM) involved first in terpolymerization³². These CSMs can possess a bromine atom³³, a nitrile³⁴, hydroxy³⁵ or thioacetoxyl³⁵ end-groups.

Several halogenated monomers such as $\text{CF}_2=\text{CX-R-Br}$, with $\text{X}=\text{H}$ or F , have already been synthesized^{33,36-39}. Among them, 4-bromo-1,1,2-trifluorobut-1-ene ($\text{CF}_2=\text{CF-CH}_2\text{-CH}_2\text{-Br}$, C_4Br) and 4-bromo-1,1-difluorobut-1-ene ($\text{CF}_2=\text{CH-CH}_2\text{-CH}_2\text{-Br}$) are interesting since they exhibit a fluorinated double bond, what makes them as suitable comonomers to show a good reactivity towards VDF. So far, those monomers have only been used as nematocides, insecticides and pesticides or as intermediates in their synthesis⁴⁰⁻⁴⁵. Furthermore, the literature shows that few copolymerizations of these halogenated monomers with VDF have

been studied. In such copolymers, bromine atom enables crosslinking methods already applied onto other copolymers, essentially elastomers. In addition, bromine considered as an interesting atom, can bring other functionalities by its modification. Thus, the main goals of this study are the optimization of the synthesis of brominated comonomers such as 4-bromo-1,1,2-trifluorobut-1-ene (C_4Br) and 4-bromo-1,1-difluorobut-1-ene, and their copolymerizations with VDF.

RESULTS AND DISCUSSION

The synthesis of functional PVDFs was investigated by the radical copolymerization of vinylidene fluoride (VDF) with other functional fluoromonomers which can be summarized by the following scheme :



Z = F and R = Br, C₄Br

R = Br, N⁺R₃Br⁻ or other groups (Scheme 1)

1. Synthesis of fluorinated monomers

This study deals with the synthesis of 4-bromo-1,1,2-trifluorobut-1-ene (CF₂=CF-CH₂-CH₂-Br, C₄Br) and 4-bromo-1,1-difluorobut-1-ene (CF₂=CH-CH₂-CH₂-Br). Indeed, those monomers can be interesting precursors for the synthesis of other fluorinated functional monomers, as described in Scheme 1.

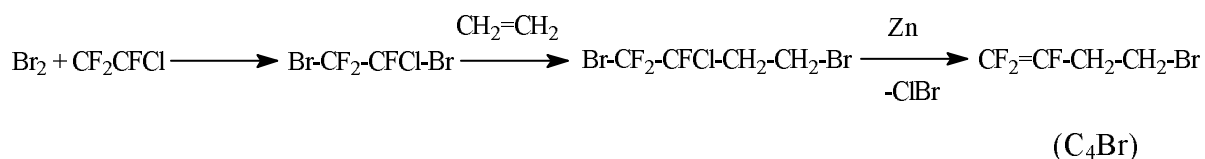
In this paper, we only focus on the synthesis of monomers bearing a quaternary ammonium function (CF₂=CZ-CH₂-CH₂-NR₃⁺/Br⁻). Indeed, those monomers lead to PVDF with quaternary ammonium sites by radical copolymerization with VDF. Such functional polymers can be used as anion exchange membranes in many fields like electrolysis in acid recycling process of industrial salted effluents.

The first goal of this study consists in the synthesis of CF₂=CZ-CH₂-CH₂-Br (Z = H or F).

1.1. Synthesis of CF₂=CF-CH₂-CH₂-Br (C₄Br)

The synthesis of this monomer was carried out in a three step-reaction : i) bromination of the chlorotrifluoroethylene (CTFE); ii) radical addition of Br-CFCI-CF₂-Br onto ethylene; iii)

dehalogenation of the precursor Br-CF₂-CFCI-CH₂-CH₂-Br with zinc dust, in order to obtain monomer C₄Br as follows :



1.1.a Synthesis of 1,2-dibromo-1-chloro-1,2,2-trifluoroethane (Br-CF₂-CFCI-Br)

In contrast to numerous studies concerning the radical addition of iodine monochloride (ICl) onto chlorotrifluoroethylene (CTFE)⁴⁶⁻⁴⁸ or that of I-Br onto CTFE⁴⁹⁻⁵⁰, the addition of bromine onto CTFE was scarcely investigated^{51,52}. These reactions were carried out in autoclave or in Carrius tube in 85% yield. We propose the optimisation of this reaction and the improvement of the process.

This reaction was first realized in batch in a Hastelloy autoclave leading to a yield of 90% about bromine and 81% about CTFE. However, as bromine is a corrosive reactant for the reactor, this method was given up. Consequently, the product was obtained from a "bubbling process" under atmospheric pressure (CTFE directly bubbled with a low flow in a bromine solution). In these conditions, the yields reached 99% about CTFE and 100% about bromine. The resulting product (Br-CF₂-CFCI-Br) was a colorless liquid (that evidenced the absence of Br₂) and was characterized by ¹⁹F NMR spectroscopy.

The ¹⁹F NMR spectrum of that halogenated ethane shows an ABX system, with the AB part centered at -60.0 ppm, and the X part located at -69.3 ppm, confirming a previous study⁵².

1.1.b Synthesis of 1,4-dibromo-2-chloro-1,1,2-trifluorobutane (Br-CF₂-CFCI-CH₂-CH₂-Br)

The telomerization of fluorinated olefins with Br-CF₂-CFCI-Br has already been described in the literature^{7,52,53} just like the ethylenation of diiodinated telogens^{54,55}. For the radical addition of Br-CFCI-CF₂-Br onto ethylene, to our knowledge only the mechanism was described⁵⁶.

This few information pushed us to study the influence of different parameters in order to optimize this reaction, i.e. to obtain the maximum yield of monoadduct [Br-CF₂-CFCI-(CH₂-CH₂)-Br], while limiting the amount of diadduct [Br-CF₂-CFCI-(CH₂-CH₂)₂-Br or Br-CH₂-CH₂-CF₂-CFCI-CH₂-CH₂-Br]. The results are summarized in Table 1. In that purpose, a

standard reaction was carried out with *tertio*-butanol as the solvent and *tertio*-butyl cyclohexyl peroxydicarbonate (P 16-S) as the initiator (exp. 1). Indeed, *tertio*-butanol does not lead to any transfer reactions and is considered as a good solvent for ethylene⁵⁷. Then, other reactions were performed with the step by step modification of one parameter : ethylene proportion, heating-rate, solvent quantity. However, the $C_0 = [\text{initiator}]_0 / [\text{ethylene}]_0$ initial molar ratio remained 0.03 in all these experiments (exp. 2 to 6).

Table 1 summarizes the conditions of these different experiments and their respective influences on the yields of the products (especially mono- and diadduct).

(i) Influence of the excess of ethylene (experiments 1 and 2)

As expected, the excess of ethylene favors the formation of the diadduct. From experiment 2 (1.12 fold excess of ethylene) we found $[\text{BrCTFE-E-E-Br}] / ([\text{BrCTFE-E-Br}] + [\text{BrCTFE-E-E-Br}]) = 32.6\%$ which means that one third of the telomer was the diadduct. So, it was worth keeping stoichiometric quantities of ethylene to 1,2-dibromo-1,1,2-trifluoroethane.

(ii) influence of the heat (experiments 3 and 4 compared to 1)

In experiments 3 and 4, the temperature of the autoclave was increased to 45°C and 55°C respectively, in contrast to experiment 1 that occurred at ambient temperature. By comparison of $[\text{BrCTFE-E-E-Br}] / [\text{BrCTFE-E-Br}]$ ratios of these three experiments, it can be deduced that heating favors the formation of the diadduct.

(iii) Influence of the solvent quantity (experiments 5 and, 6 compared to 1)

In experiment 1, six molar equivalents of *tertio*-butanol with respect to the brominated compound were introduced, while a three fold-molar excess only was used in experiment 5. This change led to an increase of the yield of monoadduct without any variation of the diadduct. Besides, this statement was confirmed by experiment 6 (1.5 equivalents of solvent). A decrease of the solvent amount, without any influence on the exotherm intensity, favored the formation of the monoadduct. This is probably due to the solubility of ethylene in *tertio*-butanol that enabled a more homogeneous medium.

The mechanism proposed in Scheme 2 is that of a classical radical telomerization.

Finally, this ethylenation reaction was optimized by controlling the heating-rate, keeping stoichiometric conditions between ethylene and Br-CF₂-CFCl-Br and decreasing the amount of solvent. The overall yields of monoadduct in these conditions reached 70% after distillation. This monoadduct was characterized by ¹H NMR and ¹⁹F NMR spectroscopy.

The ¹H NMR spectrum shows two complex multiplets centered at 2.8 and 3.6 ppm assigned to methylenes in CFCI-CH₂- and CH₂-CH₂-Br groups, respectively. The ¹⁹F spectrum exhibits an ABX system, where X and AB parts are located at -118.5 and -61.8 ppm, respectively. By comparison with the ¹⁹F NMR spectrum of Br-CF₂-CFCl-Br, it is noted that AB part (assigned to CF₂) has a quasi similar chemical shift (resp. -61.8 and -60.0 ppm) while X part (assigned to CF) has undergone a high field shift from -69.3 (in Br-CF₂-CFCl-Br) to -118.6 ppm.

In addition, the absence of Br-CH₂-CH₂-CF₂-CFCl-CH₂-CH₂-Br diadduct was evidenced by ¹H and ¹⁹F NMR spectra that show the absence of the signals assigned to CH₂-CF₂ group.

1.1.c. Synthesis of CF₂=CF-CH₂-CH₂-Br

The conditions of dehalogenation were determined from a previous study on the dechlorination of Cl-CF₂-CFCl-(CH₂)₃-OH⁵⁸. So, a 2.5 fold excess of zinc dust was used as the reductive agent about Br-CF₂-CFCl-CH₂-CH₂-Br. This reaction was catalysed by Br₂. The drop-wise addition of Br-CF₂-CFCl-CH₂-CH₂-Br was realised under ultra sound system (U.S.), at 30°C in order to limit the concentration of precursor and to limit the exotherm in the mixture. The reaction was monitored by Gas Chromatography. The conversion of Br-CF₂-CFCl-CH₂-CH₂-Br into CF₂=CF-CH₂-CH₂-Br can be measured by calculating the area of the GC peak at 5.6 min attributed to Br-CF₂-CFCl-CH₂-CH₂-Br, and that assigned to CF₂=CF-CH₂-CH₂-Br (with a retention time of 1.5 min). It was noted that the reaction was quasi instantaneous and very exothermic. Br-CF₂-CFCl-CH₂-CH₂-Br was totally converted into CF₂=CF-CH₂-CH₂-Br (C₄Br). C₄Br was obtained in 79% yield after distillation and it was characterized by ¹H and ¹⁹F NMR spectroscopy. Its ¹H NMR spectrum shows a triplet (³J_{HH} = 6.7 Hz) located at 3.5 ppm and a doublet (³J_{HF} = 21.0 Hz) of doublets (³J_{HH} = 6.8 Hz) of doublets (⁴J_{HF} = 3.5 Hz) of triplets (⁴J_{HF} = 2.9 Hz) centered at 2.81 ppm, assigned to methylene groups in CH₂-CH₂-Br and CF-CH₂-CH₂ respectively. The ¹⁹F NMR spectrum of C₄Br exhibits the characteristic doublets of doublets of triplets centered at -105, -125 and -180 ppm assigned to the three fluorine atoms in CF₂=CF-CH₂- end-group.

Finally, the $\text{CF}_2=\text{CF}-\text{CH}_2-\text{CH}_2-\text{Br}$ monomer was synthesized in three step reaction with an overall yield of 56% from CTFE.

1.2 Synthesis of $\text{CF}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{Br}$

The method is similar to that used for the synthesis of C_4Br . It consists in three steps : the bromination of 2-chloro-1,1-difluoroethylene (CDFE) to generate the $\text{Br}-\text{CF}_2-\text{CHCl}-\text{Br}$, followed by an ethylenation and finally the dehalogenation of $\text{Br}-\text{CF}_2-\text{CHCl}-\text{CH}_2-\text{CH}_2-\text{Br}$.

1.2.a. Synthesis of $\text{Br}-\text{CF}_2-\text{CHCl}-\text{Br}$

That reaction was carried out in the same conditions as these of the bromination of CTFE. Temperature was set at 35°C , but the temperature increased up to 80°C because of that exothermic reaction. After the excess of halogenated olefin was degassed, $\text{Br}-\text{CF}_2-\text{CHCl}-\text{Br}$ was distilled (b.p. = 117°C) and the yield reached 82%.

The ^{19}F NMR spectrum shows an AB system centered at -55.1 ppm while the ^1H NMR exhibits a quartet at 5.9 ppm assigned to the proton of CHClBr end group.

The brominations of fluorinated olefins such as tetrafluoroethylene and chlorotrifluoroethylene were already carried out^{51,52}, and gave also good yields with 2-chloro-1,1-difluoroethylene.

The second step concerned the ethylenation reaction of $\text{Br}-\text{CF}_2-\text{CHCl}-\text{Br}$.

1.2.b. Synthesis of $\text{Br}-\text{CF}_2-\text{CHCl}-\text{CH}_2-\text{CH}_2-\text{Br}$

$\text{Br}-\text{CF}_2-\text{CHCl}-\text{CH}_2-\text{CH}_2-\text{Br}$ has never been reported in the literature. The optimization of the above ethylenation reaction has led to the following reaction conditions : a slow increase of heating, an initial $[\text{CH}_2=\text{CH}_2]_0/[\text{Br}-\text{CF}_2-\text{CHCl}-\text{Br}]_0$ molar ratio equal to 1, initial $[\text{Br}-\text{CF}_2-\text{CHCl}-\text{Br}]_0/[\text{tBuOH}]_0$ molar ratio equal to 0.67 and an initial ($C_0 = [\text{initiator}]_0 / [\text{CH}_2=\text{CH}_2]_0$) molar ratio of 0.03. Two reactions of ethylenation of $\text{BrCF}_2\text{CHClBr}$ were attempted in these conditions at 45°C . However, in these both reactions, it was noted that neither the expected exothermal phenomenon occurred, nor any drop of pressure, which evidences that ethylene was not consumed. This was confirmed by both the total release of ethylene after degassing and by the ^{19}F NMR spectrum of the total product mixture that only showed the signals of

Br-CF₂-CHCl-Br telogen. This unsuccessful result may arise from the C-Br bond which is stronger in CHCl-Br and in CF₂-Br groups than in CFCI-Br.

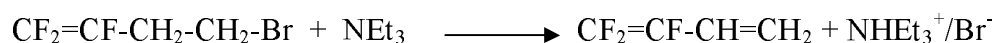
This result is surprisingly since the ethylenation of Br-CF₂-CF₂-Br was already achieved. This unsuccessful addition can be by the CHCl-Br end-group which is not electronwithdrawing enough to enable a weak dissociation energy of Br bond.

Therefore, it was not possible to synthesize Br-CF₂-CHCl-CH₂-CH₂-Br and, consequently, CF₂=CH-CH₂-CH₂-Br was not obtained, since the radical addition of Br-CF₂-CHCl-Br onto ethylene did not occur. Hence, the modification of brominated monomers was only carried out with C₄Br.

1.3. Synthesis of CF₂=CF-CH₂-CH₂-NEt₃⁺/Br⁻

Nucleophilic substitution of bromine by triethylamine enable the synthesis of original monomer bearing a quaternary ammonium. From two triethylamine molar equivalents for one C₄Br for 10 hours. The ¹⁹F NMR spectrum of the total product mixture indicated the presence of C₄Br (characteristic signals: -103.4, -123.0 and -177.5 ppm), and also the signal assigned to another characteristic system from the CF₂=CF-Y- group (Figure 1).

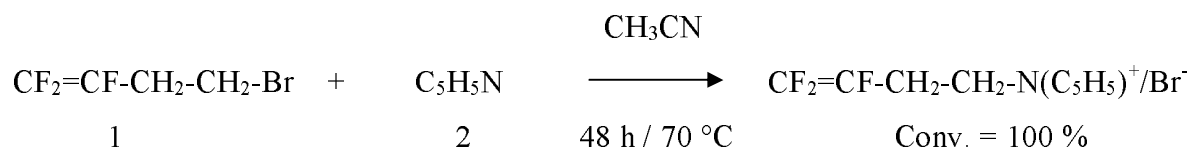
The ¹⁹F NMR spectrum of the white solid does not show any fluorine atom. Indeed, this hydrosoluble white solid, resulting from the dehydrobromination of C₄Br is hydrogenotriethylamine bromide:



The signals noted in the ¹⁹F NMR spectrum of the total product mixture (Figure 1), correspond to these of CF₂=CF-CH=CH₂ conjugated diene. It indicates that triethylamine is a strong base (pK_a = 10.75) which could easily react with the proton in α position about the double bond. That is why the second test was performed with a weaker base, pyridine, (pK_a = 5.25), in order to produce a monomer bearing a pyridinium function: CF₂=CF-CH₂-CH₂-NC₅H₅⁺/Br⁻.

1.4 Synthesis of CF₂=CF-CH₂-CH₂-NC₅H₅⁺/Br⁻ (C₄Py)

Using two pyridine equivalents about C₄Br after 48 hours at 70°C led to a quantitative transformation into quaternary ammonium CF₂=CF-CH₂-CH₂-NC₅H₅⁺/Br⁻, as follows:



After purification, the product was a dark solid at ambient temperature, that became a very viscous liquid at about 50°C. This product was characterized by ^1H (Figure 2) and ^{19}F NMR spectroscopy.

Two pseudo allylic halogenated monomers were synthesized in 56 % about CTFE yield: $\text{CF}_2=\text{CF}-\text{CH}_2-\text{CH}_2-\text{Br}$ (C_4Br) and $\text{CF}_2=\text{CF}-\text{CH}_2-\text{CH}_2-\text{NC}_5\text{H}_5^+/\text{Br}^-$ (C_4Py) which are original comonomers for the radical copolymerization with VDF. These copolymerizations have two goals : first, a kinetics of copolymerization was achieved to assess the reactivity ratios of both comonomers, and the study of potential transfer reactions to the monomer, on the CH_2 group in α position of the double bond (as known for fluoro allylic monomers)⁵⁹. Second, the synthesis of functional PVDF by chemical modification of poly(VDF-*co*- C_4Br) copolymers.

2. Radical copolymerizations of VDF with C_4Br and with C_4Py

The copolymerization of vinylidene fluoride (VDF) with C_4Py and C_4Br enables the direct synthesis of original PVDFs bearing a bromine atom and a pyridinium lateral function, respectively.

2.1 Copolymerization of VDF with C_4Py

The radical copolymerizations of VDF and C_4Py were carried out in acetonitrile, for 16 hours, in the presence of two different initiators: *tertio*-butyl peroxyvalate (TBPPI) at 70°C and di-*tertio*-butyl peroxide (DTBP) at 140°C. The initial $[\text{VDF}]_0/([\text{VDF}]_0+[\text{C}_4\text{Py}]_0)$ molar ratios were 0.90 and 0.95, respectively. After reaction and purification the total product mixtures were analyzed by ^{19}F NMR. In these spectra, only the characteristic signals of C_4Py were noted. This evidences that this monomer did not copolymerize with VDF, but even strongly inhibited the homopolymerization of VDF. This lack of reactivity may arise from the presence of a pyridinium ring as observed in the copolymerization of VDF with 4-bromotrifluorovinyloxy-benzene⁶⁰ that failed. Hence, no further investigation was carried out.

2.2 Copolymerization of VDF with C₄Br

2.2.a Kinetics of copolymerization

In order to determine the reactivity ratios of VDF and CF₂=CF-CH₂-CH₂-Br, a kinetics of copolymerization was performed. The first step of this study concerned the determination of the conditions of reaction which made the conversion of monomers lower than 10%, in order to use the Tidwell and Mortimer method⁶¹. So, four experiments were carried out in acetonitrile at 50°C. In each reaction, the initial molar ratio ([VDF]₀/([VDF]₀+ [C₄Br]₀) was 0.75. *Tertio*-butyl peroxyvalate (TBPPI) was used as initiator with an initial [TBPPI]₀/([VDF]₀+ [C₄Br]₀) molar ratio of 0.02. The respective reaction times were 0.5, 1.0, 2.0 and 4.0 hours. After reaction, the total product mixtures were analyzed by ¹⁹F NMR, the spectra of which have shown neat signals centered at -164.0 ppm (CF₂-C $\underline{\text{F}}$ (CH₂-CH₂-Br) in the co polymer) and -177.5 ppm (CF₂=C $\underline{\text{F}}$ -CH₂-CH₂-Br in the monomer) (Figure 3) with *I*₁ and *I*₂ integrals, respectively. C₄Br conversion was assessed as follows (equation 1):

$$\text{Conversion (\%)} = \frac{I_1}{I_1 + I_2} \times 100 \quad (\text{equation 1})$$

It was observed that after four hours, C₄Br conversion reached 4.9% (Table 2) and such a result was acceptable for the kinetics of copolymerization.

Nine copolymerization reactions were performed for four hours at 50°C, with initial ([VDF]₀/([VDF]₀+ [C₄Br]₀) molar ratios ranging between 0.25 and 0.96 (Table 3).

After reaction, the copolymers were precipitated in cold pentane and their compositions were determined by ¹⁹F NMR. Figure 4 represents an expansion of the zone of the ¹⁹F NMR spectrum of a poly(VDF-*co*-C₄Br) copolymer, synthesized with an initial ([VDF]₀/([VDF]₀+ [C₄Br]₀) molar ratio equal to 0.97.

As expected⁶²⁻⁶⁴, signals corresponding to the fluorinated groups in PVDF microblocks were present (Table 4) : the peak centered at -91 ppm (-CH₂-C $\underline{\text{F}}_2$ -CH₂-) resulting from a head-to-tail addition of VDF, three signals located at -94.8, -113.4 and -115.7 ppm attributed to -(CH₂-CF₂)-(CF₂-CH₂)-(CH₂-C $\underline{\text{F}}_2$)-(CH₂-, -(CH₂-C $\underline{\text{F}}_2$)-(CF₂-CH₂)-(CH₂- and -(CH₂-CF₂)-(C $\underline{\text{F}}_2$ -CH₂)-(CH₂-CF₂, respectively. These three last signals resulted from the inversion of VDF unit in the chain (head-to-head addition). Besides, both signals located between -104 and -111 ppm can be attributed to the difluoromethylene groups of VDF adjacent to C₄Br. Peaks

ranging between -118 and -130 ppm correspond to the difluoromethylene groups of C₄Br. Finally, the multiplet centered at -164 ppm was assigned to tertiary CF of C₄Br (see Table 4). This spectrum could be divided into three different zones: i) from -85 to -118 ppm, assigned to the CF₂ peaks from VDF, ii) from -118 to -130 ppm attributed to the difluoromethylene groups from C₄Br, and iii) the last signal centered on -164.0 ppm assigned to the CF from C₄Br.

These integrals were used to assess the copolymers compositions. Thanks to these integrals named I_3 , I_4 and I_5 respectively, characteristic of signals in the ¹⁹F NMR spectra, the VDF molar fractions in the copolymer was calculated according to the following equation:

$$\text{VDF molar \%} = \frac{I_3}{I_3 + I_4} \times 100 \quad (\text{equation 2})$$

Results are gathered in Table 3 and the composition diagram (i.e., the polymer-monomer curve) was given in Figure 5. According to these results, the reactivity ratios were determined using the Tidwell and Mortimer method⁶¹ : $r_{\text{VDF}} = 0.96 \pm 0.67$ et $r_{\text{C}_4\text{Br}} = 0.09 \pm 0.63$ at 50 °C. These values are compared to those assessed from the copolymerization of VDF with other fluorinated monomers (Table 5). The traditional method for the determination of the reactivity of a macroradical to several monomers was used. Indeed, it is common to compare the value $1/r_A = k_{AB}/k_{AA}$, the ratio of the rate constant of cross propagation to that of homopropagation (k_{AA}). Thus, the higher the $1/r$ value, the higher the crosspropagation reactivity of the radical. On the basis of Table 4, the increasing order of relative reactivities of monomers to macroradicals is as follows⁶⁵⁻⁸³ : $\text{F}_2\text{C}=\text{CHC}_6\text{F}_{13} < \text{F}_2\text{C}=\text{CHCF}_3 < \text{HFP} < \text{PMVE} < \text{PPVE} < \text{VDF} < \text{C}_4\text{Br} < \text{F}_2\text{C}=\text{C}(\text{CF}_3)\text{OCOC}_6\text{H}_5 < \text{TrFE} < \text{CTFE (recent value)} \approx \text{BrTFE} < \text{H}_2\text{C}=\text{CF}_2\text{OR}_F < \text{F}_2\text{C}=\text{FCO}_2\text{CH}_3 < \text{TFE} < \text{F}_2\text{C}=\text{CFC}_3\text{H}_6\text{SCOCH}_3 < \text{F}_2\text{C}=\text{CFC}_3\text{H}_6\text{OAc} < \text{H}_2\text{C}=\text{CHF} \approx \text{CTFE (old value)} < \text{H}_2\text{C}=\text{CH}_2$, although various kinetics still deserve to be investigated.

Furthermore, as $r_{\text{VDF}} \leq 1$ and $r_{\text{C}_4\text{Br}} < 1$, an azeotropic composition exists, which was calculated as follows (equation 3):

$$\text{azeotropic composition} = \frac{1-r_2}{2-(r_1+r_2)} \quad (\text{equation 3})$$

For the VDF/C₄Br copolymer, the azeotropic composition is 96 mol% of VDF monomer unit,

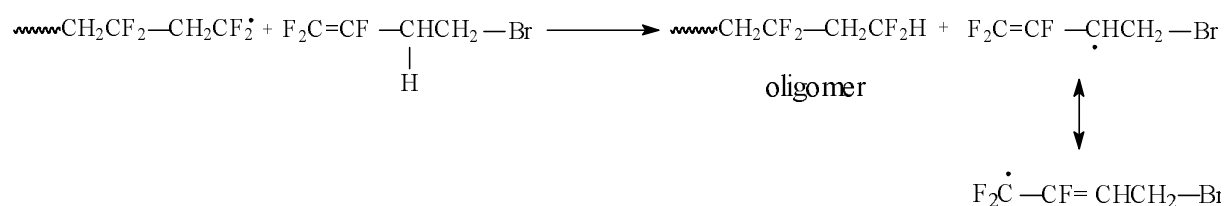
which is almost close to the one given by the composition diagram (Figure 5). Such slight difference depends upon the experimental conditions and errors.

This kinetics of copolymerization shows that C_4Br has a good reactivity towards VDF and that the synthesis of PVDF bearing brominated side groups is thus possible. Besides, the synthesis of PVDF carrying quaternary ammonium functions could not be carried out by direct copolymerization with a monomer bearing this function. Consequently, it was worth studying the chemical modifications of a VDF/ C_4Br copolymers by derivatives containing pyridinium group.

2.2.b Synthesis of a high conversion rate copolymer

In contrast to the copolymerization of VDF with C₄Br in solution, it was worth investigating the synthesis of a poly(VDF-co-C₄Br) copolymer by a suspension process. Two reactions were carried out at 60°C, in the presence of tert-amyl peroxyvalate (TAPPI) as the initiator in diethyl carbonate, CDE, starting from a feed of 1 % mol. (copolymer **I**) and 4 % mol. (copolymer **II**) of C₄Br, respectively. After reaction, copolymer **I** was worked-up, dried and obtained in 85% yield. The ¹⁹F NMR evidenced that 1% mol. of C₄Br was incorporated in the copolymer. The Melt Flow Index (MFI) gives an estimation of the molecular weight of this copolymer. The reference was PVDF whose MFI is 64.91 g.10 min⁻¹ at 230°C under 21.6 kg. The MFI measurement of copolymer **I** was 0.333 g.10 min⁻¹ at 230°C under 5 kg and 8.64 g.10 min⁻¹ at 230°C under 21.6 kg. Copolymer **II** was obtained in 41.5% yield with 6%mol. of incorporation of C₄Br evidenced by ¹H and ¹⁹F NMR spectroscopy. Its MFI could not be measurable (as soon as the polymer was introduced, it flowed). The significant decrease of the MFI indicates that chains are quite short in this copolymer. This indicates that the transfer to monomer seems to play an important role which explains the formation of a low molecular weight-copolymer :

Allylic Transfer



Both these copolymers were analyzed by thermogravimetric analysis (TGA) and differential scanning chromatography (DSC). The TGA analyses suggested that the higher the mol. content of C₄Br in the copolymer, the lower the thermal properties of the resulting copolymer. The decomposition (1% in weight loss) occurred from 383°C for copolymer **I** (1% mol. of C₄Br) and from 321°C for copolymer **II** (6% mol. of C₄Br) while the decomposition of a PVDF generally occurs from about 400°C. Results of DSC measurements are summarized in Table 6. Although T_g was not clearly observed, the DSC thermograms of these copolymers shows that the higher the C₄Br in the copolymers, the lower the crystallization and melting temperatures, this can be attributed to the presence of -C₂H₄Br grafts that deorganize the microstructure of VDF and hence upset the crystallization content.

3. Chemical modification of poly(VDF-co-C₄Br) copolymer

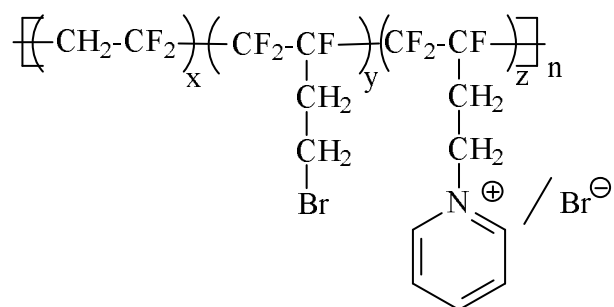
This poly(VDF-co-C₄Br) copolymer represents a potential intermediate for numerous chemical modifications as those made on the C₄Br monomer and especially in that case for introducing quaternary ammonium functions. In that purpose, the poly(VDF-co-C₄Br) copolymer containing 6 mol.% of C₄Br was mixed with pyridine. Indeed, we previously proved that the reaction between pyridine and CF₂=CF-CH₂-CH₂-Br led quantitatively to CF₂=CF-CH₂-CH₂-N(C₅H₅)⁺/Br⁻ (also avoiding any dehydrobromination).

Similar reactions were also carried out on the copolymer and the different experiments are summarized in Table 7.

The reaction was monitored by ¹⁹F and ¹H NMR. Indeed, in ¹⁹F NMR, the signal assigned to the tertiary fluorine atom, located in β position about the bromine atom, was centered at -164.0 ppm but it underwent a high field shift to -168.5 ppm when a pyridinium group was born by the side-group. Furthermore, in ¹H NMR, the methylene group, located in α position of the bromine atom, was strongly shifted due to the presence of the ammonium. The conversion rate of the reaction could thus be assessed from NMR spectra by the ratio of the integrals of both signals.

Dilution of the medium seemed to play a crucial role in the reactivity. Indeed, the higher the concentration in pyridine, the higher the yields (up to 85%). This can be explained by an easier ability for an amine and a brominated extremity to react each other when the medium was diluted in acetone and concentrated in pyridine.

Finally, a copolymer with the following composition was synthesized :



With, $x = 0.94$, $y = 0.03$, $z = 0.03$.

Such a copolymer is interesting since it can be crosslinked via the bromine side atom and the pyridinium salt may act for a potential anionic exchange membrane ⁸⁴.

EXPERIMENTAL PART

1. Materials

NaH, Br₂, zinc powder, DMF, triethylamine, acetonitrile (distilled over calcium chloride and degassed for 10 to 15 minutes with an argon flow), were provided by Aldrich, (France) whereas diethyl ether (distilled under CaH₂), chlorhydric acid (10%), celite, LiAlH₄, tertiobutanol, CaH₂ and Na₂SO₄ were supplied by SDS, Peypin (France).

Vinylidene fluoride, chlorotrifluoroethylene, t-amyl peroxyvalate, methocel K100 and 1,1,1,3,3-pentafluorobutane were kindly offered by Solvay S.A., Tavaux (France). Ethylene was provided by AGA Compagny. Bis(4-*tert*-butylcyclohexyl) peroxydicarbonate and *ditertio* butylperoxide (DTBP) were generously offered by Akzo France, 60202 Compiègne. *Tertiobutyl* peroxyvalate (TBPPI) was kindly supplied by La Chalonnaise des Peroxydes, Chalons sur Saône, France.

2. NMR Spectroscopy

The ¹H, ¹³C and ¹⁹F NMR were recorded at room temperature on Bruker AC 200 and AC 250 instruments, using deuterated chloroform or acetone as the solvents and TMS (resp. CFC_l₃) as the references for ¹H, ¹³C (resp. ¹⁹F) 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 ¹H, ¹³C and ¹⁹F 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 ¹⁹F NMR.

3. Autoclaves

Reactions of ethylenation and copolymerization were performed in 2L Hastelloy autoclave Parr System, equipped with a manometer, a rupture disk, inlet and outlet valves. An electronic device regulated and controlled both the stirring and the heating of the autoclave.

The kinetics of copolymerization of VDF with C₄Br₂ were investigated in thick borosilicate Carius tubes (length 130 mm, internal diameter 10 mm, thickness 2.5 mm; for a total volume of 8 cm³). After the introduction of the initiator (TBPPI ~ 2 mol % versus the monomer quantity), C₄Br₂ monomer and acetonitrile were added (1.5-2.0 g). The tube was connected to a manifold and then cooled into liquid nitrogen. After five freeze – thaw cycles, the adequate VDF quantity was trapped in the tube cooled in liquid nitrogen under 20 mmHg. To introduce the targeted VDF quantity, a previous calibration was made to link the VDF drop of pressure (bars) to the introduced mass (grams) (for example, a difference of pressure of 0.66 bar corresponds to 1.00 g of VDF). The tube was sealed while immersed in liquid nitrogen and left stirred at the chosen temperature for the required time (four hours were chosen to carry out the kinetics of radical copolymerization). After reaction, the mixture was analyzed by ¹⁹F NMR. Then, the copolymers were precipitated in cold pentane and dried at 70°C for 4 hours.

4. G.C. analyses

Gas chromatography (GC) was carried out on Delsi apparatus (330), fitted with an OV1 column, 2m x 1.8 mm under nitrogen pressure. The injector and the detector temperatures were 255°C and 260°C, respectively. The heating program was regulated from 35°C to 250°C, with a heating-rate of 10°C.min⁻¹. The GC apparatus was connected to a Hewlett Packard (3390) integrator equipped with automatic peak area calculation system.

Size exclusion chromatography (SEC) or Gel permeation chromatography (GPC) analyses were performed at 40°C on 2HR5E and 1HR2E columns with DMF/LiBr 0.1 mole/l as mobile phase.

5. T.G.A. analyses

Thermogravimetric analyses were performed with a TGA/SDTA 851 thermobalance from Mettler DAL 75965 and Lauda RC6 CS cryostat apparatus in air at the heating rate of 8°C.min⁻¹ from room temperature up to a maximum of 600°C.

6. D.S.C. analyses

Differential scanning calorimetry (DSC) measurements were conducted using a TA 2920 analyser from TA Instruments DA 73085, a RCS DA cooler and Sartorius MC5 weighing machine. Scans were recorded at a heating rate of $10^{\circ}\text{C}.\text{min}^{-1}$ from -20°C to 250°C and the cooling rate was $-10^{\circ}\text{C}.\text{min}^{-1}$.

7. Synthesis of $\text{CF}_2=\text{CF}-\text{CH}_2-\text{CH}_2-\text{Br}$

7.1 Synthesis of $\text{Br}-\text{CF}_2-\text{CFCl}-\text{Br}$

CTFE directly bubbled slowly from a cylinder in a solution of 190 mL (3.59 mol.) of bromine contained in a two necked round bottom flask equipped with a condenser. The decoloration of the bromine solution (assigned to the total consumption of bromine) indicated the end of the reaction. The difference of weights of the CTFE bottle (before and after the reaction) indicated that 420 g (3.62 mol.) of CTFE were necessary. 450 mL (3.58 mol.) of $\text{Br}-\text{CF}_2-\text{CFCl}-\text{Br}$, colorless liquid were obtained in 99% yield (b.p. = $99-100^{\circ}\text{C}$) (litt, $99-100^{\circ}\text{C}^{52}$).

1,2-dibromo-1,1,2-trifluoro-2-chloroethane : $\text{Br}-\text{CF}_2-\text{CFCl}-\text{Br}$, ^{19}F NMR (CDCl_3 , ppm)
 δ : -69.3 (ABX system, X part, $^3J_{\text{FF}} = 13.9$ Hz, $^3J_{\text{FF}} = 13.9$ Hz, 2F) ; -60.0 (ABX system, AB part, $^2J_{\text{FF}} = 166.7$ Hz, $^3J_{\text{FF}} = 13.9$ Hz, 1F).

7.2 Synthesis of $\text{Br}-\text{CF}_2-\text{CFCl}-\text{CH}_2-\text{CH}_2-\text{Br}$

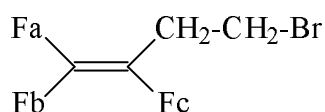
276.5 g (1.0 mol.) of $\text{Br}-\text{CF}_2-\text{CFCl}-\text{Br}$ were introduced in the 2L autoclave, with 111.3 g (1.50 mol.) of *tertio*-butanol and 11.7 g (0.03 mol.) of bis(4-*tert*-butylcyclohexyl) peroxydicarbonate. The autoclave was left closed for 20 minutes and purged with 15 bars of nitrogen pressure to prevent any leakage, before to process at two nitrogen-vacuum cycles in order to limit the presence of oxygen. Afterwards, 28.0 g (1.0 mol.) of ethylene were added. The autoclave was slowly heated at 30°C . The monitoring of the pressure is an indicator of the evolution of the reaction. When the pressure was stabilized to its minimum, it can be estimated that all the gas was consumed. After degassing and opening of the autoclave, the distillation gave 213.2 g (0.70 mol.) of $\text{Br}-\text{CF}_2-\text{CFCl}-\text{CH}_2-\text{CH}_2-\text{Br}$ (colorless liquid), (b.p. = $68^{\circ}\text{C} / 20$ mmHg) yield of monoadduct 70% and 21.3 g ($6.4 \cdot 10^{-2}$ mol.) of $\text{Br}-\text{CF}_2-\text{CFCl}-(\text{CH}_2)_4-\text{Br}$ (b.p. = $134^{\circ}\text{C} / 20$ mmHg) yield of diadduct 6.4%. The other experimental conditions of the ethylenation are listed in Table 1.

1,4-dibromo-2-chloro-1,1,2-trifluorobutane : $\text{Br-CF}_2\text{-CFCl-CH}_2\text{-CH}_2\text{-Br}$, ^{19}F NMR (CDCl_3 , ppm) δ : -118.5 (ABX system, X part, m, -CFCl- 1F) ; -61.8 (ABX system, AB part, $^3J_{\text{FF}} = 11.86$ Hz, $\text{-CF}_2\text{-}$ 2F) . ^1H NMR (CDCl_3 , ppm) δ : 2.8 (m, $\text{CFCl-CH}_2\text{-}$, 2H) ; 3.6 (t, $^3J_{\text{HH}} = 7.00$ Hz, $\text{-CH}_2\text{-CH}_2\text{-Br}$, 2H).

7.3 Synthesis of $\text{CF}_2=\text{CF-CH}_2\text{-CH}_2\text{-Br}$

A one-liter three necked round bottom flask, equipped with a cooling system, a dropping funnel and a thermometer, contained 325.2 g (5.01 mol.) of zinc and a magnetic stirrer. DMF (300 mL) was added via a cannular under nitrogen. The dropping funnel contained 602.3 g (1.98 mol.) of $\text{Br-CF}_2\text{-CFCl-CH}_2\text{-CH}_2\text{-Br}$. A fast stirring was maintained. 5 mL of bromine (0.09 mol.) were added very slowly, then $\text{Br-CF}_2\text{-CFCl-CH}_2\text{-CH}_2\text{-Br}$ was dropwise introduced. The absence of $\text{Br-CF}_2\text{-CFCl-CH}_2\text{-CH}_2\text{-Br}$ was monitored by GC, and after 2 hours its conversion was quantitative. After distillation (b.p. = 19°C / 20 mmHg), 294.17 g (1.56 mol.) of $\text{CF}_2=\text{CF-CH}_2\text{-CH}_2\text{-Br}$ were obtained (yield = 79%).

4-bromo-1,1,2-trifluorobut-1-ene :



^{19}F NMR (CDCl_3 , ppm) δ : -103.4 (ddt, $^2J_{\text{FaFa}} = 82.5$ Hz, $^3J_{\text{FaFb}} = 33.0$ Hz $^4J_{\text{FaH}} = 2.4$ Hz, Fb , 1F) ; -123.0 (ddt, $^3J_{\text{FaFc}} = 114.3$ Hz, $^2J_{\text{FaFb}} = 82.8$ Hz, $^4J_{\text{FaH}} = 3.6$ Hz, Fa , 1F) ; -177.5 (ddt, $^3J_{\text{FcFa}} = 114.3$ Hz, $^3J_{\text{FcFb}} = 33.0$ Hz, $^3J_{\text{FcH}} = 21.1$ Hz, Fc , 1F) . ^1H NMR (CDCl_3 , ppm) δ : 2.81 (dddt, $^3J_{\text{FFc}} = 21.0$ Hz, $^3J_{\text{HH}} = 6.8$ Hz, $^4J_{\text{HFa}} = 3.5$ Hz, $^4J_{\text{HFb}} = 2.9$ Hz, $\text{-CH}_2\text{-CH}_2\text{-Br}$, 2H) ; 3.50 (t, $^3J_{\text{HH}} = 6.7$ Hz, $\text{-CH}_2\text{-CH}_2\text{-Br}$, 2H).

8. Synthesis of $\text{Br-CF}_2\text{-CHCl-Br}$

162.44 g (1.015 mol.) of bromine were first introduced in the 2 L HC-276 Hastelloy autoclave. This vessel was left closed for 20 minutes and purged with 15 bars of nitrogen pressure to prevent any leakage, before to process at two nitrogen-vacuum cycles in order to limit the presence of oxygen. Then 100 g (1.015 mol.) of 2-chloro-1,1-difluoroethylene (CDFE) were transferred in the vessel. Temperature was progressively increased up to 35°C . A characteristic of this reaction was the strong exotherm (the temperature reaching 80°C) while

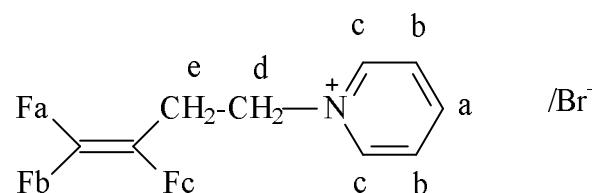
the pressure reached 8.9 bars. After reaction, degassing, opening of the autoclave, the total product mixture was distilled (the conversion rate was 95.5%). After distillation (b.p. = 117°C), 213.8 g of Br-CF₂-CHCl-Br (0.829 mol.) were obtained (yield = 81.7%).

1,2-dibromo-1,1-difluoro-2-chloroethane : Br-CF₂-CHCl-Br, ¹⁹F NMR (CDCl₃, ppm) δ : -55.1 (AB system, ²J_{F₁F₂} = 161.4 Hz, ³J_{F₁H} = 6.7 Hz, ³J_{F₂H} = 7.5 Hz) . ¹H NMR (CDCl₃, ppm) δ : 5.9 (dd, ³J_{F₁H} = 5.7 Hz, ³J_{F₂H} = 8.6 Hz).

9. Synthesis of CF₂=CF-CH₂-CH₂-NC₅H₅⁺/Br⁻

10.5 g (5.5 · 10⁻² mol.) of CF₂=CF-CH₂-CH₂-Br, 8.60 g (9.4 · 10⁻² mol.) of pyridine and 50 mL of acetonitrile were introduced in a 100 mL two necked round bottom flask equipped with a condenser. The medium was heated at 70°C for 48 hours. After reaction, the total product mixture was dried under 20 mmHg at 100°C for 3 hours. 19.0 g of a brown solid in a quasi quantitative yield were obtained.

(3,4,4-trifluorobutan-3-ene) pyridinium bromide



¹⁹F NMR (CDCl₃, ppm) δ : -103.8 (ddt, ²J_{F_bF_a} = 81.8 Hz, ³J_{F_bF_c} = 32.0 Hz, ⁴J_{F_bH_e} = 2.9 Hz, F_b, 1F) ; -122.5 (ddt, ³J_{F_aF_c} = 114.1 Hz, ²J_{F_aF_b} = 82.6 Hz, ⁴J_{F_aH_e} = 3.9 Hz, F_a, 1F) ; -174.8 (ddt, ³J_{F_cF_a} = 114.1 Hz, ³J_{F_cF_b} = 33.0 Hz, ³J_{F_cH_e} = 21.6 Hz, F_c, 1F).

¹H NMR (CDCl₃, ppm) (Figure 2) δ : 3.4 (dddt, ³J_{H_eF_c} = 22.0 Hz, ³J_{H_eH_d} = 6.8 Hz, ⁴J_{H_eF_a} = 3.9 Hz, ⁴J_{H_eF_b} = 2.9 Hz, H_e, 2H) ; 5.42 (t, ³J_{H_dH_e} = 6.7 Hz, H_d, 2H) ; 8.4 (dd, ³J_{H_bH_c} = ³J_{H_bH_a} = 7.0 Hz, H_b, 2H) ; 8.85 (t, ³J_{H_aH_b} = 8.0 Hz, H_a, 1H) ; 9.85 (d, ³J_{H_cH_b} = 5.6 Hz, H_c, 2H).

10. Radical Copolymerization of VDF with C₄Br in suspension

Two emulsion copolymerizations of VDF with C₄Br were performed in a 4 L stainless steel autoclave equipped with a rupture disk, inlet and outlet valves and a manometer, containing 3L deionised water. For these copolymerizations the initial molar ratio of C₄Br in feed was fixed to 1% and 4 % with respect to VDF.

Copolymer I: The autoclave was purged with 140 bars of nitrogen pressure to prevent any leakage and three times by evacuating and flushing with nitrogen. Then 1 kg of VDF (15.63 mol.), 29 g of C₄Br (0.15 mol.), 6 g of *tert*-amyl peroxyvalate (TAPPI) in solution in diethyl carbonate (CDE) and 0.8 g of methocel K100 (surfactant) were introduced. The temperature and the pressure were fixed at 60°C and 120 bars. After the reaction, the white powder, the size of the particules of which was about 100µm was washed, dried and 879.2 g of copolymer were obtained (yield = 85%).

Copolymer II: The same autoclave was purged with 160 bars of nitrogen pressure to prevent any leakage and three times by evacuating and flushing with nitrogen. Then 629g of VDF (10.77 mol.), 96.7 g of C₄Br (0.15 mol.), 6g of *tert*-amyl peroxyvalate (TAPPI) in solution in diethyl carbonate (CDE) and 0.8 g of methocel K100 were introduced. The temperature and the pressure were fixed at 60°C and 140 bars. After 24 hours of reaction, 5% in weight of chlorotrifluoroethylene (39.29 g, 0.34 mol.) were introduced.

After the reaction, the white powder was washed, dried and 327.5 g of copolymer were obtained (yield = 41.5%).

11. Chemical modification of Poly(VDF-co-C₄Br) copolymer

The appropriate amounts of poly(VDF-co-C₄Br) copolymer, acetone and pyridine were introduced in a 100 mL two necked round bottom flask (see Table 7). The system was stirred at the desired temperature for the chosen time. Aliquotes were sampled in the course of the reaction and characterized by ¹H and ¹⁹F NMR. The mixture was then precipitated in cold pentane, filtered and then dried at 70°C for 4 hours.

CONCLUSION

The synthesis of $\text{CF}_2=\text{CF}-\text{CH}_2-\text{CH}_2-\text{Br}$ (C_4Br) was carried out in three steps. The first step consisted in the bromination of CTFE, followed by the telomerization of ethylene with $\text{Br}-\text{CF}_2-\text{CFCl}-\text{Br}$ while the third one dealt with the synthesis of $\text{F}_2\text{C}=\text{CF}-\text{CH}_2-\text{CH}_2-\text{Br}$ by dehalogenation of its dibrominated precursor in the presence of zinc. The overall yield was 56% about CTFE. A similar strategy was carried out for the synthesis of $\text{CF}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{Br}$, but the telomerization of ethylene with $\text{Br}-\text{CF}_2-\text{CClH}-\text{Br}$ (obtained in good yield from the bromination of $\text{F}_2\text{C}=\text{CHCl}$) failed. Only C_4Br monomer underwent various chemical modifications. Triethylamine enabled a dehydrobromination leading to $\text{CF}_2=\text{CF}-\text{CH}=\text{CH}_2$, whereas the synthesis of $\text{CF}_2=\text{CF}-\text{CH}_2-\text{CH}_2-\text{NC}_5\text{H}_5^+/\text{Br}^-$ was carried out by addition of pyridine onto C_4Br monomer. However, no radical copolymerization of this monomer bearing pyridinium group occurred with VDF. Nevertheless, the kinetics of copolymerization of VDF with C_4Br enabled us the determination of the reactivity ratios ($r_{\text{VDF}} = 0.96 \pm 0.67$ and $r_{\text{C}_4\text{Br}} = 0.09 \pm 0.63$ at 50°C) and their suspension polymerization led to poly(VDF-co- C_4Br) copolymer containing 6% of C_4Br . The Melt Flow Index analyses indicated that this copolymer exhibits a low molecular weight, which may arise from allylic transfer to monomer. In order to produce a copolymer bearing quaternary ammonium functions, the chemical modification of poly(VDF-co- C_4Br) copolymer in the presence of pyridine was achieved. These poly(VDF-co- C_4Br) copolymers are interesting precursors of other functional VDF copolymers, under investigation.

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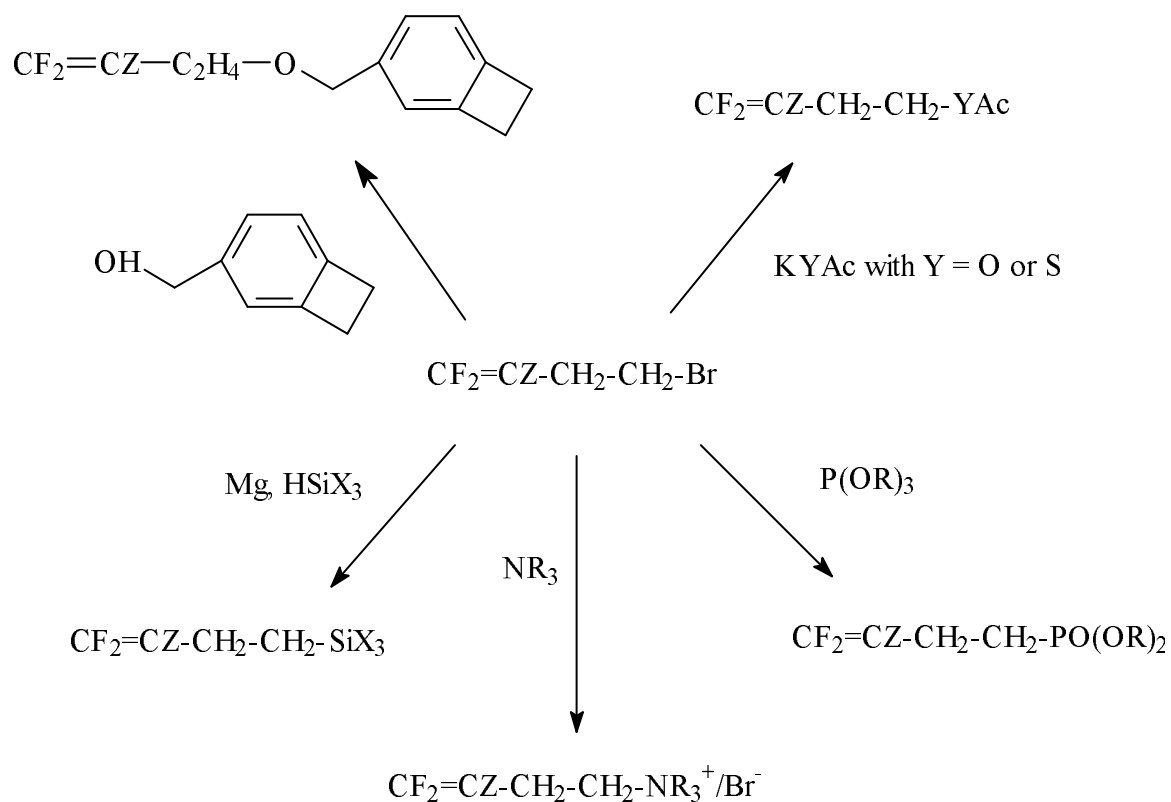
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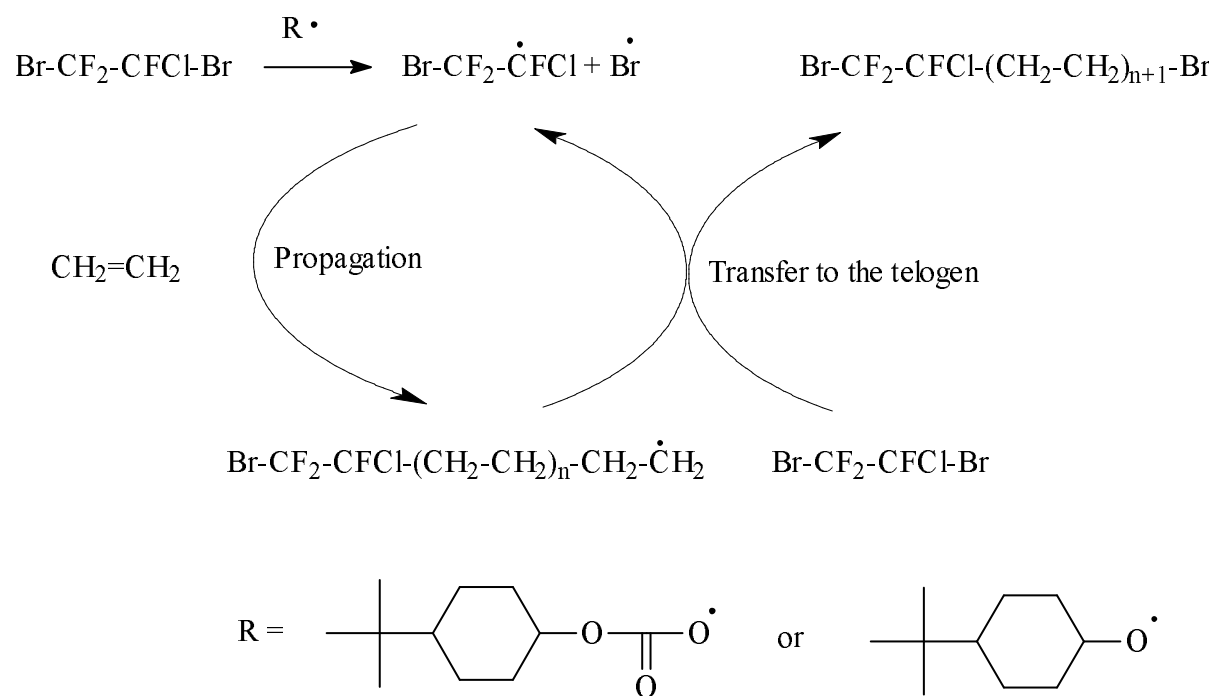
HEME CAPTIONS

Scheme 1 : Chemical modifications of $\text{CF}_2=\text{CZ}-\text{CH}_2-\text{CH}_2-\text{Br}$ (with $\text{Z} = \text{H}$ or F).

Scheme 2: Mechanism of the radical telomerization of ethylene with 1,2-dibromo-1-chloro-1,2,2-trifluoroethane



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Scheme 2: Mechanism of the radical telomerization of ethylene with 1,2-dibromo-1-chloro-1,2,2-trifluoroethane

TABLE CAPTIONS

Table 1 : Experimental conditions and results for the ethylenation reaction of Br-CF₂-CFCl-Br. $R_0 = [\text{BrCTFEBr}]_0 / [\text{C}_2\text{H}_4]_0$, $C_0 = [\text{initiator}]_0 / [\text{C}_2\text{H}_4]_0$, T = temperature, P = pressure, $P 16-S$: [tBu-C₆H₄-O-CO-O]₂, Br-CTFE-E-Br and Br-CTFE-E-E-Br stand for Br-CF₂-CFCl-CH₂-CH₂-Br and Br-CF₂-CFCl-(CH₂-CH₂)₂-Br, respectively

* bis(4-tert-butylcyclohexyl) peroxydicarbonate

Table 2 : Determination of the conversion rate of C₄Br as a function of the reaction time. Polymerization conditions: $[\text{TBPPI}]_0 / ([\text{VDF}]_0 + [\text{C}_4\text{Br}]_0) = 0.02$, 50 °C and $[\text{VDF}]_0 / [\text{C}_4\text{Br}]_0 = 75/25$.

Table 3 : Initial and final compositions of the copolymerization of VDF with C₄Br initiated by tertio-butyl peroxyvalate (TPPBI), determined by ¹⁹F NMR. Polymerization conditions : $[\text{TPPBI}]_0 / ([\text{VDF}]_0 + [\text{C}_4\text{Br}]_0) = 0.02$, $T = 50$ °C, $t = 4$ hours.

Table 4 : ¹⁹F NMR assignments of poly(VDF-co-C₄Br) copolymers (spectra recorded in d₆ acetone)

Table 5 : Monomer reactivity ratios for the copolymerization of VDF (A) with other fluoroalkenes (B) (and Ethylene).

Table 6 : Differential scanning calorimetry characteristics of PVDF and poly(VDF-co-C₄Br). T_c and T_m represent the crystallization and the melting temperatures.

Table 7 : Experimental conditions of chemical modification of the poly (VDF-co-C₄Br) copolymer with pyridine.

* During the reaction, a problem of cooling system induced an evaporation of a part of acetone.

eq. -Br = molar equivalent with respect to brominated compound.

Experiment.	1	2	3	4	5	6
Heating condition	No heating	No heating	Heating Directly to 45 °C	Heating Directly to 55 °C	No heating	No heating
BrCTFEBr (moles)	1.99	1.00	1.00	1.00	1.00	0.43
C ₂ H ₄ (moles)	1.99	1.12	1.00	0.97	1.00	0.43
P 16-S* (mole)	0.06	0.03	0.03	0.03	0.03	0.02
tBuOH (moles)	12.19	6.30	6.05	6.08	3.06	0.66
C ₀	0.03	0.03	0.03	0.03	0.03	0.03
R ₀	1.00	0.89	1.00	1.03	1.00	1.00
T max (C°)	89	79	91	97	79	59
P max (bars)	8.6	8.8	9.2	8.3	8.9	5.3
BrCTFE-E-Br (moles)	1.217	0.532	0.467	0.448	0.656	0.298
Yield monoadduct (%)	60.9	53.2	46.7	44.8	65.6	70.0
BrCTFE-E-E-Br (moles)	0.286	0.258	0.170	0.140	0.148	0.027
Yield diadduct (%)	14.3	25.8	17.0	14.1	14.8	6.4
Overall yield (%) (diadduct + monoadduct)	75.2	79.0	63.7	58.9	80.4	76.4
[BrCTFE-E-E-Br] / [BrCTFE-E-Br]	0.235	0.485	0.364	0.312	0.226	0.091

Table 1 : Experimental conditions and results for the ethylenation reaction of Br-CF₂-CFCl-Br. $R_0 = [\text{BrCTFEBr}]_0 / [\text{C}_2\text{H}_4]_0$, $C_0 = [\text{initiator}]_0 / [\text{C}_2\text{H}_4]_0$, T = temperature, P = pressure, P 16-S : [tBu-C₆H₄-O-CO-O]₂, Br-CTFE-E-Br and Br-CTFE-E-E-Br stand for Br-CF₂-CFCl-CH₂-CH₂-Br and Br-CF₂-CFCl-(CH₂-CH₂)₂-Br, respectively

* bis(4-tert-butylcyclohexyl) peroxydicarbonate

Experiment n°	Reaction time (h)	I_1	I_2	C ₄ Br conversion (%)
7	0.5	0	100	0
8	1.0	1.4	80.3	1.8
9	2.0	2.1	59.4	3.4
10	4.0	4.9	80.1	4.9

Table 2 : Determination of the conversion rate of C₄Br as a function of the reaction time. Polymerization conditions: $[TBPPI]_0/([VDF]_0 + [C_4Br]_0) = 0.02$, 50 °C and $[VDF]_0/[C_4Br]_0 = 75/25$.

Experiment n°	initial VDF molar %	VDF molar % in the copolymer
11	96.8	96.2
12	93.0	92.7
13	90.0	87.8
14	79.0	80.0
15	74.0	78.0
16	65.1	76.6
17	54.0	73.0
18	40.0	69.8
19	25.0	62.0

Table 3 : Initial and final compositions of the copolymerization of VDF with C_4Br initiated by tertio-butyl peroxyvalate (TPPBI), determined by ^{19}F NMR. Polymerization conditions : $[TPPBI]_0/([VDF]_0 + [C_4Br]_0) = 0.02$, $T = 50\text{ }^{\circ}C$, $t = 4\text{ hours}$.

Chemical shift (ppm)	Structure
-91	$-\text{CF}_2-\text{CH}_2-\text{CF}_2-\text{CH}_2-\text{CF}_2-$
-92.4	$\text{HCF}_2-\text{CH}_2-\text{CF}_2-\text{CH}_2-$
-94.8	$(\text{CH}_2-\text{CF}_2)-(\text{CF}_2-\text{CH}_2)-(\text{CH}_2-\text{CF}_2)-(\text{CH}_2-\text{CF}_2)$
- 104 to -111	$-(\text{CH}_2-\text{CF}_2)-[\text{CF}_2-\text{CF}(\text{CH}_2-\text{CH}_2-\text{Br})]-$
-113.7	$(\text{CH}_2-\text{CF}_2)-(\text{CF}_2-\text{CH}_2)-(\text{CH}_2-\text{CF}_2)-$
-114.5	$\text{HCF}_2-\text{CH}_2-\text{CF}_2-\text{CH}_2-$
-115.7	$(\text{CH}_2-\text{CF}_2)-(\text{CF}_2-\text{CH}_2)-(\text{CH}_2-\text{CF}_2)-$
- 118 to -130	$-(\text{CH}_2-\text{CF}_2)-[\text{CF}_2-\text{CF}(\text{CH}_2-\text{CH}_2-\text{Br})]-$
-164.0	$-(\text{CF}_2-\text{CF}(\text{CH}_2-\text{CH}_2-\text{Br}))-$

Table 4 : ^{19}F NMR assignments of poly(VDF-co- C_4Br) copolymers (spectra recorded in d_6 acetone).

Monomer B	r_A	r_B	$r_A r_B$	$1/r_A$	Ref.
$H_2C=CH_2$	0.05	8.5	0.42	20.00	65
$H_2C=CHOCOCH_3$	-0.40	1.67	-0.67	-2.5	66
	0.50	2.0	1.00	2.0	67
$H_2C=C(CF_3)CO_2H$	0.33	0	0	3.03	68
$FCH=CH_2$	0.17	4.2 – 5.5	0.71 – 0.94	5.88	69
	0.20 – 0.43	3.8 – 4.9	0.76 – 2.11	2.33 – 5.00	70
$H_2C=CFCH_2OR_F$	0.38	2.41	0.92	2.63	71
$F_2C=CFH$	0.70	0.50	0.35	1.43	72
$F_2C=CHCF_3$	9.0	0.06	0.54	0.11	73
$F_2C=CHC_6F_{13}$	12.0	0.90	10.80	0.08	74
$CFCl=CF_2$	0.73	0.75	0.55	1.37	75
	0.17	0.52	0.09	5.88	76
$CFBr=CF_2$	0.43	1.46	0.63	2.33	75
$CF_2=CF_2$	0.23	3.73	0.86	4.35	75,77
	0.32	0.28	0.09	3.13	78
$CF_3-CF=CF_2$	6.70	0	0	0.15	79
	2.45	0	0	0.40	77
	2.90	0.12	0.35	0.34	32
$F_2C=CFOCF_3$	3.40	0	0	0.29	74
$F_2C=CFOCF_3F_7$	1.15	0	0	0.86	32
$F_2C=CFO(HFP)OC_2F_4SO_2F$	0.57	0.07	0.04	1.75	34
$CF_2=CFCH_2OH$	0.83	0.11	0.09	1.02	14
$CF_2=CF(CH_2)_2Br$	0.96	0.09	0.09	1.00	Our work
$CF_2=CF(CH_2)_3OAc$	0.17	3.26	0.59	5.56	13
$F_2C=CF(CH_2)_3SAc$	0.60	0.41	0.25	4.07	80
$CF_2=CFCO_2CH_3$	0.30	0	0	3.33	81
$F_2C=C(CF_3)COF$	7.60	0.02	0.15	0.13	82
$F_2C=C(CF_3)OCOC_6H_5$	0.77	0.11	0.08	1.30	83

Table 5 : Monomer reactivity ratios for the copolymerization of VDF (A) with other fluoroalkenes (B) (and Ethylene).

	PVDF	Copolymer I (1% mol. of C₄Br)	Copolymer II (6% mol. of C₄Br)
T_c	139.5	130.2	92.3
T_m	174.0	167.5	122.5

Table 6 : *Differential scanning calorimetry characteristics of PVDF and poly(VDF-co-C₄Br)*
T_c and **T_m** represent the crystallization and the melting temperatures.

Exp.	Pyridine (eq. -Br)	Acetone (eq. -Br)	Temperature (°C)	Time (hours)	ammonium conversion (%)	
					by ^{19}F NMR	by ^1H NMR
20	4.6	212	Ambient	100	0	0
21	5.0	424	50	140	0	0
22	4.8	424	55	120	0	0
23	10.7	<212*	55	72	15	16
24	11.5	50	55	30	23	21
25	11.5	50	55	47	36	40

Table 7 : Experimental conditions of chemical modification of the poly (VDF-co- C_4Br) copolymer with pyridine.

* During the reaction, a problem of cooling system induced an evaporation of a part of acetone.

eq. -Br = molar equivalent with respect to brominated compound

FIGURE CAPTIONS

Figure 1 : ^{19}F NMR spectrum of the expansion of the -100 to -190ppm zone of the total product mixture of the reaction between C_4Br and Et_3N recorded in deuterated acetone (Experimental conditions : two molar equivalents of triethylamine, under acetonitrile reflux, 10 hours).

Figure 2 : ^1H NMR spectrum of $\text{CF}_2=\text{CF}-\text{CH}_2-\text{CH}_2-\text{NC}_5\text{H}_5^+/\text{Br}^-$ recorded in CDCl_3 .

Figure 3 : Expansion of the -161 to -179 ppm zone of ^{19}F NMR spectrum of poly(VDF-co- C_4Br) reactional mixture, recorded in deuterated acetone Reaction conditions : $[\text{TBPPI}]_0/([\text{VDF}]_0 + [\text{C}_4\text{Br}]_0) = 0.02$, 50°C , 4 hours and $[\text{VDF}]_0/[\text{C}_4\text{Br}]_0 = 75/25$.

Figure 4 : ^{19}F NMR spectrum of poly(VDF-co- C_4Br) copolymer recorded in deuterated acetone (exp. 11). Polymerization conditions : $[\text{TBPPI}]_0/([\text{VDF}]_0 + [\text{C}_4\text{Br}]_0) = 0.02\%$, $T = 50^\circ\text{C}$, $t = 4$ hours et $[\text{VDF}]_0/[\text{C}_4\text{Br}]_0 = 97/03$.
(The chemical shifts are uncorrected with a slight upfield shift of 2ppm)

Figure 5 : Polymer/monomer composition diagram of poly(VDF-co- C_4Br) copolymers (at 50°C , 4 hours, initiated by tertio-butyl peroxyvalate (TPPBI)).

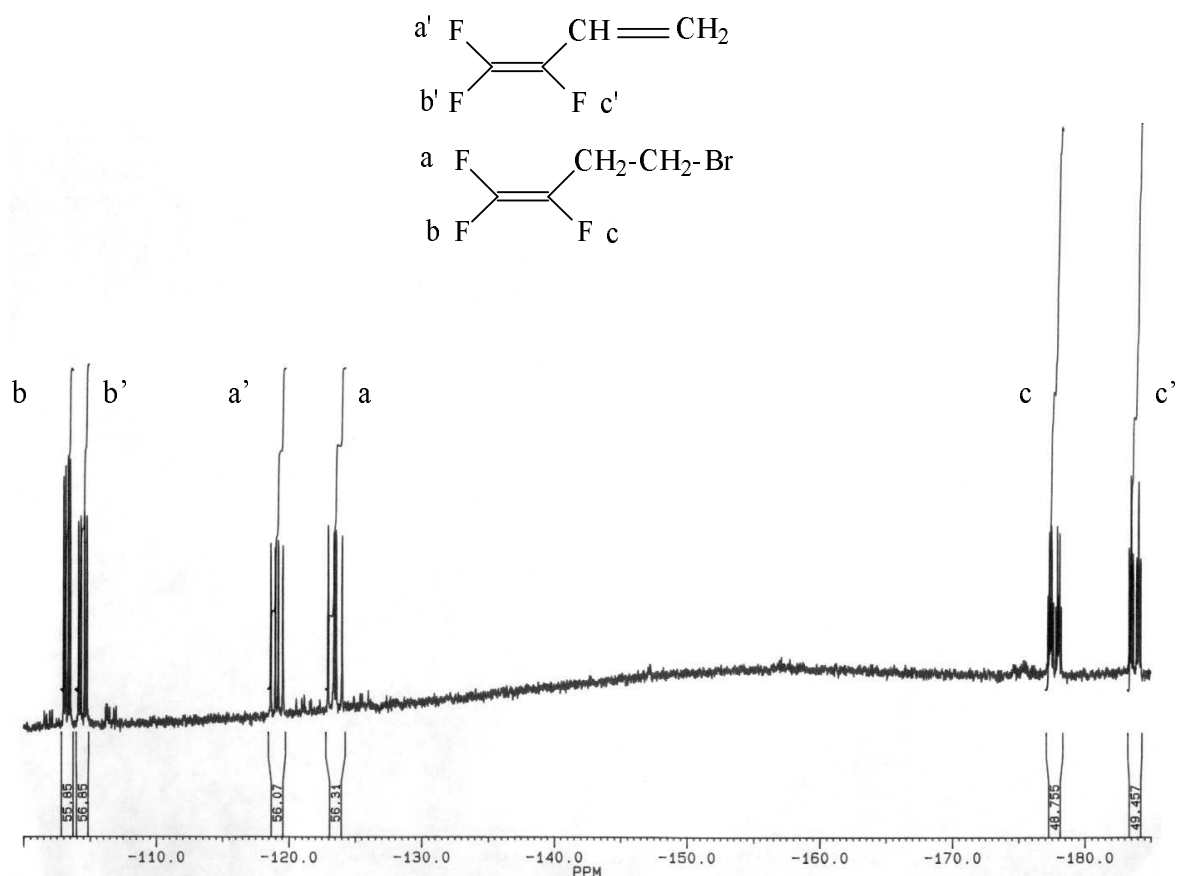


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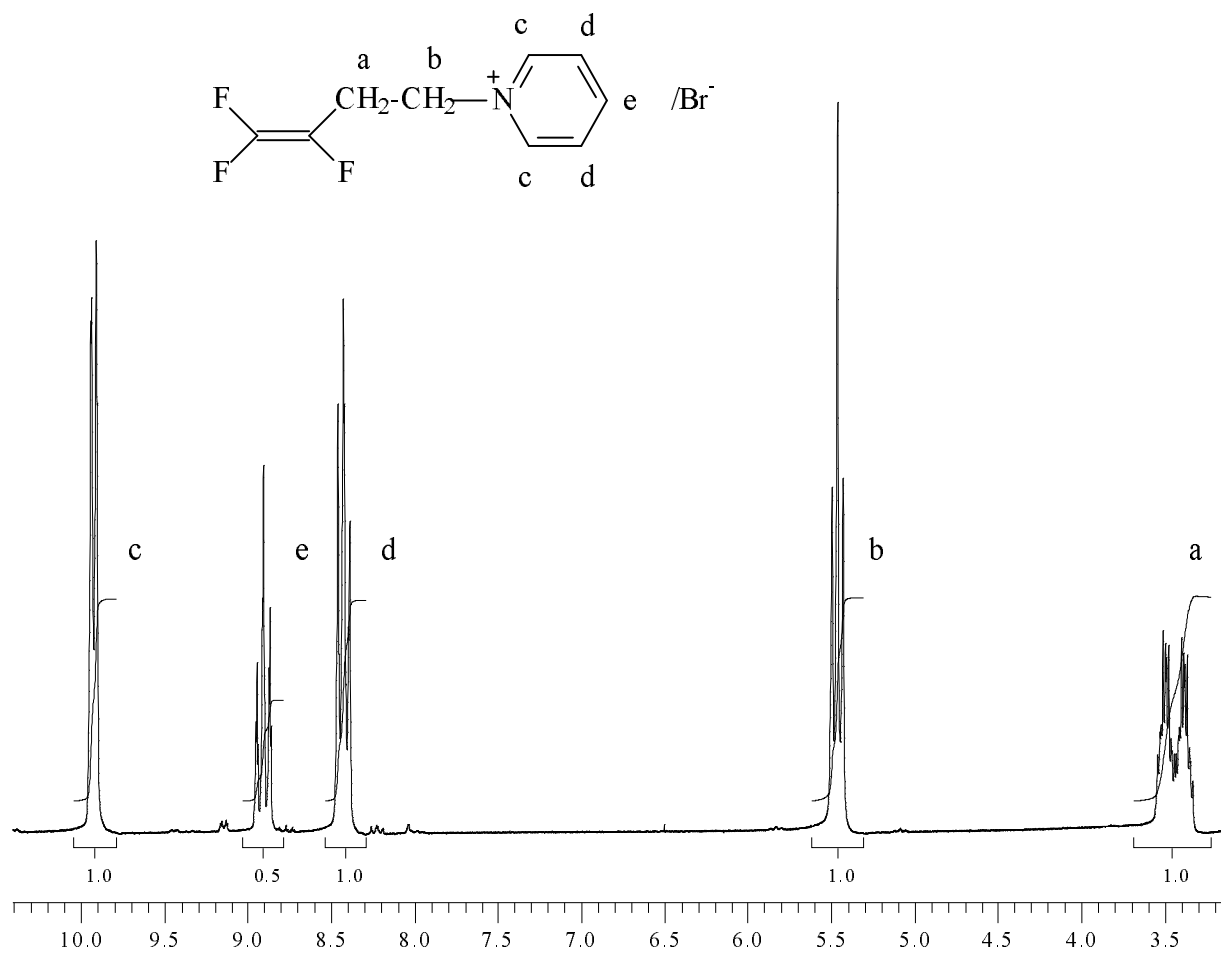


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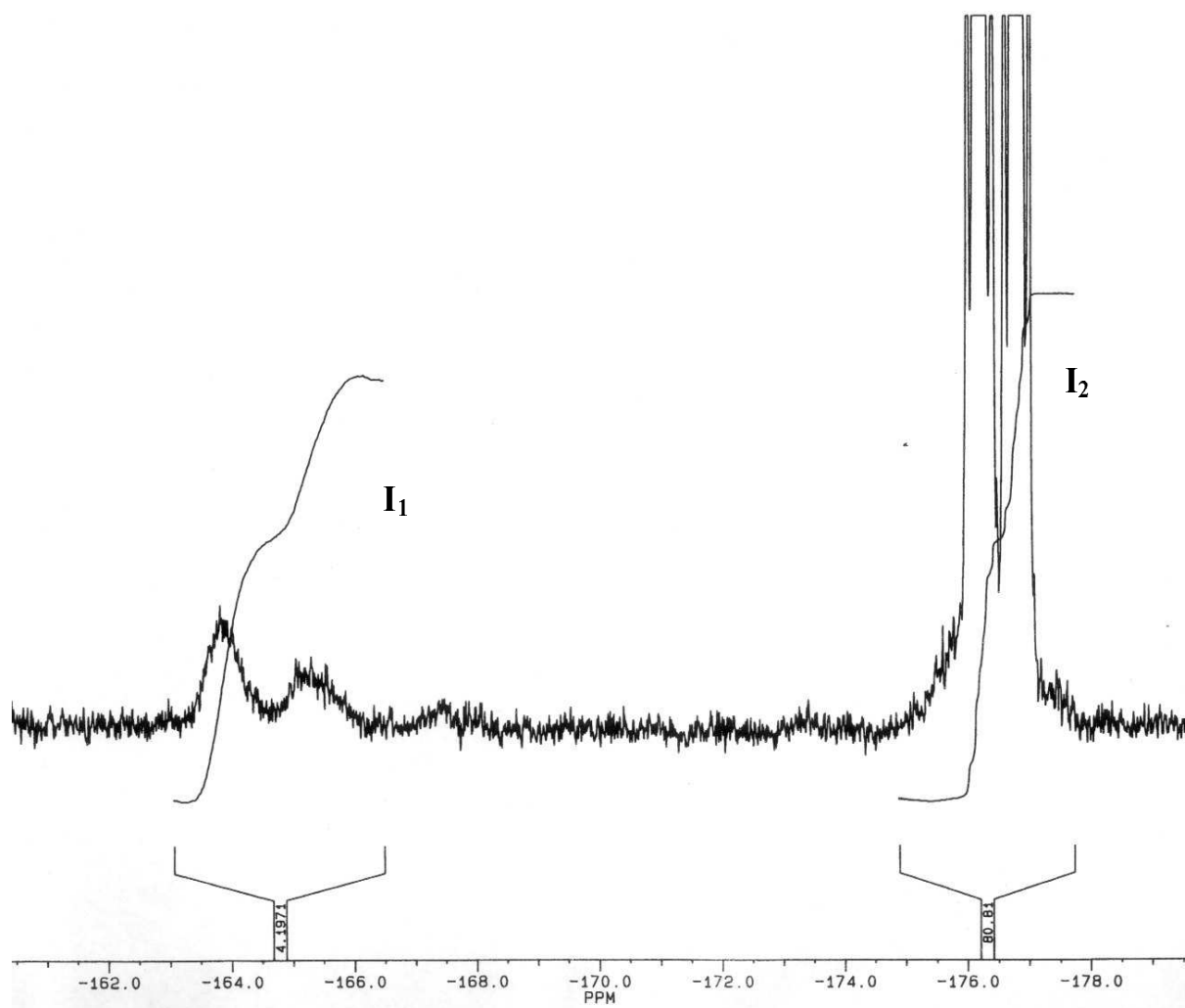


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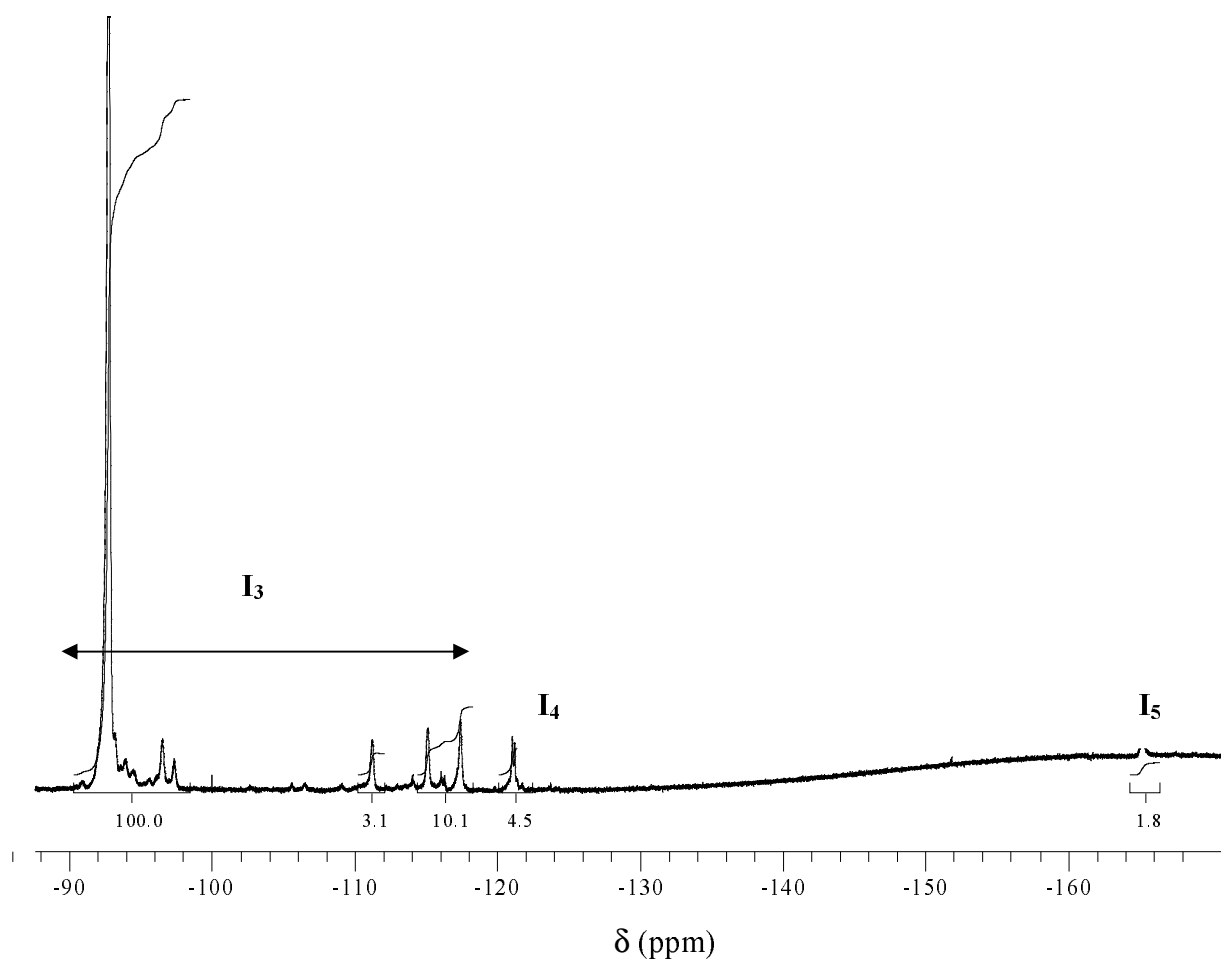


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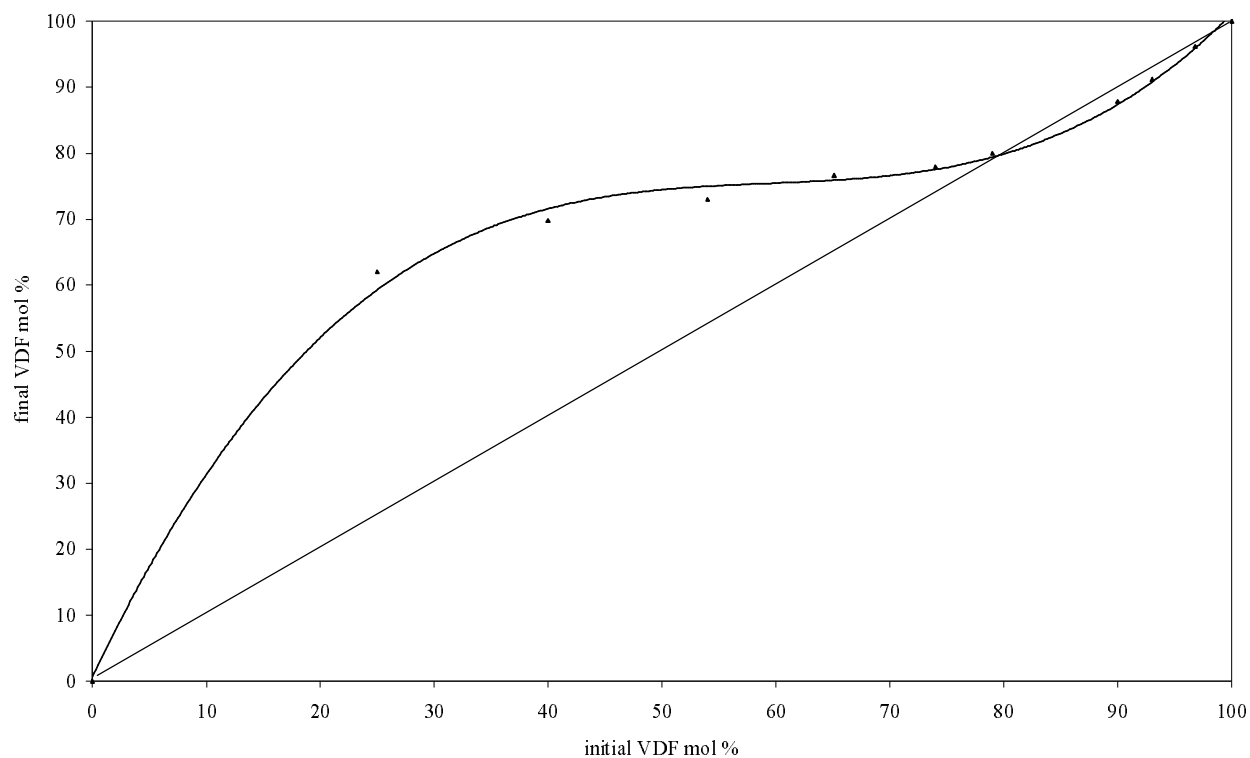


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