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Final Report

TITLE: Development of Synthesis and Large Scale Production
Technology for Ultrahigh Energy and Density Fluoro-Organic
Compounds

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EXECUTIVE SUMMARY

This Phase II STTR project addressed the laboratory production and testing and commercialization aspects of producing high-density fluorine-rich compounds that are significantly more reactive and energetic than conventional explosives to neutralize and destroy chemical and biological agents. The project combined the scientific research base of the University of Florida Department of Chemistry and Department of Mechanical & Aerospace Engineering with the analytical skills and technology marketing expertise of New Era Technology, Inc. (NeTech) to conduct this Phase II STTR, R&D effort.

Development of fluorine-rich compounds—particularly SF_5 bearing polymers—is important because of the deadly nature of the threat posed by biological and nerve agents (BANA). Accordingly the main project goals included:

- To design and synthesize polymeric materials containing a high concentration of SF5 substituents

- To design and synthesize polymeric materials with variable amounts of fluorine on the backbone of the polymer

- Lastly, to test the combustion properties of these new materials

The primary synthetic goals followed both poly-SF5-butane and SF5-containing polymers formed by free radical chain (FRC) process. The achievement of both synthetic goals was accomplished as a result of the invention of *a new and efficient method* for incorporating SF5 substituents into aliphatic compounds and reported on in *Org. Lett.* 2002, *4*, 3013-3015.

For the first time, polymers with a significant degree of incorporation of an SF5-bearing monomer were prepared and characterized. These preparations were accomplished within a collaboration with Dr. Bruno Ameduri (CNRS, Laboratory of Macromolecular Chemistry, Ecole Nat Sup de Chimie de Montpellier, France).

Synthesis of three different SF5 containing monomers were investigated as a prerequisite for polymerization:

- Pentafluorosulfanylethene, M-I ($H_2C=CHSF_5$).

- 1,1-Difluoro-2-pentafluorosulfanylethene, M-II ($F_2C=CHSF_5$).
- 1,1,2-Trifluoro-2-pentafluorosulfanylethene, $SF_5CF=CF_2$, (M-III)

These three monomers, denoted M-I, M-II, and M-III, were used in polymerization studies to form SF5 bearing polymers. Neat Et_3B instead of its 1 M solution in hexanes was used for these reactions, which allowed us to avoid a step of solvent removal. Monomers M-I and M-II were prepared in a manner similar to those described in the literature, but using our new Et_3B-initiation methodology to add SF_5Cl to ethylene and VDF, respectively. For the synthesis of pentafluorosulfanyl ethene M-I, a method developed by Wessel was adopted. Treatment of the chloro precursor with $KOH/H_2O/i$-PrOH allowed preparation of monomer M-I in high yields. Attempts to use this method for preparation of M-II proved less effective resulting in a messy mixture containing the product as well as its decomposition products. A procedure adapted from Winter and Gard successfully prepared M-II starting from 1-bromo-1,1-difluoro-2-pentafluorosulfanylethane. Fortunately, the chloro precursor underwent dehydrochlorination smoothly under the same conditions with no formation of decomposition products being observed upon its treatment with 42.5% KOH solution. M-III monomer ($F_2C=CFSF_5$) was obtained from the radical addition of $BrSF_5$ onto trifluoroethylene followed by a dehydrobromination step.

For the preparation of SF_5- containing polymers with vinylidene fluoride (VDF) and hexafluoropropene (HFP) two batch processes were examined. First, copolymerizations of VDF with $CF_2=CFRf$ were examined. The radical copolymerization of VDF with $F_2C=CFSF_5$ was carried out and compared to those of VDF with HFP, VDF and perfluoromethyl vinyl ether (PMVE) and VDF with perfluoropropyl vinyl ether (PPVE).

It was found that M-III monomer does not homopolymerize but copolymerizes with VDF by free radical initiation. Its reactivity with VDF when compared to that of other fluoroalkenes (HFP, PMVE and PPVE) gives the following decreasing series:

$$HFP>PPVE>PMVE>SF_5M$$

i.e. the M-III monomer has the lowest reactivity due to the SF_5 bulky-side groups.

Because of the difficulty to introduce an SF_5 comonomer into a copolymerization, it was deemed necessary to carry out terpolymerizations of VDF, HFP and different SF_5 containing-monomers – M-I, M-II, M-III, since it was known that the presence of HFP can enhance the reactivity of VDF and of the comonomer. This is the case when one reactive couple of monomers can involve the third low- reactive monomer in terpolymerization.

Studies were conducted of the radical binary and terpolymerization of the different SF_5 containing monomers, their reactivity with VDF and HFP, and the detailed characterization of the copolymers obtained. Batch terpolymerizations of VDF (with HFP) and the SF_5-containing monomers resulted in highly viscous or rubber-like polymers. The expected terpolymers should contain an increased amount of fluorine in the polymer backbone (compared to the usual level of incorporation of HFP), which should improve the physico-chemical properties of the resulting fluoropolymers.

The terpolymerization of SF_5 containing monomers with VDF, HFP in organic solvent, and peroxide initiator has been described for the first time. Indeed, it has been shown that radical polymerization of SF_5M can be successfully performed in 1,1,1,3,3-pentafluorobutane initiated by di(*tert*-butylperoxide). Interestingly, the terpolymerization of VDF with HFP and SF_5M shows that $CH_2=CHSF_5$ monomer was more reactive than $CF_2=CHSF_5$ and even more reactive than $CF_2=CFSF_5$.

$$CH_2=CH(SF_5) > F_2C=CF(SF_5) > F_2C=CH(SF_5)$$

Additionally, analyses indicated that the terpolymers II and III incorporating SF_5 side groups exhibited better thermal properties and higher molecular weights than terpolymer I.

These laboratory quantities produced in Phase II were used in laboratory-scale combustion testing of these target SF_5 bearing polymers. Combustion testing was performed in an externally heated reactor containing air and other oxidative gaseous mixtures under pressure utilized to measure ignition delay time for the SF_5 compounds. The test samples of polymer III were heated in the reactor to a temperature of 1400 ± 100 K. Using NaCl windows on the testcell to enable a spectral range of 900-4200 cm^{-1} for Fourier Transform Infrared Spectroscopy (FTIR), a full spectrum was acquired with a

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resolution of 2 cm^{-1} every 10 s. The concentrations of eight selected major species were analyzed. The addition of dimethyl methanephosphonate (DMMP) was also analyzed.
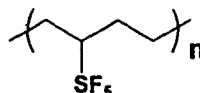
1.0 INTRODUCTION

1.1 Project Goals:

- To design and synthesize polymeric materials containing a high concentration of SF5 substituents
- To design and synthesize polymeric materials with variable amounts of fluorine on the backbone of the polymer
- Lastly, to test the combustion properties of these new materials

1.2 Primary Synthetic Goals:

- A. Poly-SF5-butane

- SF5-containing polymers formed by free radical chain (FRC) process

$$—(CXYCZSF_5)_{\overline{a}}—(CF_2CFCF_3)_{\overline{b}}—(CH_2CF_2)_{\overline{c}}—$$
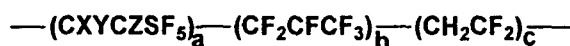
VDF/HFP/(SF$_5$-monomer) Terpolymer

Polymer I, X = Y = H
Polymer II, X = F, Y = H
Polymer III, X = Y = F

2.0 Summary of Project Synthetic Achievements

Achievement of both synthetic goals was accomplished as a result of our invention of *a new and efficient method* for incorporating SF5 substituents into aliphatic compounds (*Org. Lett.* 2002, *4*, 3013-3015)
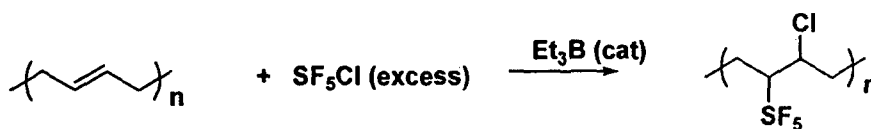
$$CH_2=CH_2 \ + \ SF_5Cl \ \xrightarrow{\text{Et}_3\text{B}} \ SF_5CH_2CH_2Cl$$

$$SF_5CH_2CH_2Cl \ \xrightarrow{\text{NaOEt}} \ SF_5CH=CH_2 \quad \text{Monomer I}$$

$$CH_2=CF_2 \ + \ SF_5Cl \ \xrightarrow{\text{Et}_3\text{B}} \ SF_5CH_2CF_2Cl$$

$$SF_5CH_2CF_2Cl \ \xrightarrow{\text{NaOEt}} \ SF_5CH=CF_2 \quad \text{Monomer II}$$

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For the first time, polymers with a significant degree of incorporation of an SF5-bearing monomer were prepared and characterized. These preparations were accomplished within a collaboration with Dr. Bruno Ameduri (CNRS, Laboratory of Macromolecular Chemistry, Ecole Nat Sup de Chimie de Montpellier, France).

$$n \begin{array}{c} X \\ \backslash \\ / \\ X \end{array} \!\!=\!\! \begin{array}{c} SF_5 \\ / \\ \backslash \\ Y \end{array} \quad + \quad m\ CF_2\!=\!CFCF_3 \quad + \quad p\ CH_2\!=\!CF_2 \quad \xrightarrow[\substack{CF_3CH_2CF_2CH_3 \\ di\text{-}^tBu\ peroxide}]{143\ ^oC,\ 5\ h}$$

SF$_5$-monomer   HPF   VDF

$$-\!(CXYCZSF_5)_a\!-\!(CF_2CFCF_3)_b\!-\!(CH_2CF_2)_c\!-$$
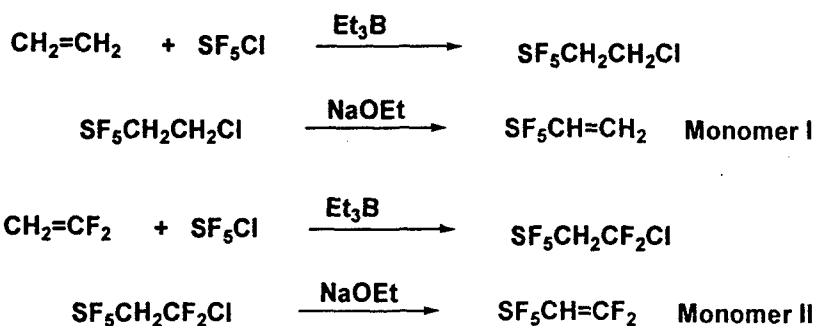
VDF/HFP/(SF$_5$-monomer) Terpolymer
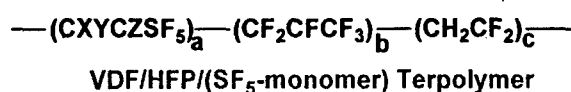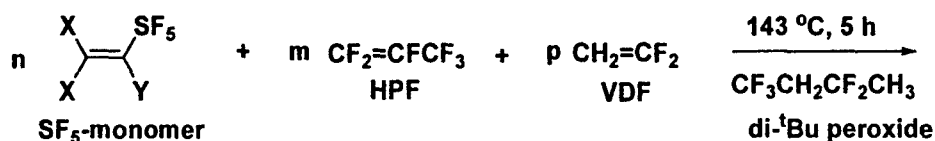
Polymer I,   X = Y = H
Polymer II, X = F, Y = H
Polymer III, X = Y = F

3.0 Discussion of Project Results

3.1 Introduction to fluoropolymers

Fluoropolymers find relevant application in many fields of high technology: aeronautics[1,2], microelectronics, engineering, chemical and automotive industries, optics [3], textile finishing [4] and military use[5]. The specific properties (adhesion, solubility, curability, surface properties, good hydrophilicity, heat or chemical resistance) of a fluoropolymer are determined by the nature of the specific functional group that is present in the lateral position of the copolymer backbone. The synthesis of fluoropolymers can be realized by copolymerization of fluoroalkenes with other fluorinated or nonhalogenated monomers. In contrast to such copolymers, fluorinated homopolymers (e.g., polyvinylidene fluoride, polytetrafluoroethylene or polychlorotrifluoroethylene) exhibit a high crystallinity rate that induces high costs in the processing at the molten state, poor solubility in organic common solvents and difficult crosslinking.

Among the well-known fluorinated copolymers, those incorporating vinylidene fluoride (VDF) monomeric units are of particular interest, because they can be either thermoplastics [6], or elastomers [7], or thermoplastic elastomers [1d,8]. Usually, such fluoropolymers can be synthesized by radical copolymerization of VDF with other

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fluoroalkenes leading to statistical copolymers[7,9] except for copolymers prepared from hexafluoroisobutylene [10] (commercialized by the Allied Company under the CMX® trade mark), methyl trifluoroacrylate [11] and α-trifluoromethyl acrylic acid [12] which are unexpected alternating copolymers. In fact, VDF has been copolymerized with various fluorinated monomers with the resulting copolymers bearing functions such as: hydroxy [13], acetoxy [13,14], thioacetoxy [15], sulfonyl fluoride [16], nitrile [17], bromine [18] or a perfluoroalkyl group [19].

3.2 Introduction to SF$_5$-containing fluoropolymers

Monomers bearing the SF$_5$-group have previously led to a number of materials that can be used as high-performance lubricants and optical materials, water repellent and oil-resistant sealants, antifoaming agents, surface-active agents, and protective surface coatings[20-23]. Recent studies have prepared not only SF$_5$-polyfluoroalkylacrylates [24], SF$_5$-polyfluoroalkylsiloxanes [25], SF$_5$-polyfluoroalkylepoxides[26] but also aromatic polymers that include polyimides containing the SF$_5$(CF$_2$)$_n$C$_6$H$_3$- groups (n= 0, 2) [26,27], polyacrylate and polystyrene containing the SF$_5$CF$_2$CF$_2$-group [28]. Additional properties brought about by the SF$_5$-group include low wettability, low refractive index, low surface energy, high dielectric strength, high chemical and thermal stability. The use of SF$_5$-monomers has resulted in the preparation of the first organic superconductor with an organic anion [29], the first SF$_5$-organic metals/organic semiconductors [30], the first SF$_5$-containing ionic liquids [31] and the preparation of novel liquid crystals [32]. Different SF$_5$- containing copolymers (acrylates, silicones, epoxides) exhibit nonstoichiometric enrichment of the film surface with fluorinated monomers bearing SF$_5$ groups.

Prior to the present studies, in 1969 and 1974, Banks et al. [33-34] reported the preparation of SF$_5$– containing polymers with VDF and hexafluoropropene (HFP) in emulsion using an aqueous redox initiation system and perfluorooctanoic acid. However, no data was supplied about the copolymer compositions. In addition, the microstructure, the molecular weight and Tg values of copolymers obtained were not described. We considered it to be worthwhile to revisit that copolymerization system and to provide characterization of the binary and ternary systems with different SF$_5$ comonomers (hydrogenated and perfluorinated).

Hence, the objective of this paper deals with the radical binary and terpolymerization of different SF_5 containing monomers, their reactivity with VDF and HFP and the detailed characterization of the copolymers obtained.

3.3 Synthesis of polymers

3.3.1 Materials

Vinylidene fluoride (VDF), hexafluoropropene (HFP) and 1,1,1,3,3-pentafluorobutane (kindly provided by Solvay Solexis S.A., Tavaux, France and Brussels, Belgium), di(*tert*-butylperoxide, DTBP (Aldrich) were used as delivered by the supplier. Acetonitrile, dimethylsulfoxyde of analytical grade (Aldrich), were distilled over calcium hydride prior to use.

3.3.2 Analysis

The compositions of the co- and terpolymers (the molar contents of VDF, HFP, and SF_5-containing monomers) were determined by ^{19}F and ^{1}H NMR spectroscopy. The NMR spectra were recorded on Bruker AC 200 and AC 250 instruments, using deuterated acetone as the solvent and TMS (or $CFCl_3$) as the references for ^{1}H (or ^{19}F) nuclei. Coupling constants and chemical shifts are given in Hz and ppm, respectively. The experimental conditions for ^{1}H (or ^{19}F) NMR spectra were the following: 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 64), and a pulse width of 5 μs for ^{19}F NMR.

Differential scanning calorimetry (DSC) measurements were conducted using a Perkin-Elmer Pyris 1 instrument connected to a microcomputer. The apparatus was calibrated with indium and n-decane. After its insertion into the DSC apparatus, the sample was initially cooled to −105°C for 15 min. Then, the first scan was made at a heating rate of 40°C.min^{-1} up to 80°C, where it remained for 2 min. It was then cooled to −105°C at a rate of 320°C.min^{-1} and left for 10 min at that temperature before a second scan was started at a heating rate of 20°C.min^{-1}. Finally, another cycle was performed and a third scan at a heating rate of 20°C.min^{-1} was initiated, giving the values of Tg reported herein, taken at the half-height of the heat capacity jump of the glass transition.

Thermogravimetric analyses were performed with a Texas Instrument TGA 51-133 apparatus in air at a heating rate of $10°C.min^{-1}$ from room temperature up to a maximum of 600 °C.

Gel Permeation Exclusion Chromatography (GPC) or Size Exclusion Chromatography (SEC) was carried out in tetrahydrofuran at 30 °C, at a flow rate of 0.8 mL/min, by means of a Spectra Physics Winner Station, a Waters Associate R 401 differential refractometer and a set of four columns connected in series: Styragel (Waters) HR4 5μ, HR3 analyses 5μ, PL Gel (Polymer Laboratories) 5μ 100 Å. Monodispersed (PMMA) standards were used for calibration. Aliquots were sampled from the reaction medium, diluted with tetrahydrofuran up to a known concentration ($C_{p,t}$) ca. 4% wt.-%, filtered through a 20 μm PTFE Chromafil Membrane and finally analyzed by GPC under the conditions described above.

3.3.3 Synthesis of SF₅-containing monomers

1-chloro-2-pentafluorosulfanylethane (ClCH₂CH₂SF₅). A 50 mL three-necked flask containing 30 mL of methylene chloride and bearing a dry ice condenser was cooled to – 60 °C, and ethylene was bubbled vigorously through the solution for five minutes, after which 3.2g (0.020mol) of SF₅Cl was bubbled into the mixture. Triethylborane (1 mL) was then added dropwise to the mixture, with stirring, and the bubbling of ethylene was recommenced for another 5 minutes. After 1 h at -60 °C, the solution was allowed to warm to -30 °C, where it was maintained for another 2 h. The solvent was removed by distillation to give 2.5g (yield: 65%) of a residue that was essentially pure 1-chloro-2-pentafluorosulfanylethane, which was used directly in the next reaction. Bp: 92-93 °C ; ¹H NMR: δ 4.15-3.85 (m) ; ¹⁹F NMR: δ 81.57 (q, 1F), 64.92 (d, 4F).

Pentafluorosulfanylethene, M-I (H₂C=CHSF₅). To 3.5 g potassium hydroxide in 4 mL of water was added 10.5 mL of isopropanol in a 50 mL three-necked flask equipped with an addition funnel and a reflux condenser connected to a trap cooled by a dry ice/acetone bath. The solution was brought to reflux and then 4.5 g (0.024mol) of the 1-chloro-2-pentafluorosulfanylethane was added dropwise. The mixture was refluxed for 2 h, with 2.9 g (yield: 79%) of the desired product being collected in the cooled trap: ¹H

NMR, δ 5.74 (m, 1H), 6.01 (d, J = 15 hz, 1H), 6.68 (m, 1H); ^{19}F NMR: AB$_4$ system, δ 81.5 (pent, 1F) and 59.7 (d, 4F), J$_{AB}$ = 146 Hz [35].

1-Chloro-1,1-difluoro-2-pentafluorosulfanylethane (ClCF$_2$CH$_2$SF$_5$). In a 50 mL three-necked flash bearing a dry ice condenser and cooled to – 50 °C was condensed 20 mL of ClCF$_2$CH$_3$ (Forane 142b) and 4.4g (4 equiv) of CF$_2$=CH$_2$ (VDF). To this mixture was added 2.7 g (0.017mol) of SF$_5$Cl. Then 1.5 mL of Et$_3$B was added to the mixture drop wise and the mixture stirred at – 20 to – 30 °C for 3 h, after which the flask was stoppered and allowed to stand at -20 °C for three days. Then the fluorinated solvent was evaporated, leaving 1.5g (yield: 40%) of almost pure product, 1-chloro-1,1-difluoro-2-pentafluorosulfanylethane, which was used directly in the next reaction. Bp 70 °C ; ^{1}H NMR: δ 4.4-4.2 (m) ; ^{19}F NMR: δ 77.04 (q, 1F), 70.06 (d, 4F), -55.35 (s, 2F).

1,1-Difluoro-2-pentafluorosulfanylethene, M-II (F$_2$C=CHSF$_5$). A 50-ml round-bottom flask equipped with a magnetic stirrer and a 20-cm reflux condenser that was connected to a cold trap   (-78°C) was charged with an aqueous potassium hydroxide solution (13 g, 42.5% by weight). 1-Chloro-1,1-difluoro-2-pentafluorosulfanylethane (4.4 g, 19 mmol) was added at room temperature to the solution. The mixture was slowly heated to 100 °C. Heating was continued for 2 hrs with simultaneous collection of the product **M-II** in a cold trap, 2.1 g (13 mmol, yield: 70%). Bp 26 °C ; ^{1}H NMR: δ 5.7 (m) ; ^{19}F NMR: δ 78.89 (m, 1F, SF$_5$), 72.78 (d, 4F, SF$_5$), -65.80 (m, 1F), -83.96 (m, 1F) [36-38].

1,1,2-Trifluoro-2-pentafluorosulfanylethene, SF$_5$CF=CF$_2$, (M-III) was prepared from SF$_5$CHFCF$_2$Br as described in the literature [38]. The purity of the starting material was checked via IR and NMR spectroscopy.
IR (cm^{-1}): 1782 (s, C=C), 1351 (s), 1246 (s), 1089 (m), 898 (vs), 862 (vs), 706 (m), 654 (wm), 613 (s). The absorptions at 898 and 862 cm^{-1} are due to S-F stretching while that at 613 cm^{-1} is due to one of the SF$_5$-deformation modes.
NMR (CDCl$_3$, CFCl$_3$): 69.7 (nine-line pattern, 1F, SF$_5$); 59.0 (d, 4F, SF$_5$); -163 (m, 1F, **CF=**); - 99.5 (m, 2F,**=CF$_2$**).

3.3.4 Copolymerization

The batch copolymerizations of VDF with **CF$_2$=CFRf** were performed in thick borosilicate Carius tubes (length 130 mm, internal diameter 10 mm, thickness 2.5 mm; for a total volume of 8 cm^3). After the introduction of the initiator (di *tert*-butyl peroxide ~ 1.0 mol % *versus* the monomer quantities) and acetonitrile (1.5-2.0 g), the tube was connected to a manifold and then cooled with liquid nitrogen. After five freeze – thaw cycles, the appropriate gas quantities were trapped in the tube cooled in liquid nitrogen under 20 mm Hg. To introduce the targeted VDF quantities, a previous calibration was made to link the gas pressure (bars) to the introduced weight (grams) (for example, a difference of pressure of 0.66 bar represents 1.00 g of VDF). The tube was sealed while immersed in liquid nitrogen and then stirred at the chosen temperature (140 °C) for the required time (0.5 hours was chosen for carrying out the process of radical copolymerization). After reaction, the total product mixture was analyzed by ^{19}F NMR and ^{1}H NMR. Then, the copolymers were precipitated from cold pentane and dried until constant weight was reached.

Batch terpolymerizations of VDF (with HFP) and the SF$_5$-containing monomers were performed in a 160 ml HASTELLOY (HC 276) autoclave, equipped with an inlet valve, a manometer, and a rupture disk. The autoclave was purged with 20 bars of nitrogen pressure and left closed for 20 minutes to test for leakage. After releasing the pressure, a 20 mm Hg vacuum was operated for 15 min, and then the initiator di(*tert*-butylperoxide), SF$_5$ monomers, and 1,1,1,3,3-pentafluorobutane were introduced successively via a funnel tightly connected to the introduction valve. Next, VDF and HFP were respectively introduced by double weighing. The autoclave was then heated at 143 °C for 5 hours. After reaction, the vessel was cooled to room temperature and then put in an ice bath. The non-reacted monomers were separated and the conversion vs. monomers was determined. Then, the solvent was evaporated, the co- or terpolymer was precipitated from cold pentane and the total product mixture was dried at 0.1 mm Hg at 40 °C for 15hrs (to constant weight). Highly viscous or rubber-like polymers were obtained.

4.0 Results and Discussion

4.1 Synthesis of Monomers containing SF5 (SF5M)

Monomers **M-I** and **M-II** were prepared in a manner similar to those described in the literature, but using our new Et_3B-initiation methodology [39] to add SF_5Cl to ethylene and VDF, respectively.

M-I, R = H
M-II, R = F
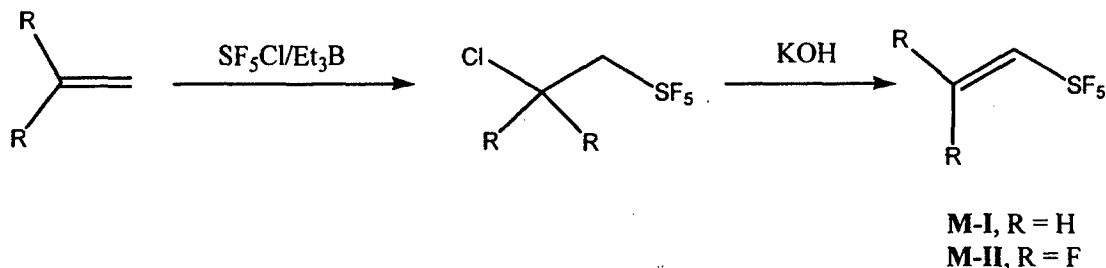
The reaction of SF_5Cl with ethylene proceeded smoothly in dichloromethane at –30° to –20°C over 2 hrs furnishing 1-chloro-2-pentafluorosulfanylethane in good yield, but the synthesis of 1-chloro-1,1-difluoro-2-pentafluorosulfanylethane proved to be more difficult. As pointed out by Case et al. [40], reactions of SF_5Cl with fluorocarbon olefins do not take place as easily as those with hydrocarbon olefins. Thus, significantly harsher conditions were required for the reaction with VDF to occur. Only trace amounts of product were obtained after treatment of VDF with SF_5Cl in dichloromethane or pentane. On the other hand, when the reaction was carried out in $ClCF_2CH_3$ (Forane 142B) as a solvent, it was possible to increase the yield up to 70-80%. Neat Et_3B instead of its 1 M solution in hexanes was used for these reactions, which allowed us to avoid a step of solvent removal. Since the boiling point of $ClCF_2CH_3$ is only –10°C, essentially pure products were obtained by simply warming the reaction to room temperature. These chloro, pentafluorosulfanylethane intermediates were used in the next step without further purification.

For the synthesis of pentafluorosulfanyl ethene **M-I**, a method developed by Wessel et al. [35] was adopted. Treatment of the chloro precursor with $KOH/H_2O/i$-PrOH allowed preparation of monomer **M-I** in high yields.

When we attempted to use this method for preparation of **M-II**, a messy mixture containing the product as well as its decomposition products was obtained. Winter and

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Gard successfully prepared **M-II** starting from 1-bromo-1,1-difluoro-2-pentafluorosulfanylethane[37]. Fortunately, the chloro precursor underwent dehydrochlorination smoothly under the same conditions with no formation of decomposition products being observed upon its treatment with 42.5% KOH solution. **M-III** monomer ($F_2C=CFSF_5$) was obtained from the radical addition of $BrSF_5$ onto trifluoroethylene followed by a dehydrobromination as reported in a previous work [38,39]

4.2 Radical copolymerization of SF_5-containing monomers with VDF and HFP

4.2.1 Radical copolymerization of $F_2C=CFSF_5$ with VDF

Initially, the radical homopolymerization of $F_2C=CFSF_5$ was attempted under classic conditions of homopolymerization starting from a [di *tert*-butyl peroxide, DTBP]$_0$ to [$F_2C=CFSF_5$]$_0$ molar ratio of 2 mol %, 5.0g (0.024 moles) of $CF_2=CFSF_5$, solvent 1,1,1,3,3-pentafluorobutane (70 wt %), temperature 143 °C and reaction time 5 hrs. It was noted that no reaction occurred, probably because of the bulky SF_5 substituent which, as in the case of HFP, PPVE, PMVE or PFP prevents these fluoromonomers from undergoing homopolymerizations.

Then, the radical copolymerization of VDF with $F_2C=CFSF_5$ was carried out and compared to those of VDF with hexafluoropropene (HFP), VDF and perfluoromethyl vinyl ether (PMVE) and VDF with perfluoropropyl vinyl ether (PPVE). For each couple, three different copolymerization were carried out using VDF mol. percentages of ca. 20, 50 and 75% under the same conditions of batch (initiator di*tert*-butyl peroxide in 1,1,1,3,3-pentafluorobutane as the solvent). Because of the high volatilities of VDF and SF_5-containing monomers, the precise assessment of monomer conversions was difficult to obtain. Nevertheless, the monomer conversions were established to be less than 10 wt %.

Both comonomeric units in each of the copolymers were assessed by ^{19}F NMR spectroscopy. Those of poly(VDF-co-HFP) [41], poly(VDF-co-PMVE) [19b,42] and poly(VDF-co-PPVE) [19b,42] copolymers had been previously characterized by ^{19}F NMR while that of poly(VDF-co-SF$_5$M) copolymers has never been reported in the literature Table 1. For example, Figure 1 represents the ^{19}F NMR of the copolymers prepared by

radical copolymerization of VDF and SF_5-monomer III ($CF_2=CFSF_5$) starting from an initial feed percentage of VDF/M-III = 70/30. This spectrum shows a peak centered at about –91.1 ppm (noted $I_{91.1}$) characteristic of the difluoromethylene groups of the head-to-tail VDF chaining (i.e., normal VDF addition). Furthermore, a series of other signals centered at -94.9 (noted I_{94}), -113.7 (noted $I_{113.7}$) and -115.7 (noted $I_{115.7}$) ppm can be assigned to the CF_2 groups in $(CH_2-CF_2)-(CF_2-CH_2)-(CH_2-C\underline{F}_2)-(CH_2-CF_2)$; $-(CH_2-C\underline{F}_2)-(CF_2-CH_2)-(CF_2-CH_2)-$; $(CH_2-CF_2)-(C\underline{F}_2-CH_2)-(CH_2-CF_2)$ sequences, respectively, and correspond to the reverse VDF addition (i.e., head-to-head addition) [43] as noted for the chemical shifts observed for ^{19}F NMR spectra of poly(VDF-co-HFP) [41] or poly(VDF-co-PVME) [42]. The multiplet signals from +75 to +50 ppm are ideally an AB_4 system and are assigned to the five fluorine atoms in the SF_5 groups; the first one was a nine-line pattern, each line split into a triplet, and the second one was a skewed doublet of a pentet. The difluoromethylene group of VDF adjacent to $CF_2CF(SF_5)$ leads to a signal centered at – 109.8 ppm while those centered at -118.8 and -136.7 ppm are related to the -CF_2 and -CF groups, respectively, deriving from the perfluorovinyl group of the M-III monomer (Table 2).The microstructure of the copolymers was assessed by mol % SF_5 = ($I_{+50\ to}$ $_{+75}$)/5 for the multiplet centered at –135ppm for –$CF(SF_5)$ fluorine atom. Indeed, both fluorine atoms in the difluoromethylene group adjacent to –$CF(SF_5)$ were anisochronous,hence leading to an AB system. This arises from the bulky –SF_5 group which stiffens the molecule as we had noted in $C_4F_9CF_2CF(CF_3)I$ obtained by telomerization of HFP with C_4F_9I[45].In that monoadduct containing a bulky iodine, the central CF_2 group yielded an AB system. This AB system was also noted on CF_2 of VDF adjacent to -$CF_2CF(CF_3)$ as in the case of $C_3F_7CF_2CF(CF_3)I$. Because of the overlapping of different signals in that region it was difficult to assess the mol % CF_5M from $\delta\ cf_2$ atoms. Interestingly, no doublet of multiplets centered at –114.8 ppm corresponding to -$CH_2C\underline{F}_2H$ end-group was observed, proving the absence of transfer reaction [41,43,44,45]. The mol percentage of VDF in the copolymer was assessed from the following formulae taking into account that integrals of signals centered at –113 and –116 ppm are the same with some overlapping of those centered at –116 and –118.8 ppm :

Mol. % VDF= [$I_{-91}+I_{-94}+I_{-107}+2I_{-113.7}$]/ [$I_{-91}+I_{-94}+I_{-107}+2I_{-113.7}$]+ $2I_{-136.7}$ (eq.1)

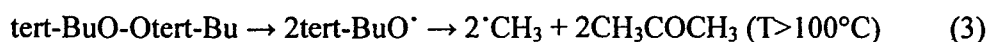^1H NMR spectrum (Fig.2) exhibits one multiplet signal centered at 3.0 ppm assigned to

the –CH₂ protons of normal VDF units and traces of signals at 2.3-2.4 ppm that can be related to the CH₂ groups in the reverse structure of VDF (or tail to tail addition) [41,43]. Interestingly, no triplet of triplets is seen, which would be characteristic of –CH₂CF₂H arising from an H-transfer from solvent or polymer.

Table 1 summarizes the results obtained from the four different series of radical copolymerization involving VDF. It is observed that comparing all cases, the SF₅ monomer is the least reactive and the decreasing reactivity series is suggested:

$$HFP > PPVE > PMVE > SF_5M \tag{2}$$

That low reactivity of SF₅M may arise from both the bulky electron withdrawing SF₅ groups and the delocalization of the electron in the radical ~ CF₂C˙F(SF₅) terminal groups. This observation results in low molecular weight copolymers in the range of 1700-5400 g/mol. From a mechanistic point of view, when DTBP is thermally decomposed two different radicals can be produced as follows:

$$\text{tert-BuO-Otert-Bu} \rightarrow 2\text{tert-BuO}^{\bullet} \rightarrow 2{}^{\bullet}\text{CH}_3 + 2\text{CH}_3\text{COCH}_3 \ (T>100°C) \tag{3}$$

It is assumed that tert-BuO˙ undergoes a thermal fragmentation (T>100°C) to generate ˙CH₃ [43d]. The radicals produced can react onto both sides of VDF in a non-regioselective manner:

$$R^{\bullet} + H_2C=CF_2 \rightarrow RCH_2C^{\bullet}F_2 + RCF_2C^{\bullet}H_2 \tag{4}$$

$$R:CH_3, \text{tert-BuO}$$
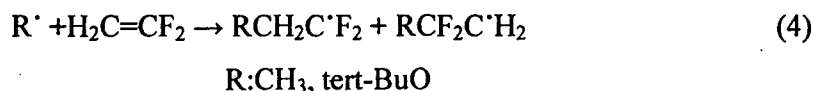
These hydrogenated end-groups can be evidenced by ¹H NMR as follows:

CH₃CH₂CF- at 1.2 ppm, CH₃CF₂CH₂ – at 11.8 ppm , (CH₃)₃C-OCH₂CF₂- at 1.1 ppm and (CH₃)₃C-OCF₂CH₂– at 1.15 ppm. In addition, signals of small intensities are observed in the ¹⁹F NMR spectra at –60 and –65 ppm. They are assigned to CF₂ of (CH₃)₃C-OCF₂CH₂– and confirm previous works dealing with the addition of tert-BuO˙ onto the CF₂ site of VDF[43d] or onto the CF₂ site of PMVE[16e].

Both ¹⁹F and ¹H NMR spectra were used to assess the molecular weight of poly(VDF-co-CF₅MIII) copolymers:

$$N_{VDF} = [(I_{2.3-2.5} + I_{2.8-3.2})/2]/[(I_{1.2} + I_{1.8})/6] \tag{5}$$

where N_{VDF} is number of VDF units in copolymer and I_i are the integrals of H signals at given ppm, assuming recombination of macroradicals as a main termination reaction[1d].

^{19}F NMR spectra yield the SF$_5$/VDF molar ratio α in the copolymer. Hence, the molecular weights can be deduced from the following equation :

$$Mn = N_{VDF} \times 64 + \alpha\, N_{VDF} \times 208 + 30 \qquad (6)$$

Table 3 lists the molecular weights of binary poly(VDF-co-SF$_5$MIII) copolymers obtained from equation (6).

In addition the solution polymerization used leads to lower molecular weights in contrast to polymerizations carried out in aqueous media (such as emulsion, miniemulsion or suspension) that result in higher molecular weights (as for poly(VDF-co-HFP) copolymers)[5].

Hence, because of the difficulty to introduce an SF$_5$ comonomer into a copolymerization, we have found it worthwhile to carry out terpolymerizations of VDF, HFP and different SF$_5$ containing-monomers – M-I, M-II, M-III, since it is known that the presence of HFP can enhance the reactivity of VDF and of the comonomer as recently reported in the case of F$_2$C=CFO-C$_6$H$_4$-Br[44]. This is the case when one reactive couple of monomers can involve the third low- reacticve monomer in terpolymerization.

4.2.2 Radical terpolymerization of SF$_5$-containing monomers with VDF and HFP

The expected terpolymers should contain an increased amount of fluorine in the polymer backbone (compared to the usual level of incorporation of HFP), which should improve the physico-chemical properties of the resulting fluoropolymers.

A series of terpolymerizations were performed using an initial [initiator]$_0$/[total monomers]$_0$ molar ratio of 1%. These radical-initiated polymerizations were carried out in a high pressure autoclave at 143 °C for 5 hrs using di(*tert*-butyl)peroxide as the radical initiator and 1,1,1,3,3-pentafluorobutane as the solvent (Figure 3). Upon completion of the reaction, the solvent was evaporated and, after precipitation and drying, the products were characterized by their ^{1}H and ^{19}F NMR spectra, which allowed characterization of the microstructures of these terpolymers. Depending on the identity of the SF$_5$-containing monomer and of the initial molar ratios, three different types of terpolymers were obtained: (a) a brown high viscous liquid oligomer (I) when using the SF$_5$ monomer **M-I**, which bears three H atoms on the vinyl group; (b) a brown rubber-like polymer (II) when using SF$_5$ monomer (**M-II**); and (c) a grey rubber-like polymer (III) when using the

perfluorinated monomer **M-III**. Regarding solubilities of the polymers, all of them were soluble in acetone, THF and in 1,1,1,3,3-pentafluorobutane, whereas terpolymer **III**, based on the perfluorinated SF_5 monomer was also soluble in dichloromethane and partially in chloroform. It was also noted that the higher the fluorine content of the SF_5 comonomer, the higher the yield of the reaction, and the higher the initiator concentration, the greater the yield (Table 4).

On the basis of such analyses, it was concluded that in all cases statistical terpolymers were obtained wherein the different monomeric units were randomly distributed in the backbone, and where microblocks of oligo(VDF)s could be noted in the terpolymer. The relative amounts of the monomers in the terpolymers were assessed by ^{19}F NMR spectroscopy (Figures 4 and 6). In addition, all ^1H NMR spectra(Figures 5 and 7) exhibit signals that can be assigned to the methylene groups of VDF units adjacent to difluoromethylene groups in the 2.5 - 3.5 ppm range (with the high amounts of VDF units in the terpolymer, small amounts of head-to-head addition can also be seen, which gives rise to signals at about 2.2 - 2.4 ppm). The low intensity of the signals and absence of any triplet of triplets and of doublet of multiplets centered at 6.3 and 5.6 ppm, assigned to – CH_2CF_2H and CF_2CFHCF_3, respectively, gave evidence that very little (Figure 5) or no (Figure 7) chain transfer reaction occurred.

4.2.2.1 Determination of the terpolymer compositions by using ^{19}F NMR spectra

Radical terpolymerizations in solution with organic initiators of SF_5-containing monomers such as **M-I**, **M-II** and **M-III**, have not been previously reported in the literature. The main goal of this part was thus to identify those peaks characteristic of such comonomers in the terpolymers. In contrast, the determination of the various NMR signals deriving from VDF and HFP units in co- and terpolymers has been the subject of various papers[7,16e,41,44,46].

4.2.2.2 Terpolymerization of SF_5 Monomers with VDF and HFP

The ^{19}F NMR spectra of polymers **I** and **III** (Fig. 4 ,6) as well as polymer **II** exhibit the characteristic signals centered at -91, -94, -107, -110, -113.7 and -116 ppm assigned to the difluoromethylene groups of VDF in the normal addition, adjacent to a $F_2C=CFSF_5$

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unit, and to reverse addition : -CH$_2$<u>CF$_2$</u>-CF$_2$CH$_2$-CH$_2$CF$_2$- and -CH$_2$CF$_2$<u>CF$_2$</u>CH$_2$-CH$_2$CF$_2$- [43], respectively as observed in NMR spectra of copolymers (Table 2). The signals located at -108 ppm (noted I$_{-108}$) and −110.1 (noted I$_{-110.1}$) range are assigned to the difluoromethylene groups of the VDF unit adjacent to HFP and SF$_5$M unit, respectively.

In addition, the chemical shifts centered at -71.2 (noted I$_{-71.2}$), -74.8 (noted I$_{-74.8}$) are assigned to the trifluoromethyl side group of HFP in the terpolymer: -CH$_2$CF$_2$CF$_2$CF(CF$_3$)- CF$_2$-CH$_2$-, -CH$_2$-CF$_2$-CF$_2$-CF(CF$_3$)-CH$_2$-CF$_2$-, while those centered at −118.8 (noted I$_{-118.8}$) and −183.5 (noted I$_{-183.5}$) ppm are attributed to the HFP difluoromethylene groups in -CH$_2$CF$_2$CF$_2$CF(CF$_3$)- sequences and to the tertiary fluorine in CF$_2$CF(CF$_3$) of HFP [41], respectively.

Finally, the multiplets centered at − 114.0 ppm (noted I$_{-114.0}$) and − 112.0 ppm (noted I$_{-112.0}$) are attributed to the difluoromethylenes of the SF$_5$M unit in terpolymers **III** and **II**: -(CF$_2$-CF(SF$_5$))- and CF$_2$-CH(SF$_5$))-, respectively. Also, the peaks located in the -137.6 ppm region (noted I$_{-137}$) are assigned to the tertiary fluorine atom in the CF group of -(CF$_2$-CF(SF$_5$))- monomer unit in polymer **III**. The multiplets centered at +55 and +75 ppm in the ^{19}F NMR are consistent with the presence the SF$_5$ group. The SF$_5$ group, as found by Muller et al. [47], contains four magnetically equivalent and one non-equivalent fluorine atoms (AB$_4$ system). The equatorial, A$_4$, resonance is split into a doublet while the apex, A, resonance is grossly a pentet with a 'fine structure'. Cross et al. [48] reported that the compounds in which the SF$_5$ group is bound to aliphatic hydrocarbons, a very intense broad band centered on or about 870 cm^{-1} is found. They assigned this to the S-F stretching modes. We observed the same behavior with our compounds.

The integrals in the ^{19}F NMR spectra (denoted above), allow the determination of the molar fractions of VDF, HFP and SF$_5$M units in the terpolymers, and they are given by the following equations (Eq. 7):

$$\text{Mol \% of VDF in the terpolymer} = \frac{I_J}{I_J + I_K + I_L} \times 100 \qquad \text{(Eq. 7a)}$$

$$\text{Mol \% of HFP in the terpolymer} = \frac{I_K}{I_J + I_K + I_L} \times 100 \qquad \text{(Eq. 7b)}$$

$$\text{Mol \% of SF}_5\text{M in the terpolymer} = \frac{I_L}{I_J + I_K + I_L} \times 100 \qquad \text{(Eq. 7c)}$$

where,

$$I_J = \frac{I_{-91.1} + I_{-94.9} + I_{-109.8} + I_{-110.1} + 2 \times I_{-115.7}}{2} \qquad \text{(Eq.8a)}$$

$$I_K = \frac{I_{-71.2} + I_{-74.8}}{3} \quad \text{or} \quad I_K = I_{-119}/2 \qquad \text{(Eq.8b)}$$

$$I_L = I_{+50 \text{ to } +75}/5 \quad \text{or} \quad I_L = I_{-135} \qquad \text{(Eq.8c)}$$

The degrees of incorporation of each monomer in the terpolymers are listed in Table 4.

4.2.2.3 Characterization of the terpolymers

Table 4 lists the final molar percentages of each termonomer and also the physico-chemical properties of each terpolymer. In the same experimental conditions (experiments I, II and III: terpolymer VDF / HFP / SF$_5$M, starting from the same SF$_5$M feed molar percentages of ca. 8.6 mol % led to copolymers containing 17.4, 2.1, and 5.3 mol. %, respectively (Table 4). The increasing mol. % of SF$_5$M in feed means increasing its mol. % in the terpolymer and the yield. Usually, the final molar percentages of VDF is higher than the molar percentages in feed. As a matter of fact, this result is the evidence of the presence of oligo(VDF) blocks separated by one SF$_5$ monomeric unit in the terpolymer. The poor reactivity of $F_2C=CH(SF_5)$ monomer is not surprising when its behavior is compared to that of $F_2C=CH(CF_3)$[49] or $F_2C=CH(C_6F_{13})$,1HPFO[50]. Actually, kinetics of copolymerization of both of these fluorinated monomers led to the following reactivity ratios:

$$r_{PFP} = 0.06 ; \qquad r_{VDF} = 9.0 \qquad \text{at } 40°C$$

$$r_{1HFPO} = 0.9; \qquad r_{VDF} = 12.0 \qquad \text{at } 75°C$$

These values show the low reactivity of the above mentioned fluorinated alkenes vs. VDF.

While the ^{19}F NMR spectroscopy shows the insertion of VDF and HFP base units in the terpolymers, several methods were used to characterize these fluorinated terpolymers: the molecular weights by size exclusion chromatography (SEC with PMMA standards, the polymers were soluble in THF) and the thermal properties by differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA).

In all cases, the SEC chromatograms (Figure 8) showed one main maximum with two shoulders. This can be surprising for terpolymers for which monomodal distribution is expected, although more detailed experiments required to be done. The value of the average molecular weights, $\overline{M_n}$, of poly(VDF-ter-HFP-ter-SF$_5$M) terpolymers (experiments I, II and III with ca. 8.6 mol % in feed of fluorinated SF$_5$ monomer) or poly(VDF-ter-HFP-ter-SF$_5$M) terpolymers (experiment IV), 13.6 mol % in feed of perfluorinated SF$_5$ monomer) were about 2540, 8290, 10030, and 6650 g.mol^{-1}, respectively (Table 4). The SEC chromatograms shown in Figure 8 also indicate some low molecular weight-products tailing in the range of monomers. The maximum of the SEC traces shifted towards higher molecular weight with increasing of fluorine atom in SF$_5$M for the main part of the copolymer obtained. In the case of experiments III and IV, the lower molecular weight in the latter is, as expected, due to the higher concentration of DTBP initiator (3 mol % vs. 1 mol%). However, these measurements cannot be considered quite accurate because of the lack of standards for VDF polymers. The polydispersity index of terpolymers synthesized is in the range of the statistic distribution (2.0-2.4).

The transfer reaction on the macroradical appears to be quite negligible on the basis of the small presence of transfer signals in ^{19}F and ^{1}H NMR spectra (few presence of triplet of triplets and doublet of multiplets centered at 6.1 and 5.5 ppm assigned to -CH$_2$CF$_2$H and -CF$_2$CF(CF$_3$)H, respectively. On the other hand using the same strategy of binary poly(VDF-co-SF$_5$MIII) copolymers, the molecular weights of terpolymers can be assessed by ^{1}H and ^{19}F NMR analyses. The equation 6 can be modified as follows:

$$Mn = N_{VDF} \times 64 + \alpha_1 N_{VDF} \times 150 + \alpha_2 N_{VDF} \times M_{SF_5M_i} + 30 \qquad (9)$$

where α_1 and α_2 are the molar ratios of HFP and SF_5M_i monomer units vs. VDF and $M_{SF_5M_i}$ are the molecular weights of SF_5MI, SF_5MII and SF_5MIII monomers, respectively. The results obtained are shown in Table 3 and compared to SEC molecular weights. They follow the same tendency, but they have higher values than SEC ones as was discussed before.

Thermogravimetry curves (Figure 9) show that these terpolymers exhibit a good thermal stability since their decomposition started from 170 to 250°C, for poly(VDF-ter-HFP-ter- SF_5) terpolymers. For example, terpolymer I (curve I) is the least thermal stable because of the entirely hydrogenated vinyl group in M-I. The higher the fluorine content, the higher thermostability of the obtained terpolymer.

The glass transition temperatures (Tg) of the different fluorinated terpolymers were assessed by differential scanning calorimetry (DSC) and the results are listed in Table 3. In the poly(VDF-ter-HFP-ter-SF5M) terpolymers, Tgs were ranging from -40 to -50 °C without any other transitions, showing amorphous behaviour. With such T_gs, and as reported in the literature [8,9], it is known that fluoropolymers containing VDF and HFP base units only, exhibit average T_g of -26°C and are fluoroelastomers.

Finally, regarding the results gathered in Table 4, it appears that the hydrogenated monomer M-I is more reactive than M-II and M-III monomers containing two and three F- atoms in the vinyl group, respectively.
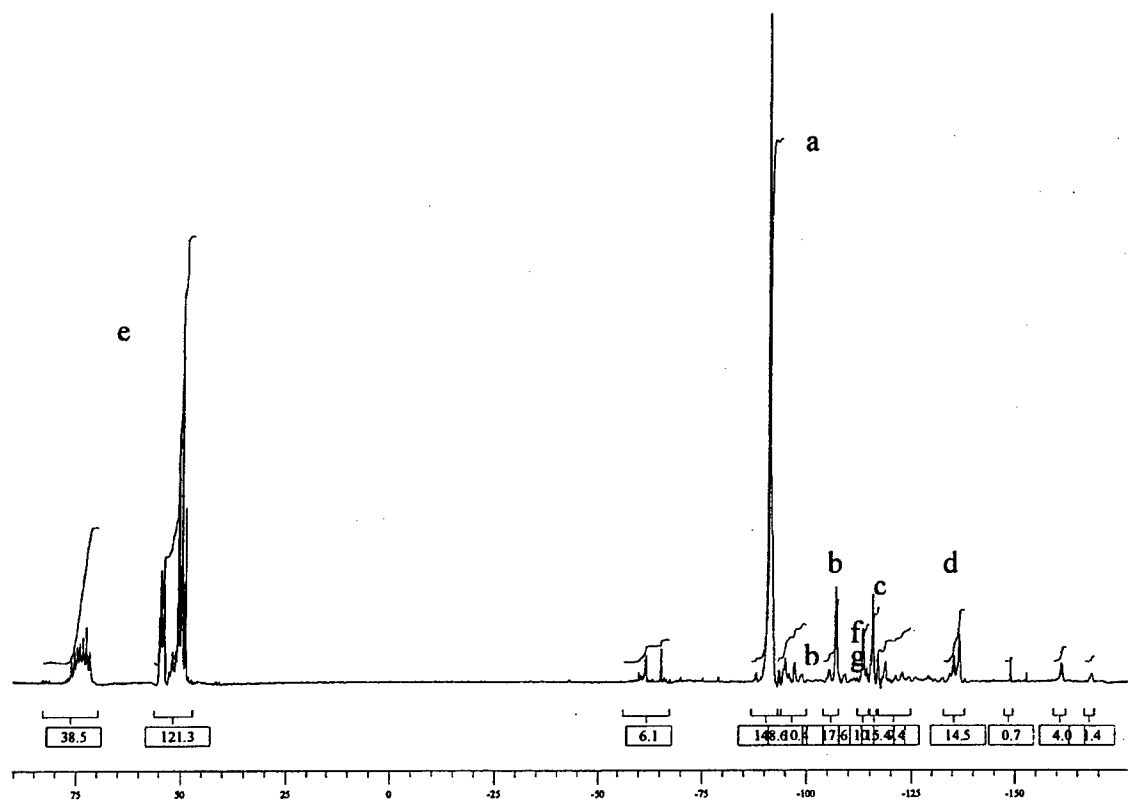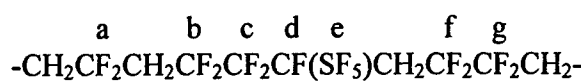
a   b   c   d   e   f   g
-CH₂CF₂CH₂CF₂CF₂CF(SF₅)CH₂CF₂CF₂CH₂-

Fig.1 ¹⁹F NMR spectrum of VDF/CF₂=CF(SF₅) copolymer at 70/30 mol % monomer
ratio in the feed

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a   b   c

-$CH_2CF_2CH_2CF_2CF_2CF(SF_5)CF_2CH_2CH_2CF_2$-

Fig. 2 ^1H NMR spectrum of VDF/CF_2=CF(SF_5)copolymer at 70/30 mol % monomer ratio in the feed

$$nH_2C=CF_2 \;+\; mF_2C=CFCF_3 \;+\; pXCY=CZSF_5 \;\xrightarrow{\text{radical}}\; \left[(CH_2CF_2)_t - (CF_2CF)_u - CF_3 \right.$$

$$\left. (CXYCZ)_v \right]_q SF_5$$
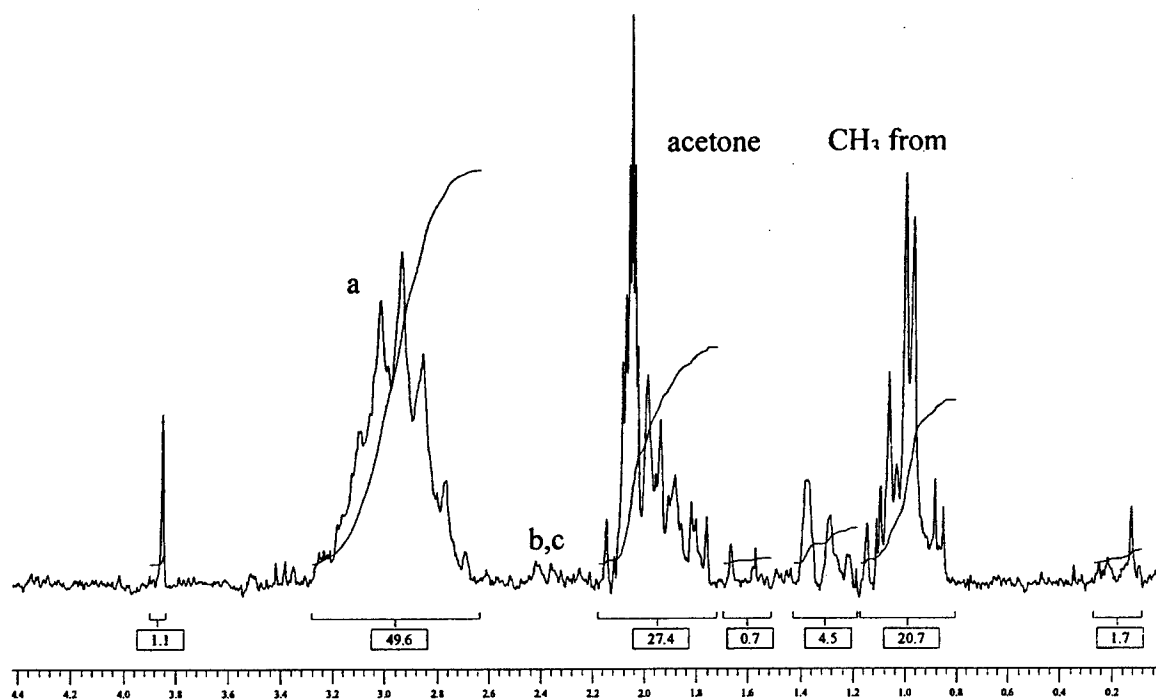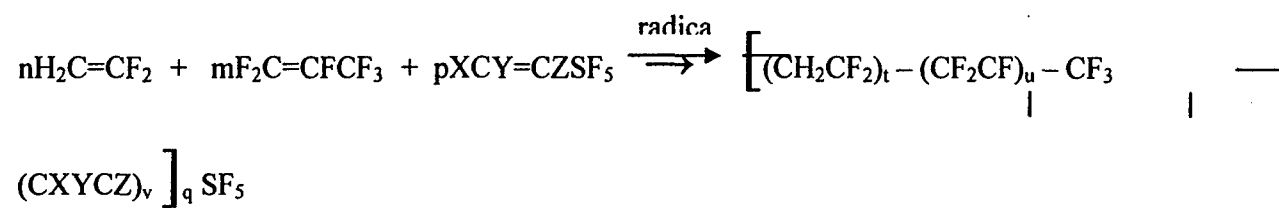
Fig. 3: Radical terpolymerization of SF₅ monomers with VDF and HFP
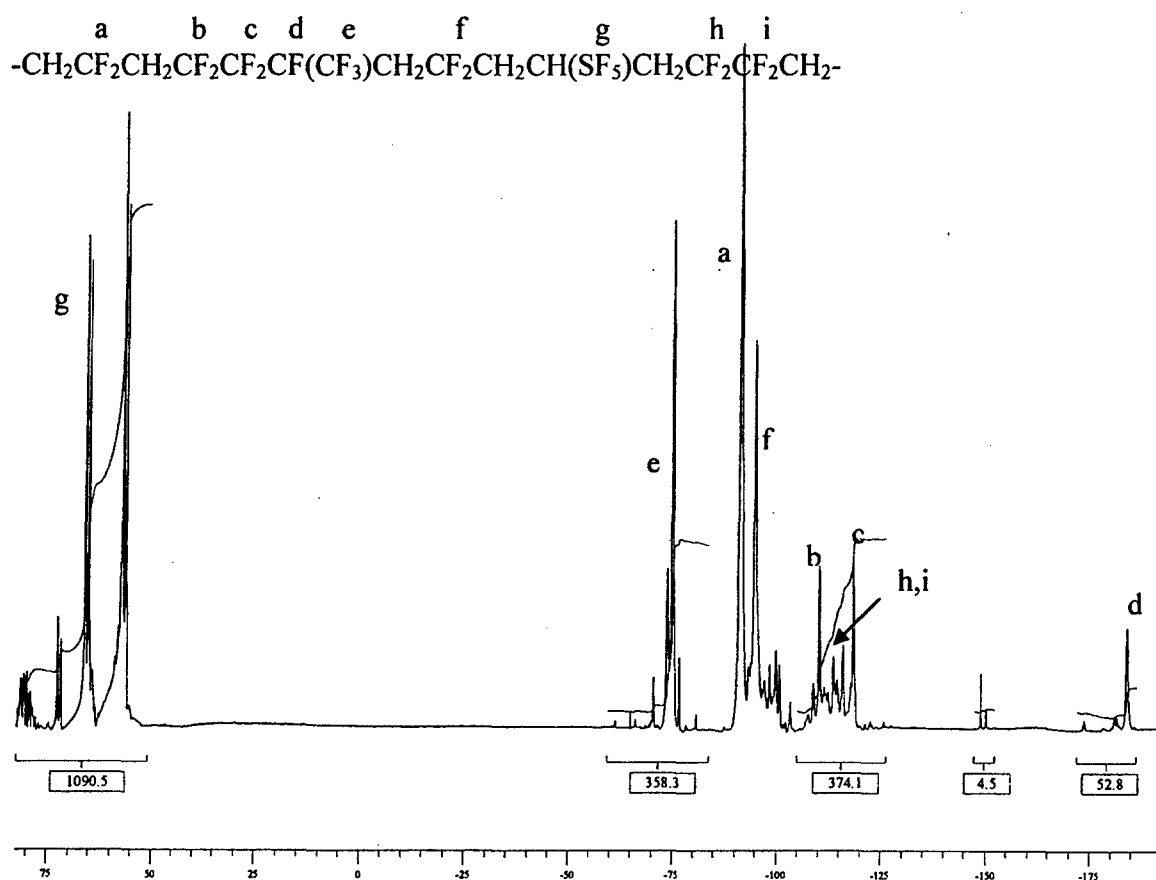
Fig.4 ^{19}F NMR spectrum of VDF/HFP/SF$_5$(M-I) terpolymer I at initial monomer ratio in the feed =72.0/19.4/8.6 mol %

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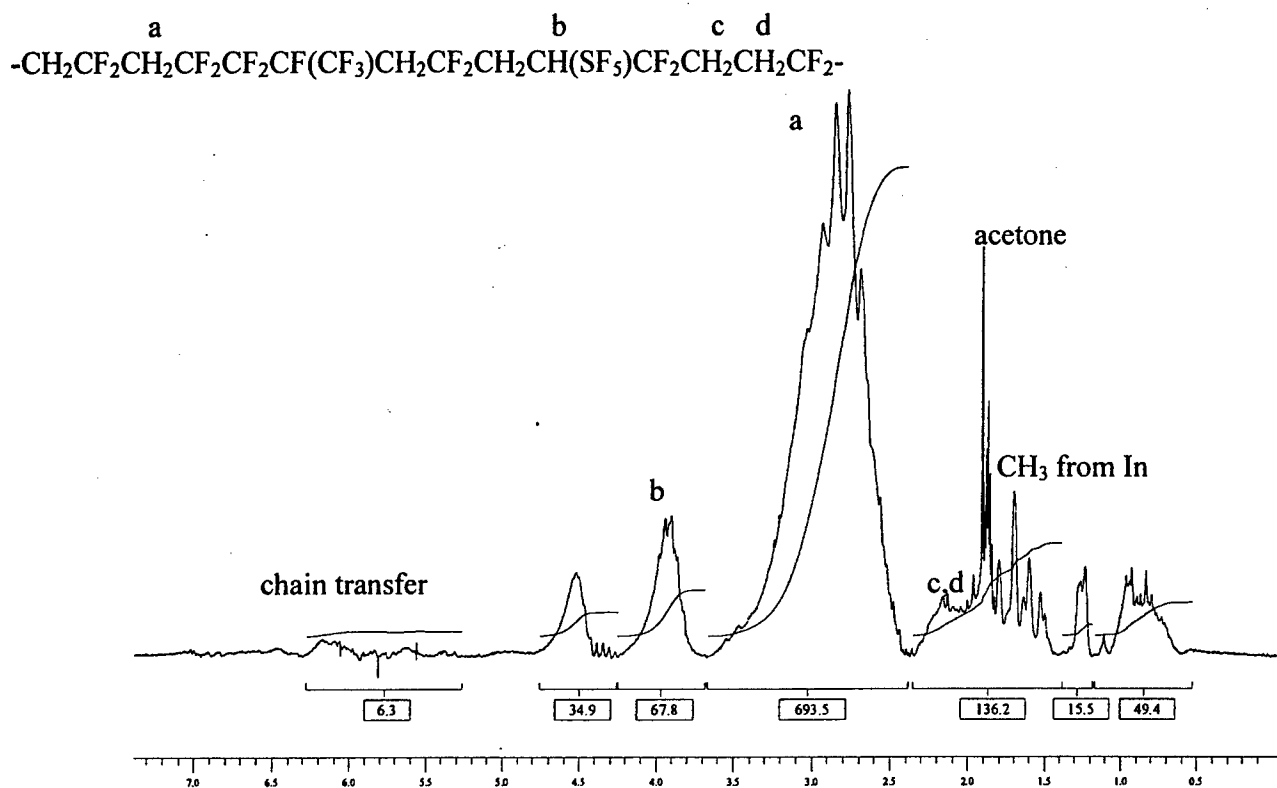
Fig .5 ^{1}H NMR spectrum of VDF/HFP/SF$_5$(M-I) terpolymer I at initial monomer ratio in the feed =72.0/19.4/8.6 mol %

a   b   c d   e   f g h k   l m
-CH₂CF₂CH₂CF₂CF₂CF(CF₃) CH₂CF₂CF₂CF(SF₅)CH₂CF₂CF₂CH₂-

Fig. 6 ¹⁹F NMR spectrum of VDF/HFP/SF₅(M-III) terpolymer III recorded in deuterated acetone at initial monomer ratio 73.1/18.3/8.6 mol %

$$\underset{\text{a}}{\text{-CH}_2\text{CF}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF(CF)}}\ {}_3\text{CH}_2\text{CF}_2\text{CF}_2\underset{\text{b}}{\text{CF}}\underset{\text{c}}{\text{(SF}_5)}\text{CF}_2\text{CH}_2\text{CH}_2\text{CF}_2\text{-}$$
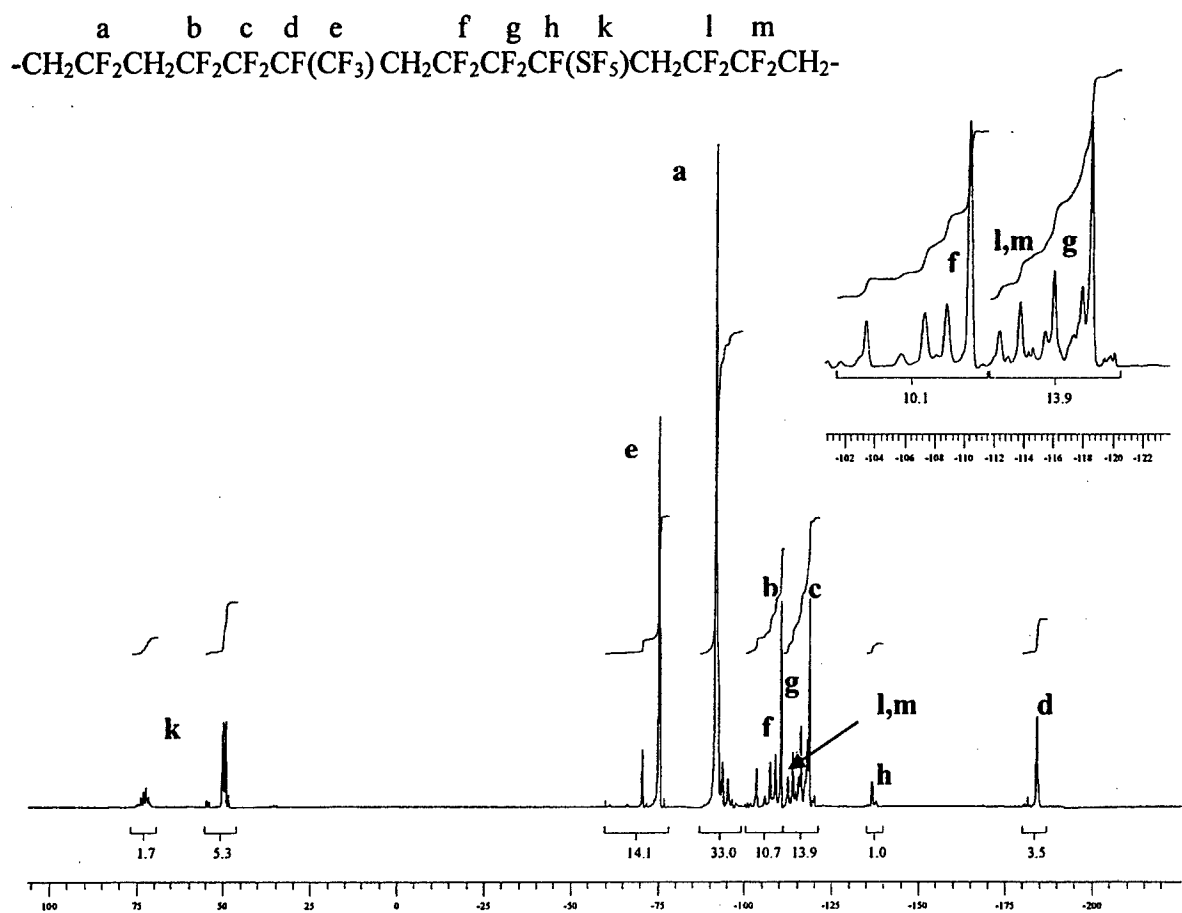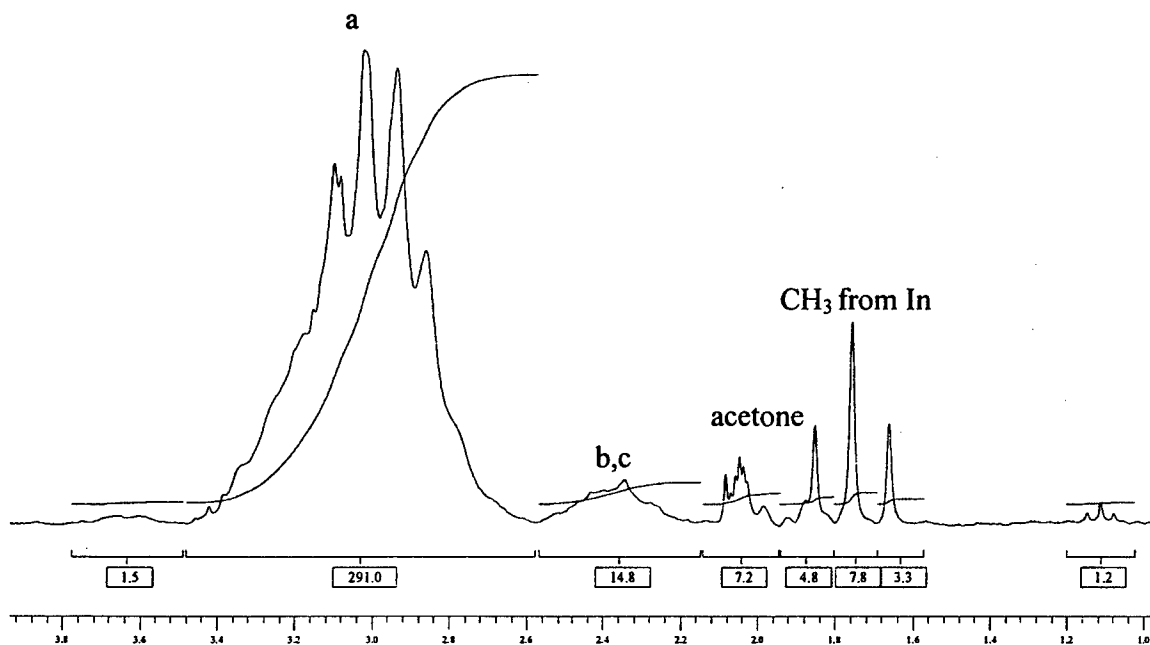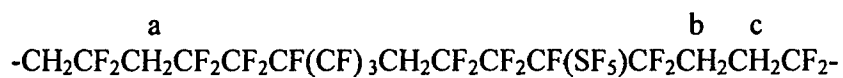

Fig.7 ^{1}H NMR spectrum of VDF/HFP/SF5(M-III) terpolymer III recorded in deuterated acetone at initial monomer ratio 73.1/18.3/8.6 mol %
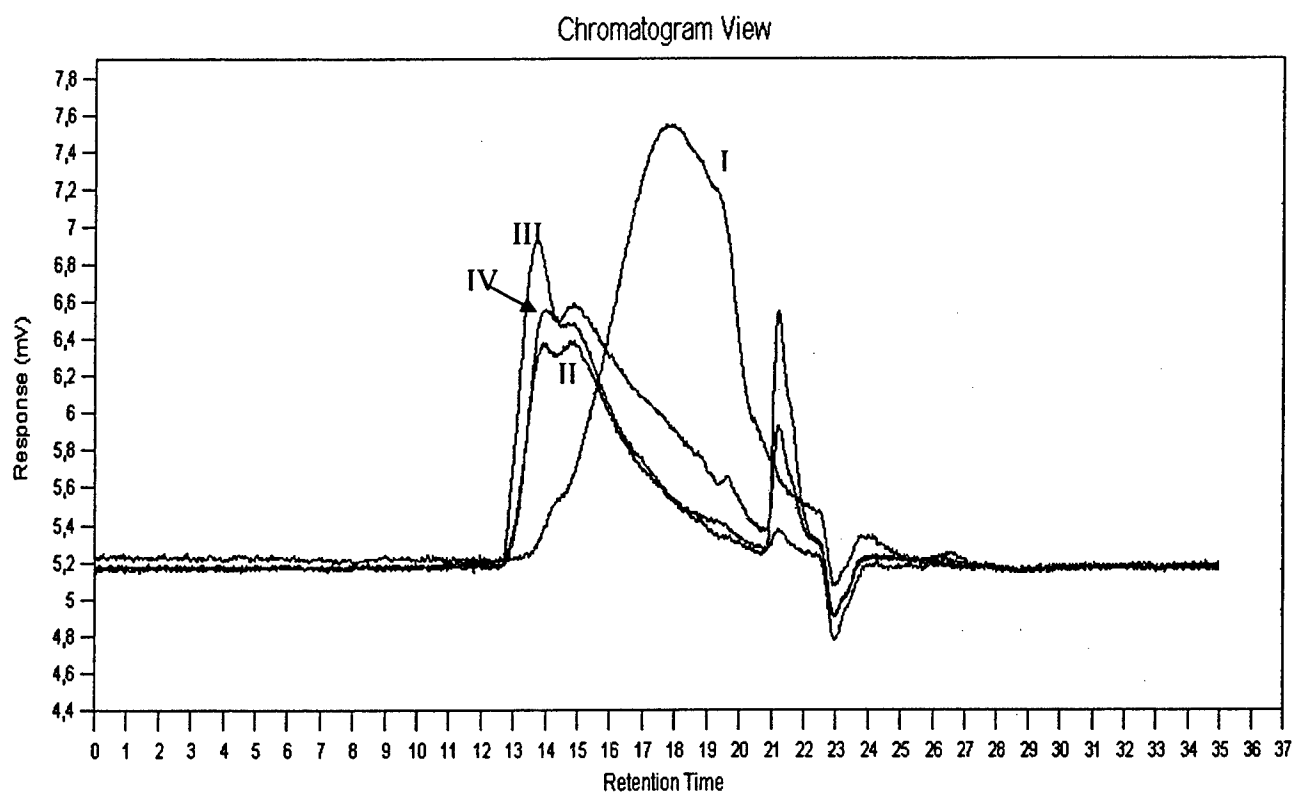
Fig. 8 SEC Chromatograms of poly(VDF-ter-HFP-ter-SF$_5$M) terpolymers. Terpolymer compositions of VDF/HFP/SF$_5$M in mol % :I -71.0/11.6/17.4 ;II- 83.8/14.1/2.1; III – 78.3/16.4/5.3; IV – 78.1/13.5/8.3

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Fig.9 Thermogravimetric curves of VDF/HFP/-SF$_5$M terpolymers in air of
VDF/HFP/SF$_5$ terpolymers. Terpolymer compositions of VDF/HFP/SF$_5$M in mol % :I -
71.0/11.6/17.4 ;II-83.8/14.1/2.1; III – 78.3/16.4/5.3; IV – 78.1/13.5/8.3

Table 1.Comparative study of different reactivities of VDF with various monomers in
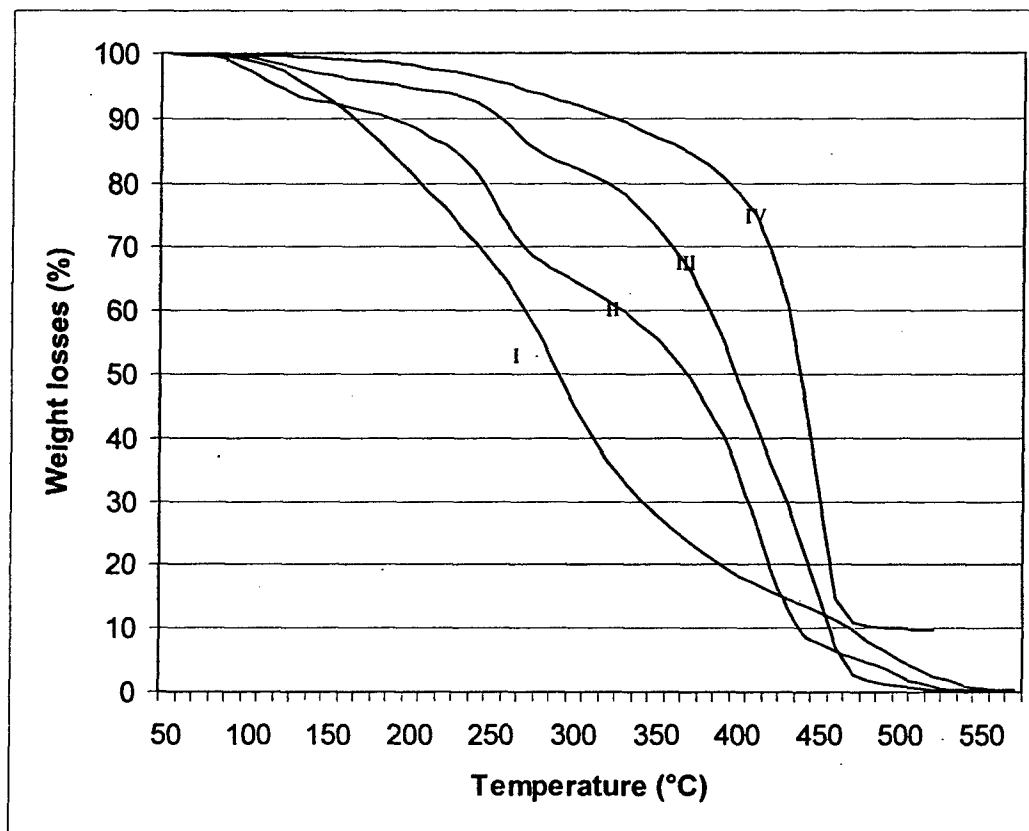
Run No	Mol % monomer in the feed					Mol % monomer in the copolymer				
	VDF	HFP	PMVE	PPVE	-SF$_5$	VDF	HFP	PMVE	PPVE	-SF$_5$
1	21.6	78.4	-	-	-	53.4	46.6	-	-	-
2	49.5	50.5	-	-	-	78.1	21.9	-	-	-
3	75.0	25.0	-	-	-	89.3	10.7	-	-	-
4	20.0	-	80.0	-	-	61.8	-	38.2	-	-
5	50.8	-	49.2	-	-	73.6	-	26.4	-	-
6	78.9	-	21.1	-	-	85.5	-	14.5	-	-
7	20.4	-	-	79.6	-	57.0	-	-	43.0	-
8	50.1	-	-	49.9	-	73.0	-	-	27.0	-
9	70.1	-	-	29.9	-	74.6	-	-	25.4	-
10	20.0	-	-	-	80.0	81.2	-	-	-	18.8
11	49.6	-	-	-	50.4	83.6	-	-	-	16.4
12	69.8	-	-	-	30.2	86.4	-	-	-	13.6

radical copolymerization[a]

a) no homopolymerization of $CF_2=CFSF_5$ monomer

Table 2: ^{19}F-NMR assignments of fluorinated groups in the poly(VDF-ter-HFP-ter-CF$_2$=CFSF$_5$) terpolymers recorded in deuterated acetone.

Chemical shift (ppm)	structure	Integrals in Eq. 1,3
-71.2	-CH$_2$CF$_2$CF$_2$CF(**CF$_3$**)-CF$_2$-CH$_2$-	I$_{-71.2}$
-74.8	-CH$_2$-CF$_2$-CF$_2$-CF(**CF$_3$**)-CH$_2$-CF$_2$-	I$_{-74.8}$
-91.1	-CF$_2$-CH$_2$-**CF$_2$**-CH$_2$-CF$_2$-	I$_{-91.1}$
-94.9	(CH$_2$-CF$_2$)-(CF$_2$-CH$_2$)-(CH$_2$-C**F**$_2$)-(CH$_2$-CF$_2$)	I$_{-94.9}$
-108	-CH$_2$CF$_2$CF$_2$CF(SF$_5$)-	I$_{-108}$
-110.1	-(CH$_2$-CF$_2$)CF$_2$CF(CF$_3$)-	I$_{-110.1}$
-113.7	- (CH$_2$-CF$_2$)-(**CF$_2$**-CH$_2$)-(CF$_2$-CH$_2$)-	I$_{-113.7}$
-113.8	- CF$_2$CH$_2$ (CH$_2$-CF$_2$)-[**CF$_2$**-CH$_2$]-	I$_{-113.8}$
-115.7	-(CH$_2$-CF$_2$)-(C**F$_2$**-CH$_2$)-(CH$_2$-CF$_2$)-	I$_{-115.7}$
-118.8	-CH$_2$CF$_2$CF$_2$CF(SF$_5$)-	I$_{-118.8}$
-136.7	-(CH$_2$-CF$_2$)-[CF$_2$-C**F**SF$_5$]-	I$_{-136.7}$
-183.5	-CH$_2$CF$_2$CF$_2$C**F**(CF$_3$)-	I$_{-183.5}$

Table 3. Molecular weights of poly(VDF-co-SF$_5$MIII) and poly (VDF-ter-HFP-ter-SF$_5$Mi) copolymers assessed by ^{1}H and ^{19}F NMR analyses

Exp. No[a]	Feed, mol %			N$_{VDF}$	Molar ration in copolymers[b]			Mn g/mol
	VDF	SF$_5$Mi	HFP		α	α$_1$	α$_2$	
1	20.0	80.0	-	15	0.23	-	-	1750
2	49.6	50.4	-	16	0.20	-	-	1740
3	69.8	30.2	-	55	0.16	-	-	5350
4	72.0	8.6	19.4	35	-	0.16	0.25	4900
5	75.2	8.7	16.1	130	-	0.17	0.03	12400
6	73.1	8.6	18.3	154	-	0.21	0.07	16900
7	71.1	13.6	15.3	65	-	0.17	0.11	7300

a) Experiments No 1 to 3 concern Run No 10-12 in Table 1 ; Experiments No 4 to 7 concern Exp. numbers in Table 4

b) α = mol% SF$_5$MIII / mol %VDF in copolymer, α$_1$ =% HFP / mol %VDF in terpolymer ;

α$_2$= mol %SF$_5$Mi / mol % VDF in terpolymer

Table 4. Monomer – polymer compositions of poly(VDF-ter-HFP-ter-SF$_5$M) terpolymers and their main characteristics. Reaction conditions : initiator DTBP – 1 mol %; solvent pentafluorobutane – 70 wt % ; 143 ^{0}C ; 5 h

Exp No Monomer	Feed (mol %)			Terpo (mol%)			Y (wt %)	Mn (g/mol)	PDI	Tg (^{0}C)
	VDF	HFP	SF$_5$M	VDF	HFP	SF$_5$M				
Polymer I* H$_2$C=CH(SF$_5$)	72.0	19.4	8.6	71.0	11.6	17.4	45.0	2540	2.0	-50
Polymer II* F$_2$C=CH(SF$_5$)	75.2	16.1	8.7	83.8	14.1	2.1	52.2	8290	2.3	-41
Polymer III* F$_2$C=CF(SF$_5$)	73.1	18.3	8.6	78.3	16.4	5.3	72.5	10030	2.4	-40
Polymer IV** F$_2$C=CF(SF$_5$)	71.1	15.3	13.6	78.1	13.5	8.3	91.2	6650	2.4	-50

*DTBP concentration 1 mol %
**DTBP concentration 3 mol %

Polymer solubility : soluble in acetone ,THF, C$_4$F$_5$H$_5$; Polymers I and II not soluble in CHCl$_3$ and CH$_2$Cl$_2$ whereas polymers III and IV are soluble in CH$_2$Cl$_2$ and partially in CHCl$_3$

5.0 Combustion Experiments on polymer III

5.1 Test conditions, methodology, and FTIR results for Polymer III

Combustion studies

In each experiment, a sample of fluorinated polymer was applied to a glow spiral in a sealed test cell in an FT-IR spectrometer. When current was applied, the sample decomposed and underwent combustion, during which time IR absorption spectra of the released gases were acquired. Following is schematics and description of the FT-IR Combustion apparatus that was used in this study:
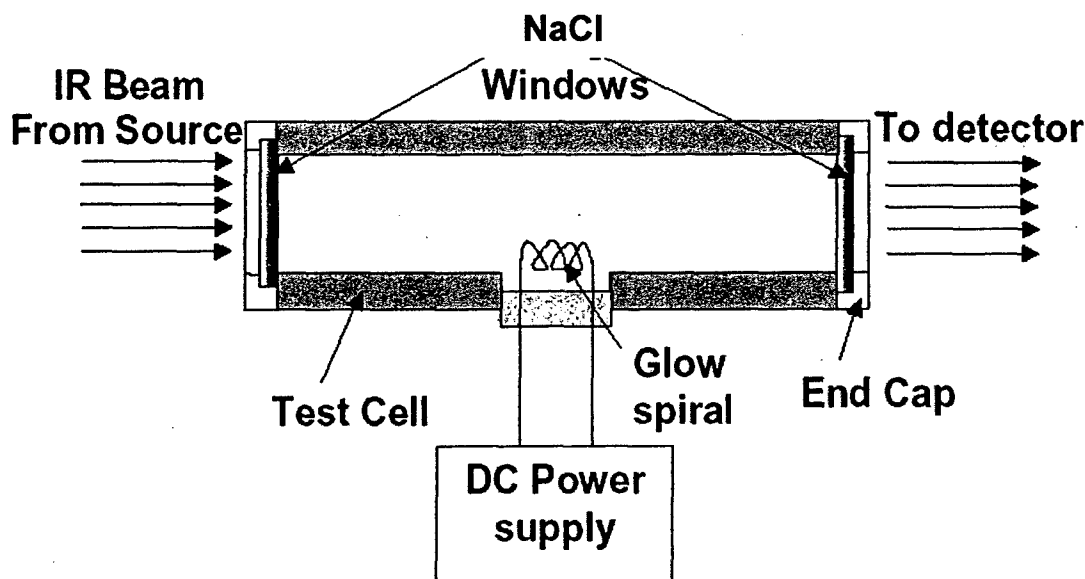

- **Pt wire 0.010" diam.**
- **Ni-coated SS cell**
- **Power ~20W, >100K/s heat rate**
- **cell body 105°C**

The test samples were applied to a platinum heat spiral held between two titanium posts through a ceramic base plate. This assembly was mounted inside a nickel-coated stainless steel 10-cm pathlength testcell, which was fitted with an electric heater to provide a cell body temperature of 380 K prior to the test to avoid condensation problems. When a dc current of 3A was applied to the heat spiral, its surface temperature, as monitored using a resistance calibration, increased by 140 K/s initially. The equilibrium temperature was 1400 ± 100 K. Using NaCl windows on the testcell to enable a spectral range of 900-4200 cm^{-1}, a full spectrum could be acquired with a resolution of 2 cm^{-1} every 10 s. The concentrations of eight selected major species shown below were obtained after baseline correction and application of a Classical Least Squares (CLS) fit of the measured spectra to a database containing the pure spectra of 31 species, listed in Table 5.

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Table 5. Species used in CLS fit to measured spectra.

| species	Amax (cm^2)
SF6	2.82E-17
COF2	3.13E-19
HF	6.20E-19
CO	1.99E-19
H2S	2.96E-21
OCS	3.54E-18
C2F6	1.12E-17
C2H4F2	2.21E-18
C3H6O	3.10E-19
CF4	3.20E-17
CH3OH	4.07E-19
CH4	5.25E-19
CHF3	6.57E-18
CO2	2.01E-18
CS2	2.41E-18
H2O	1.40E-19
SO2	7.70E-19
CF2=CF2	2.72E-18
CH2=CF2	7.88E-19
CH3-CHF2	1.79E-18
CHF2-CHF2	3.33E-18
CF2=CF-CF3	2.46E-18
CH3-CF3	4.08E-18
CH2F2	1.85E-18
CH2FCF3	1.95E-18
CH3CF2CF3	6.54E-18
CHF2CF3	2.57E-18
CHF2CH2CF3	3.14E-18
SiF4	4.25E-18
GB3	1.36E-18
DMMP	1.00E-18

Polymer III in air
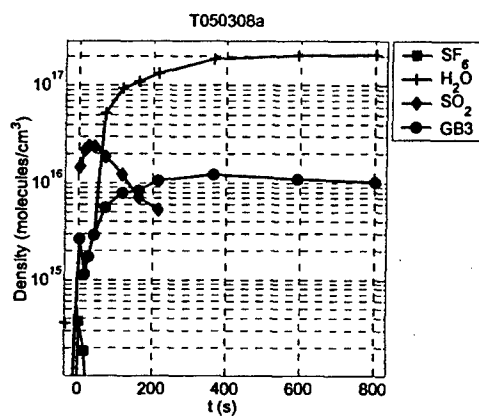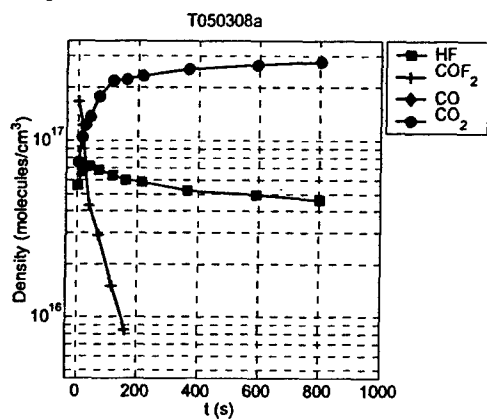
Polymer III in argon
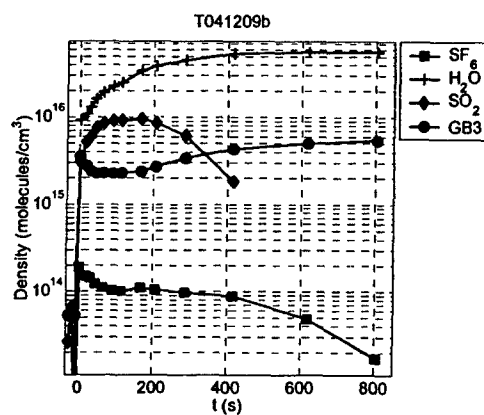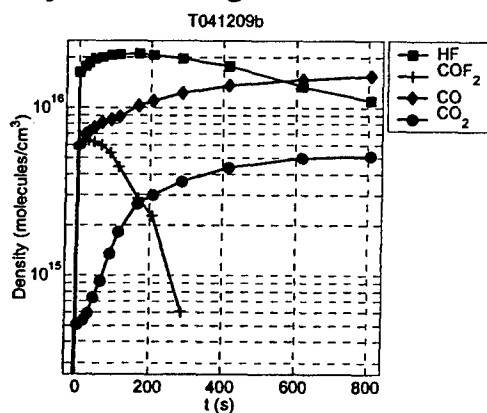
Polymer III +DMMP in air
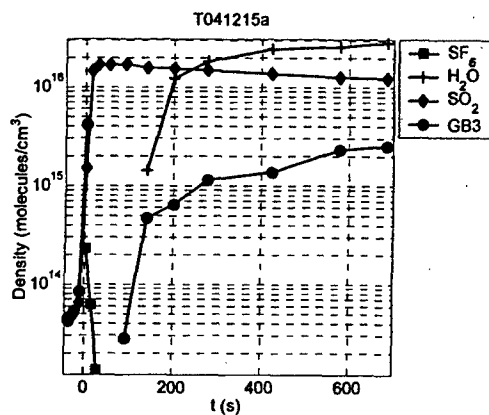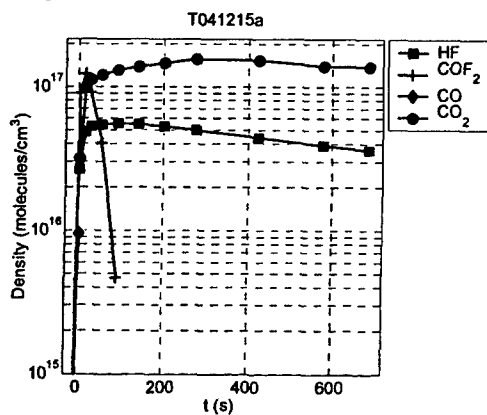
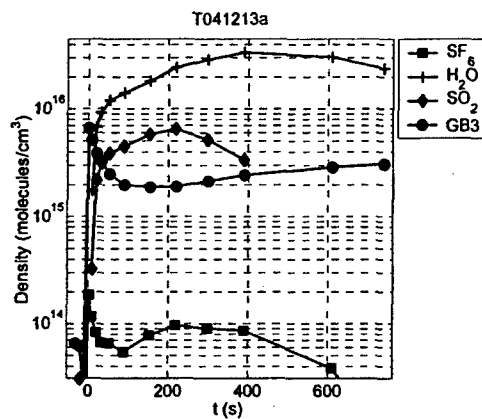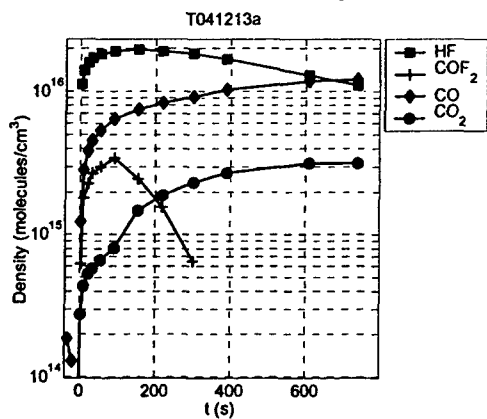## Polymer III+DMMP in argon

Fig 10. FTIR results for Polymer III with and without DMMP. Results shown for air and argon. Eight species were analyzed in each of the four test conditions.

6.0 Conclusions

6.1 Conclusions of synthesis studies

Monomers $CH_2=CHSF_5$, M-I and $CF_2=CHSF_5$,M-II were prepared by using a new Et_3B-initiation methodology to add SF_5Cl to ethylene and VDF, respectively.$CF_2=CFSF_5$, M-III monomer was synthesized by radical addition of $BrSF_5$ onto trifluoroethylene followed by a dehydrobromination. It was found that M-III monomer does not homopolymerize but copolymerizes with VDF by free radical initiation. Its reactivity with VDF when compared to that of other fluoroalkenes (HFP, PMVE and PPVE) gives the following decreasing series:

$$HFP>PPVE>PMVE>SF_5M$$

i.e. the M-III monomer has the lowest reactivity due to the SF_5 bulky-side groups.

The terpolymerization of SF_5 containing monomers with vinylidene fluoride (VDF), hexafluoropropene (HFP) in organic solvent and peroxide initiator has been described for the first time. Indeed, it has been shown that radical polymerization of SF_5M can be successfully performed in 1,1,1,3,3-pentafluorobutane initiated by di(*tert*-butylperoxide). Interestingly, the terpolymerization of VDF with HFP and SF_5M shows that $CH_2=CHSF_5$ monomer was more reactive than $CF_2=CHSF_5$ and even more reactive than $CF_2=CFSF_5$.

$$CH_2=CH(SF_5)>F_2C=CF(SF_5)>F_2C=CH(SF_5)$$
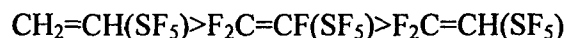
Both ${}^1H$ and ${}^{19}F$ NMR analyses enabled the calculation of molecular weight of binary and ternary SF_5M copolymers.

Finally, DSC, TGA and GPC analyses indicated that the terpolymers II and III incorporating SF_5 side groups exhibited better thermal properties and higher molecular weights than terpolymer I. Further work on these materials, including combustion tests, is in progress.

6.2 Conclusions of combustion studies

- The addition of DMMP to the test sample had little impact on the result compared to the pure Polymer III sample under the same atmosphere.

- Comparing tests under argon and air atmosphere, significantly (1-2 orders of magnitude) larger peak concentrations of CO_2 and COF_2 were noted under air than under argon atmospheres.

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- No measurable CO concentration was found in the air tests, while the peak CO concentration was a factor ~4 higher than the CO_2 concentration under the argon tests.

- No DMMP was found in the gas phase during any of the tests, but Polymer III was found in all tests throughout the sampling.

- SF_6 was found just after ignition in all tests at concentrations which fell more rapidly in air than in argon.

- SiF4 is found in high and growing concentrations in all runs. The source of this contamination is unknown - it is speculated that it may be due to F_2 or HF reacting with residual Si in the cell body.

- Several fluorinated hydrocarbons, primarily CF_4, C_2F_6 and C_2F_4, are found at concentrations near the detection threshold in all runs and decrease in concentration over the course of the run.

- CS_2 was not found at detectable concentrations in any run and H_2S only briefly after ignition in the Polymer III+DMMP in argon run.

- COS is found in concentrations near the detection threshold in argon runs, but is not detected in the air atmosphere runs.

- The only noteworthy effects of the addition of DMMP to the sample are lowered concentrations of H_2O and Polymer III in air. Note that DMMP dominated over Polymer III in the samples applied by a factor 5-10 on mass basis.

Note: The addition of Polymer III the spectral database eliminated the false H_2S match found previously. Since Polymer III was measured in solid form in the current spectrometer, no quantitative cross section is available for this species and the concentrations quoted are based on a nominal peak absorption cross section of $1.36 \times 10^{-18} cm^2$.

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14. ABSTRACT
The research addressed the laboratory production and testing and commercialization aspects of producing high-density fluorine-rich compounds that were significantly more reactive and energetic than conventional explosives to neutralize and destroy chemical and biological agents. The primary synthetic goals followed both poly-SF5-butane and SF5-containing polymers formed by the free radical chain (FRC) process. For the first time, polymers with a significant degree of incorporation of an SF5-bearing monomer were prepared and characterized. Synthesis of three different SF5-containing polymers was investigated as a prerequisite for polymerization. These monomers were: pentafluorosulfanylethene, 1,1-difluro-2-pentafluorosulfanylethene, and 1,1,2-trifluoro-2-pentafluorosulfanylethene. Combustion testing was performed in an externally heated reactor containing air and other oxidative gaseous mixtures under pressure.

15. SUBJECT TERMS
Fluorine-rich compounds, energetic fluoro-organic, SF-5 monomer, SF5-bearing polymers.

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