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Original SF₅-Containing Fluorinated Copolymers Based on Vinylidene Fluoride

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ABSTRACT: The radical co- and terpolymerization of fluorinated monomers bearing an SF₅ group, XYC=CZSF₅ (where X, Y and Z represent either H or F atoms) with 1,1-difluoroethylene (vinylidene fluoride, VDF or VF₂) and hexafluoropropene (HFP), is presented. Although these SF₅ monomers do not homopolymerize under radical initiation, they do copolymerize (and terpolymerize) in solution, in the presence of radical initiators with VDF, (and with VDF and hexafluoropropylene (HFP)), hence leading to original copolymers bearing SF₅ side groups. NMR characterizations and yields enabled one to compare the relative reactivities of F₂C=CFSF₅, HFP, perfluoromethyl vinyl ether, and perfluoropropyl vinyl ether in the copolymerization of VDF with these fluoroolefins. The degree of fluorine substitution on the ethylenic unit of the SF₅ monomers had an influence on their reactivity, their relative incorporation in the copolymers and on the molar masses of the resulting terpolymers – the higher the fluorine in the SF₅ monomer, the higher molecular weight. Interestingly, the greater the degree of fluorine substitution of the SF₅-containing monomer, the greater the yield of the reaction. The yield also increased as the amount of initiator was increased. The relative concentrations of the comonomers in each copolymer were assessed by ¹⁹F and ¹H NMR spectroscopy. The thermal properties (thermal stability and glass transition temperature) of these resulting SF₅-containing fluoropolymers were also examined.

INTRODUCTION

Fluoropolymers are of great interest because of their unique combination of outstanding properties¹ such as chemical inertness (to acids, bases, solvents and petroleum), low dielectric constants and dissipation factors, low water absorptivities, excellent weatherabilities and very interesting surface properties. Hence, these high value added products can find relevant applications in many fields of high technology: aeronautics², microelectronics, engineering, chemical and automotive industries, optics³, textile finishing⁴ and military use⁵. 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 these fluorinated copolymers, those incorporating vinylidene fluoride (VDF) monomeric units are of particular interest, because they can be either thermoplastics⁶, or elastomers⁷, or thermoplastic elastomers^{1d,8}. Usually, such fluoropolymers can be synthesized by radical copolymerization of VDF with other fluoroalkenes leading to statistical copolymers^{7,9} except for copolymers prepared from hexafluoroisobutylene¹⁰ (commercialized by the Allied Company under the CMX[®] trade mark), methyl trifluoroacrylate¹¹ and α -trifluoromethyl acrylic acid¹² which are unexpected alternating copolymers. In fact, VDF has been copolymerized with various fluorinated monomers with the resulting copolymers bearing functions such as: hydroxy¹³, acetoxy^{13,14}, thioacetoxy¹⁵, sulfonyl fluoride¹⁶, nitrile¹⁷, bromine¹⁸ or a perfluoroalkyl group¹⁹.

Interestingly, monomers bearing the SF₅-group have 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 coatings²⁰⁻²³. Recent studies have prepared not only SF₅-polyfluoroalkylacrylates²⁴, SF₅-polyfluoroalkylsiloxanes²⁵, SF₅-polyfluoroalkylepoxides²⁶ but also aromatic polymers that include polyimides containing the SF₅(CF₂)_nC₆H₃- groups (n= 0, 2)^{26,27}, polyacrylate and polystyrene containing the SF₅CF₂CF₂-group²⁸. Additional properties brought about by the SF₅-group include low wettability, low refractive index, low surface energy, high dielectric strength, high chemical and thermal stability. The use of SF₅-monomers has resulted in the preparation of the first organic superconductor with an organic anion²⁹,

the first SF₅-organic metals/organic semiconductors³⁰, the first SF₅-containing ionic liquids³¹ and the preparation of novel liquid crystals³².

Different SF₅-containing copolymers (acrylates, silicones, epoxides) exhibit nonstoichiometric enrichment of the film surface with fluorinated monomers bearing SF₅ groups.

Prior to our studies, in 1969 and 1974, Banks et al.³³⁻³⁴ reported the preparation of SF₅-containing polymers with VDF and 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 SF₅ comonomers (hydrogenated and perfluorinated).

Hence, the objective of this paper deals with the radical binary and terpolymerization of different SF₅-containing monomers, their reactivity with VDF and HFP and the detailed characterization of the copolymers obtained.

EXPERIMENTAL

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 Chimie, 38299 Saint Quentin-Fallavier, France). They were used as supplied. Acetonitrile, dimethylsulfoxide of analytical grade (Aldrich Chimie, 38299 Saint Quentin-Fallavier, France), were distilled over calcium hydride prior to use.

Analysis

The compositions of the co- and terpolymers (the molar contents of VDF, HFP, and SF₅-containing monomers) were determined by ¹⁹F and ¹H NMR spectroscopy. The NMR spectra were recorded on Bruker AC 200 and AC 250 instruments, using deuterated acetone as the solvent and TMS (or CFC₁₃) as the references for ¹H (or ¹⁹F) nuclei. Coupling constants and chemical shifts are given in Hz and ppm, respectively. The experimental conditions for ¹H (or ¹⁹F) 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 ¹⁹F NMR.

Differential scanning calorimetry (DSC) measurements were conducted using a Perkin-Elmer Pyris 1 instrument connected to a micro-computer. 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 $40^{\circ}\text{C}\cdot\text{min}^{-1}$ up to 80°C , where it remained for 2 min. It was then cooled to -105°C at a rate of $320^{\circ}\text{C}\cdot\text{min}^{-1}$ and left for 10 min at that temperature before a second scan was started at a heating rate of $20^{\circ}\text{C}\cdot\text{min}^{-1}$. Finally, another cycle was performed and a third scan at a heating rate of $20^{\circ}\text{C}\cdot\text{min}^{-1}$ was initiated, giving the values of T_g 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 $10^{\circ}\text{C}\cdot\text{min}^{-1}$ 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 $0.8\text{ mL}/\text{min}$, 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 \AA . 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 $20\text{ }\mu\text{m}$ PTFE Chromafil Membrane and finally analyzed by GPC under the conditions described above.

Synthesis of SF_5 -containing monomers

1-chloro-2-pentafluorosulfanylethane ($\text{ClCH}_2\text{CH}_2\text{SF}_5$). 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 a five minutes, after which 3.2g (0.020mol) of SF_5Cl 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: $92\text{-}93^{\circ}\text{C}$; ^1H NMR: δ 4.15-3.85 (m); ^{19}F NMR: δ 81.57 (q, 1F), 64.92 (d, 4F).

Pentafluorosulfanylethene, M-I ($\text{H}_2\text{C}=\text{CHSF}_5$). To 3.5 g KOH 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, $J = 15\text{ Hz}$, 1H), 6.68 (m, 1H); ^{19}F NMR: AB_4 system, δ 81.5 (pent, 1F) and 59.7 (d, 4F), $J_{\text{AB}} = 146\text{ Hz}$ ³⁵.

1-Chloro-1,1-difluoro-2-pentafluorosulfanylethane (ClCF₂CH₂SF₅). To a 50 mL three-necked flask bearing a dry ice condenser and cooled to -50 °C was condensed 20 mL of ClCF₂CH₃ (Forane 142b) and 4.4g (4 equiv) of CF₂=CH₂ (VDF). To this mixture was added 2.7 g (0.017mol) of SF₅Cl. Then 1.5 mL of Et₃B 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 ; ¹H NMR: δ 4.4-4.2 (m) ; ¹⁹F NMR: δ 77.04 (q, 1F), 70.06 (d, 4F), -55.35 (s, 2F).

1,1-Difluoro-2-pentafluorosulfanylethene, M-II (F₂C=CHSF₅). 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 ; ¹H NMR: δ 5.7 (m) ; ¹⁹F NMR: δ 78.89 (m, 1F, SF₅), 72.78 (d, 4F, SF₅), -65.80 (m, 1F), -83.96 (m, 1F) ³⁶⁻³⁸.

1,1,2-Trifluoro-2-pentafluorosulfanylethene, SF₅CF=CF₂, (M-III) was prepared from SF₅CHFCF₂Br 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 SF₅-deformation modes.

NMR (CDCl₃, CFCl₃): 69.7 (nine-line pattern, 1F, SF₅); 59.0 (d, 4F, SF₅); -163 (m, 1F, CF=); -99.5 (m, 2F, =CF₂).

Copolymerization

The batch copolymerizations of VDF with CF₂=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 cm³). 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 ^1H NMR. Then, the copolymers were precipitated from cold pentane and dried until constant weight was reached.

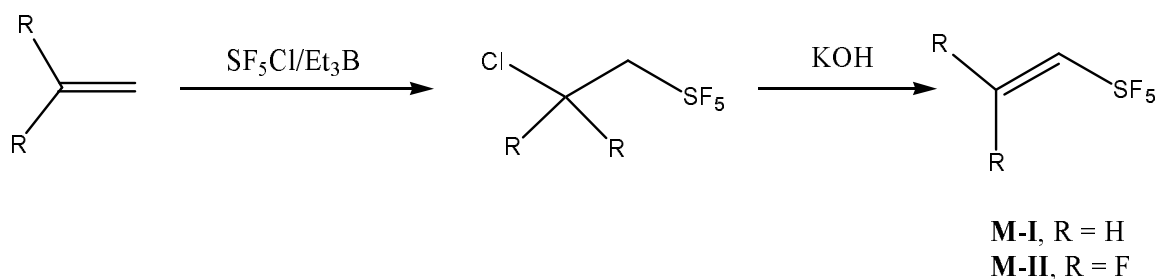
Batch terpolymerizations of VDF (with HFP) and the SF_5 -containing monomers were performed in a 160 ml Hastelloy (HC 276) autoclave, equipped with an inlet valve, a manometer, and a rupture disk. The autoclave was purged with 20 bars of nitrogen pressure and left closed for 20 minutes to test for leakage. 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.

RESULTS AND DISCUSSION

(I) 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 methodology³⁹ to add SF_5Cl to ethylene and VDF, respectively.



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 SF₅Cl in dichloromethane or pentane. On the other hand, when the reaction was carried out in ClCF₂CH₃ (Forane 142B) as a solvent, it was possible to increase the yield up to 70-80%. Neat Et₃B 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 ClCF₂CH₃ 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 ethylene **M-I**, a method developed by Wessel *et al.*³⁵ was adopted. Treatment of the chloro precursor with KOH/H₂O/*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 Gard successfully prepared **M-II** starting from 1-bromo-1,1-difluoro-2-pentafluorosulfanylethane³⁷. 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 (F₂C=CFSF₅) was obtained from the radical addition of BrSF₅ onto trifluoroethylene followed by a dehydrobromination as reported in a previous work^{38,39}

(II). Radical copolymerization of SF₅-containing monomers with VDF and HFP

(II-1) Radical copolymerization of F₂C=CFSF₅ with VDF

Initially, the radical homopolymerization of F₂C=CFSF₅ was attempted under classic conditions of homopolymerization starting from a [di *tert*-butyl peroxide, DTBP]₀ to [F₂C=CFSF₅]₀ molar ratio of 2 mol %, 5.0g (0.024 moles) of CF₂=CFSF₅, 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 SF₅ 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 F₂C=CFSF₅ 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 copolymerizations 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 SF₅-containing monomers, the precise assesment 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.

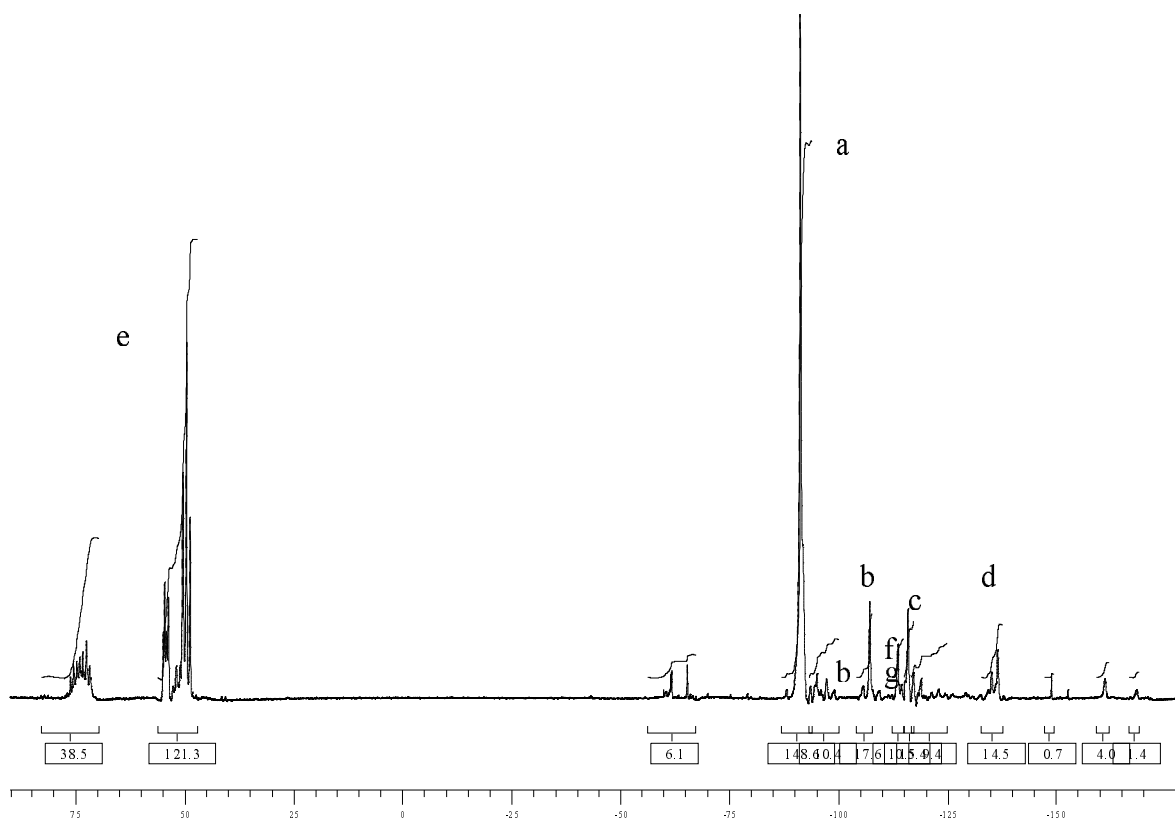
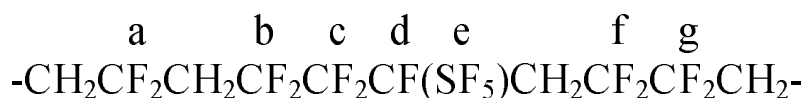


Fig. 1 ^{19}F NMR spectrum of VDF/ $\text{CF}_2=\text{CF}(\text{SF}_5)$ copolymer at 70/30 mol % monomer ratio in the feed

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-SF₅M) 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 SF₅-monomer III ($\text{CF}_2=\text{CFSF}_5$) 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 CF₂ groups in $(\text{CH}_2\text{-CF}_2)\text{-}(\text{CF}_2\text{-CH}_2)\text{-}(\text{CH}_2\text{-CF}_2)\text{-}(\text{CH}_2\text{-CF}_2)$; $\text{-(CH}_2\text{-CF}_2)\text{-}(\text{CF}_2\text{-CH}_2)\text{-}(\text{CF}_2\text{-CH}_2)\text{-}$; $(\text{CH}_2\text{-CF}_2)\text{-}(\text{CF}_2\text{-CH}_2)\text{-}(\text{CH}_2\text{-CF}_2)$ sequences, respectively, and correspond to the reverse VDF addition

(i.e., head-to-head addition) ⁴³ as noted for the chemical shifts observed for ¹⁹F 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 AB₄ system and are assigned to the five fluorine atoms in the SF₅ 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 CF₂CF(SF₅) leads to a signal centered at -109.8 ppm while those centered at -118.8 and -136.7 ppm are related to the -CF₂ 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 % SF₅ = (I_{+50 to +75})/5 for the multiplet centered at -135 ppm for -CF(SF₅) fluorine atom. Indeed, both fluorine atoms in the difluoromethylene group adjacent to -CF(SF₅) were anisochronous, hence leading to an AB system. This arises from the bulky -SF₅ group which stiffens the molecule as we had noted in C₄F₉CF₂CF(CF₃)I obtained by telomerization of HFP with C₄F₉I⁴⁵. In that monoadduct containing a bulky iodine, the central CF₂ group yielded an AB system. This AB system was also noted on CF₂ of VDF adjacent to -CF₂CF(CF₃) as in the case of C₃F₇CF₂CF(CF₃)I. Because of the overlapping of different signals in that region it was difficult to assess the mol % CF₂M from δ_{CF₂} atoms. Interestingly, no doublet of multiplets centered at -114.8 ppm corresponding to -CH₂CF₂H 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 :

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

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:



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:



It is assumed that tert-BuO^\bullet undergoes a thermal fragmentation ($T > 100^\circ\text{C}$) to generate $^\bullet\text{CH}_3$ ^{43d}. The radicals produced can react onto both sides of VDF in a non-regioselective manner:



R: CH_3 , tert-BuO

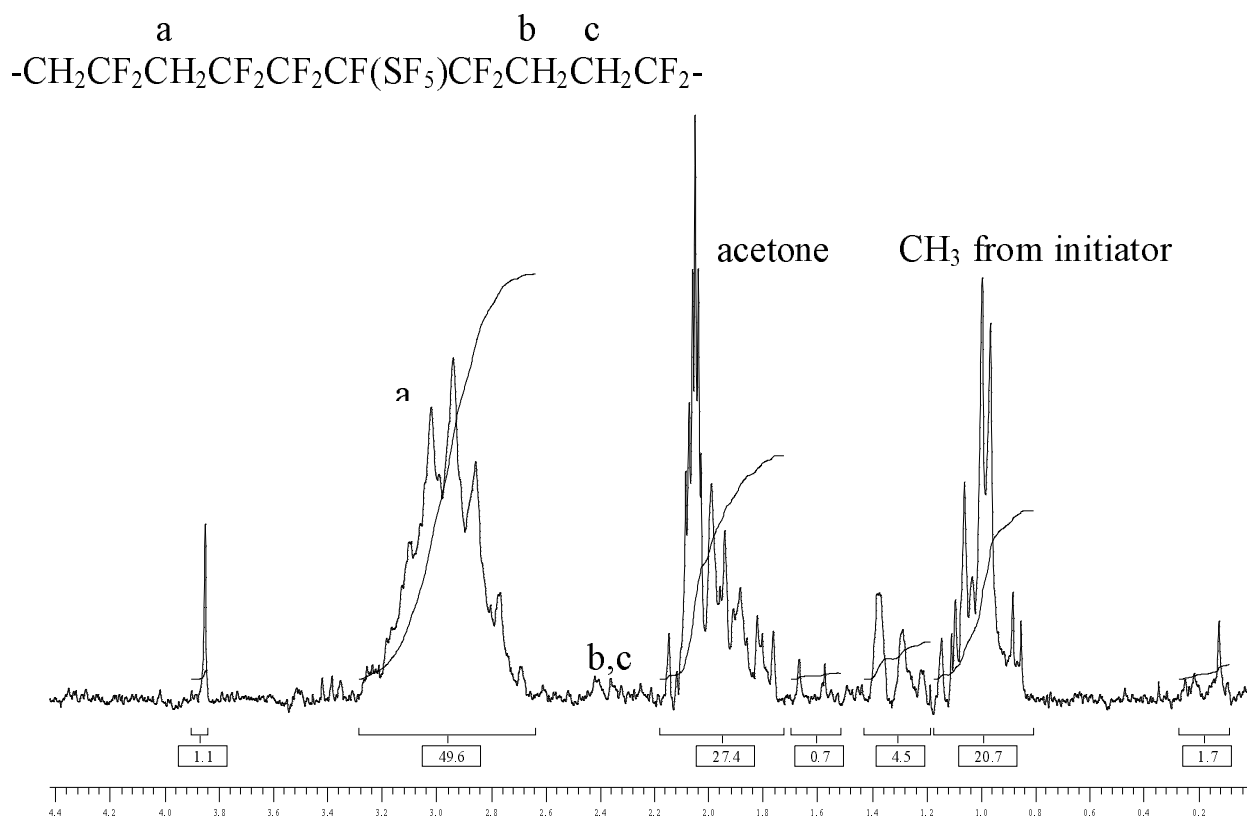


Fig. 2 ^1H NMR spectrum of VDF/ $\text{CF}_2=\text{CF}(\text{SF}_5)$ copolymer at 70/30 mol % monomer ratio in the feed.

^1H NMR can evidence these hydrogenated end-groups as follows:

$\text{CH}_3\text{CH}_2\text{CF}-$ at 1.2 ppm, $\text{CH}_3\text{CF}_2\text{CH}_2-$ at 1.15 ppm, $(\text{CH}_3)_3\text{C-OCH}_2\text{CF}_2-$ at 1.1 ppm and $(\text{CH}_3)_3\text{C-OCF}_2\text{CH}_2-$ at 1.15 ppm. In addition, signals of small intensities are observed in the ^{19}F NMR spectra at -60 and -65 ppm. They are assigned to CF_2 of $(\text{CH}_3)_3\text{C-OCF}_2\text{CH}_2-$ and confirm previous works dealing with the addition of tert-BuO^\bullet onto the CF_2 site of VDF^{43d} or onto the CF_2 site of PMVE^{16e}.

Both ^{19}F and ^1H NMR spectra were used to assess the molecular weight of poly(VDF-co- CF_5MIII) copolymers:

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

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 :

$$M_n = N_{\text{VDF}} \times 64 + \alpha N_{\text{VDF}} \times 208 + 30 \quad (6)$$

Table 3 lists the molecular weights of binary poly(VDF-co- SF_5MIII) 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 $\text{F}_2\text{C}=\text{CFO}-\text{C}_6\text{H}_4-\text{Br}$ ⁴⁴. This is the case when one reactive couple of monomers can involve the third low- reactive monomer in terpolymerization.

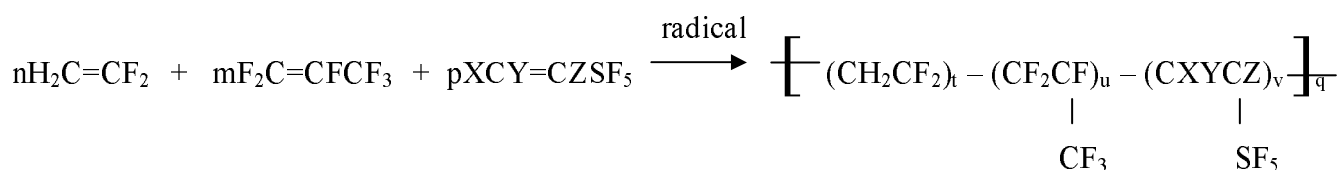


Fig. 3: Radical terpolymerization of SF_5 monomers with VDF and HFP.

(II-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 $[\text{initiator}]_0/[\text{total monomers}]_0$ 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 ^1H 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).

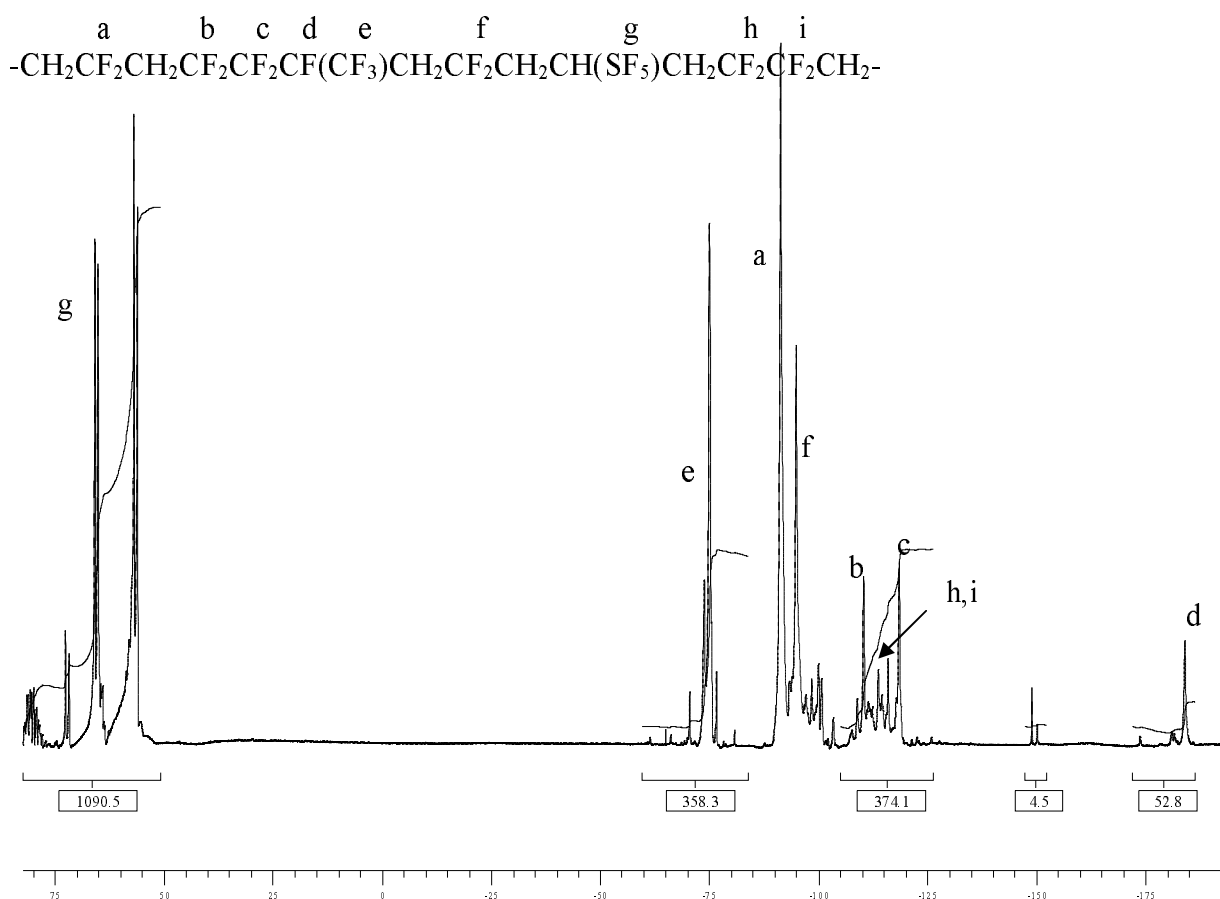


Fig. 4 ^{19}F NMR spectrum of poly(VDFter-HFP-ter-SF₅(M-I)) terpolymer I at initial monomer ratio in the feed =72.0/19.4/8.6 mol %

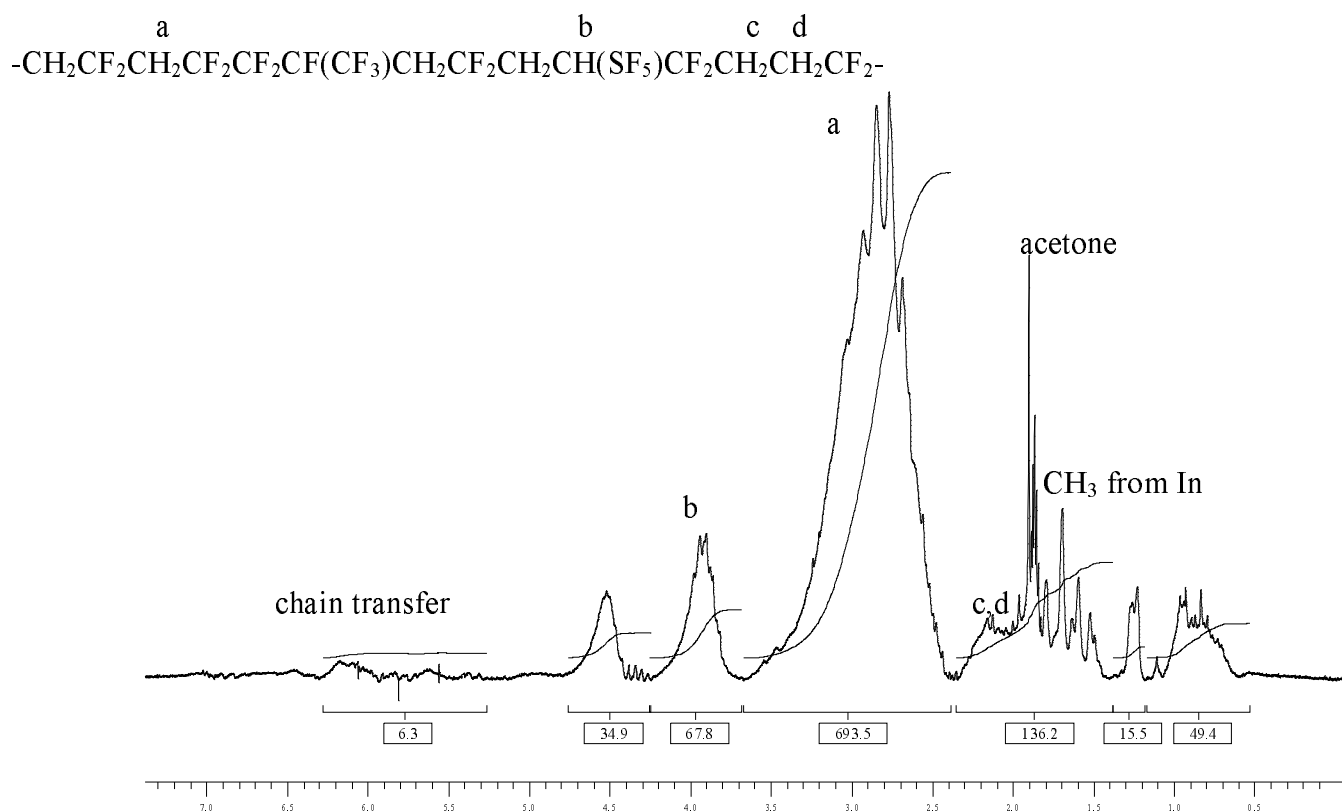


Fig. 5 ^1H NMR spectrum of poly(VDFter-HFP-ter-SF₅(M-I)) terpolymer I at initial monomer ratio in the feed =72.0/19.4/8.6 mol %

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 $-\text{CH}_2\text{CF}_2\text{H}$ and $\text{CF}_2\text{CFHCF}_3$, respectively, gave evidence that very little (Figure 5) or no (Figure 7) chain transfer reaction occurred.

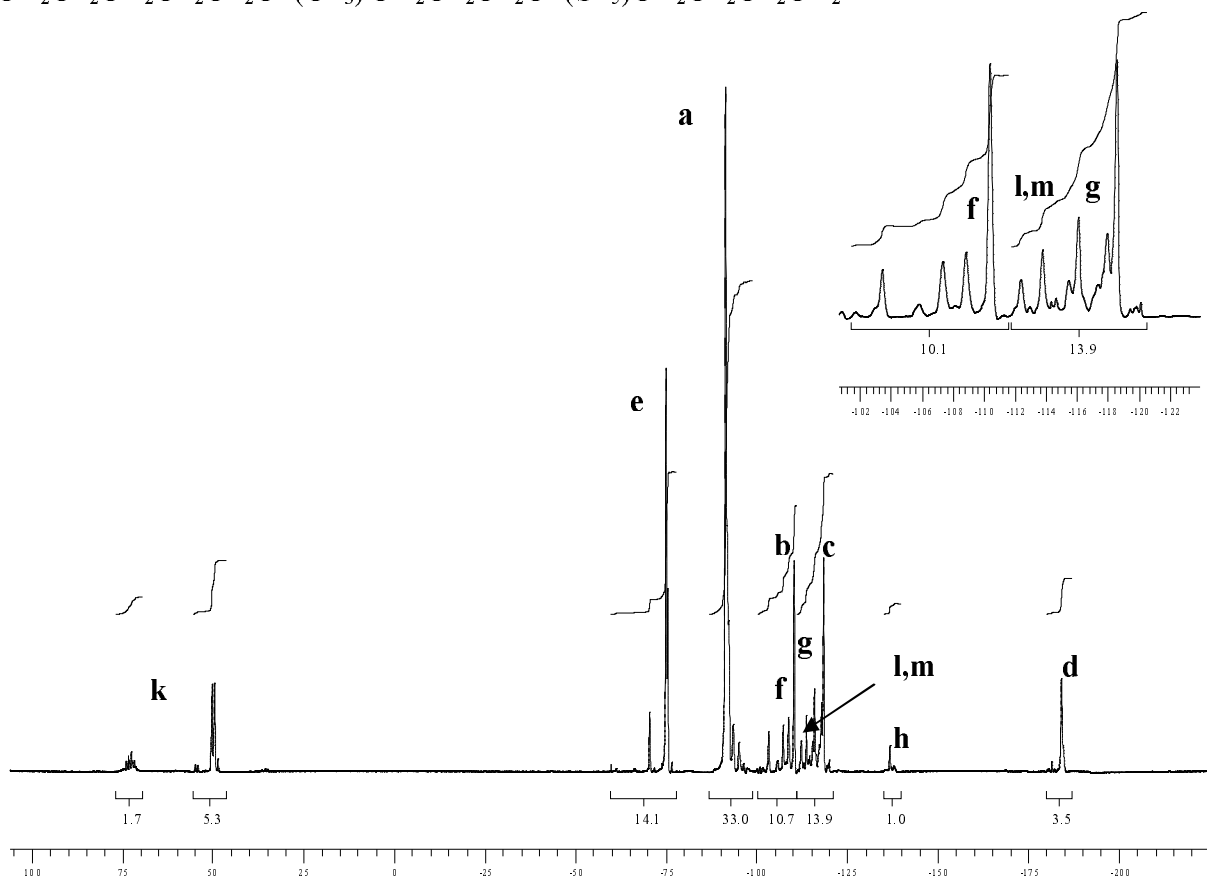
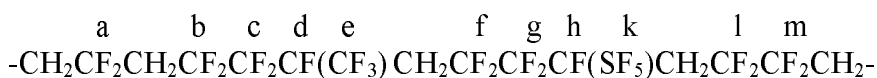


Fig. 6 ^{19}F NMR spectrum of poly(VDFter-HFP-ter-SF₅(M-III)) terpolymer III recorded in deuterated acetone at initial monomer ratio 73.1/18.3/8.6 mol %

II-2-1) Determination of the terpolymer compositions by using ^{19}F NMR spectra

Radical terpolymerizations in solution with organic initiators of SF₅-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}.

II-2-2) Terpolymerization of SF₅ 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 $\text{F}_2\text{C}=\text{CFSF}_5$ unit, and to reverse addition : $-\text{CH}_2\text{CF}_2-\text{CF}_2\text{CH}_2-\text{CH}_2\text{CF}_2-$ and $-\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2-\text{CH}_2\text{CF}_2-$ ⁴³, respectively as observed in NMR spectra of copolymers (Table 2). The signals located at -108 ppm (noted I₁₀₈) and -110.1 (noted I_{-110.1}) range are

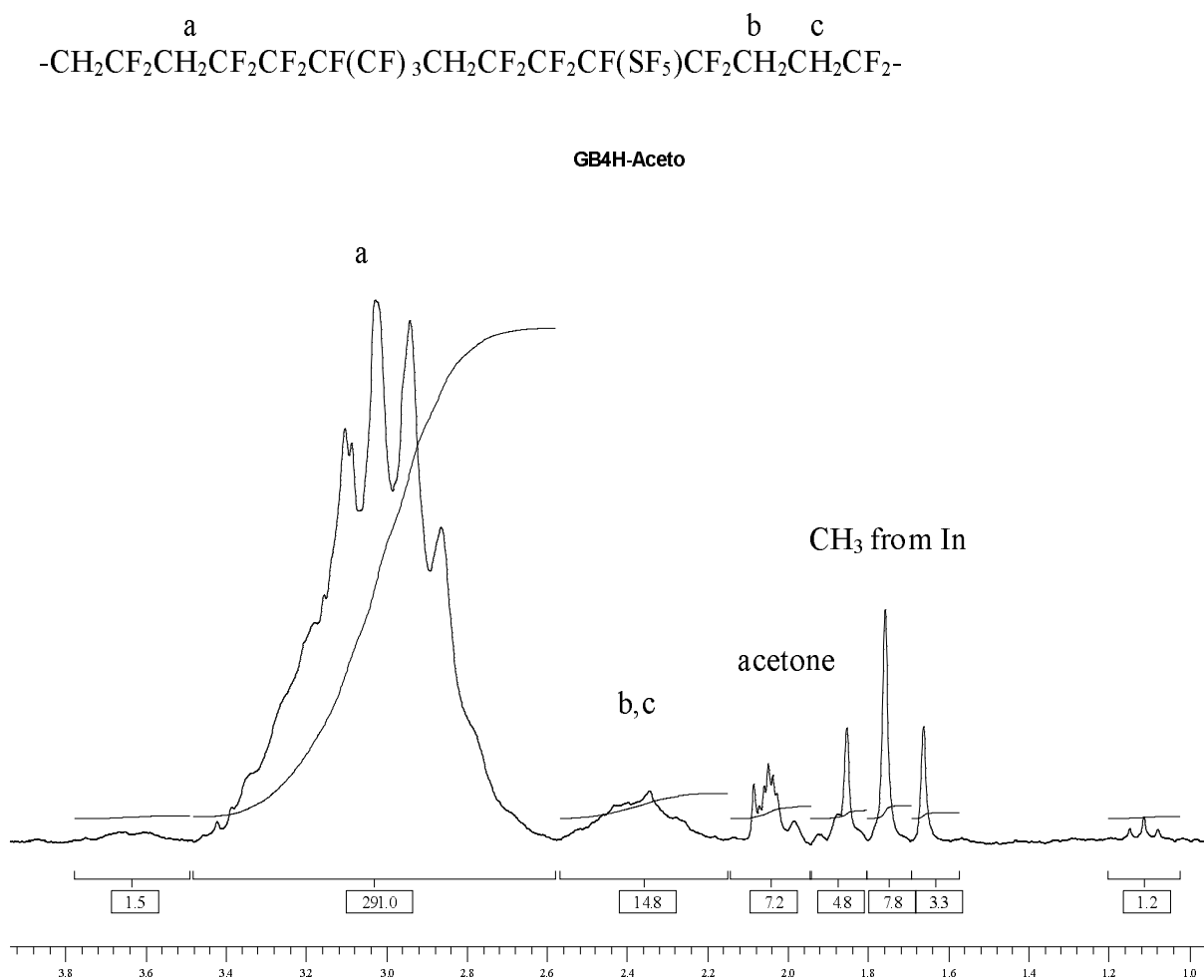


Fig. 7 ^1H NMR spectrum of poly(VDFter-HFP-ter-SF₅(M-III)) terpolymer III recorded in deuterated acetone at initial monomer ratio 73.1/18.3/8.6 mol %

assigned to the difluoromethylene groups of the VDF unit adjacent to HFP and SF₅M 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: $-\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)-\text{CF}_2-\text{CH}_2-$, $-\text{CH}_2-\text{CF}_2-\text{CF}_2-\text{CF}(\text{CF}_3)-\text{CH}_2-\text{CF}_2-$, 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 $-\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)-$ sequences and to the tertiary fluorine in $\text{CF}_2\text{CF}(\text{CF}_3)$ of HFP⁴¹, 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_5M 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_5M units in the terpolymers, and they are given by the following equations (Eq. 7):

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

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

$$\text{Mol \% of } SF_5M \text{ in the terpolymer} = \frac{I_L}{I_J + I_K + I_L} \times 100 \quad (\text{Eq. 7c})$$

where,

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

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

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

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

III-5) Characterization of the terpolymers

Table 4 lists the final molar percentages of each monomer and also the physico-chemical properties of each terpolymer.

In the same experimental conditions (experiments I, II and III: terpolymer VDF / HFP / SF₅M, starting from the same SF₅M 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 SF₅M in feed makes 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 SF₅ monomeric unit in the terpolymer. The poor reactivity of F₂C=CH(SF₅) monomer is not surprising when its behavior is compared to that of F₂C=CH(CF₃)⁴⁹ or F₂C=CH(C₆F₁₃),1HPFO⁵⁰. Actually, kinetics of copolymerization of both of these fluorinated monomers led to the following reactivity ratios :

$$\begin{array}{lll} r_{\text{PFP}}=0.06 ; & r_{\text{VDF}} = 9.0 & \text{at } 40^{\circ}\text{C} \\ r_{\text{1HFPO}}=0.9; & r_{\text{VDF}} = 12.0 & \text{at } 75^{\circ}\text{C} \end{array}$$

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

While the ¹⁹F 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).

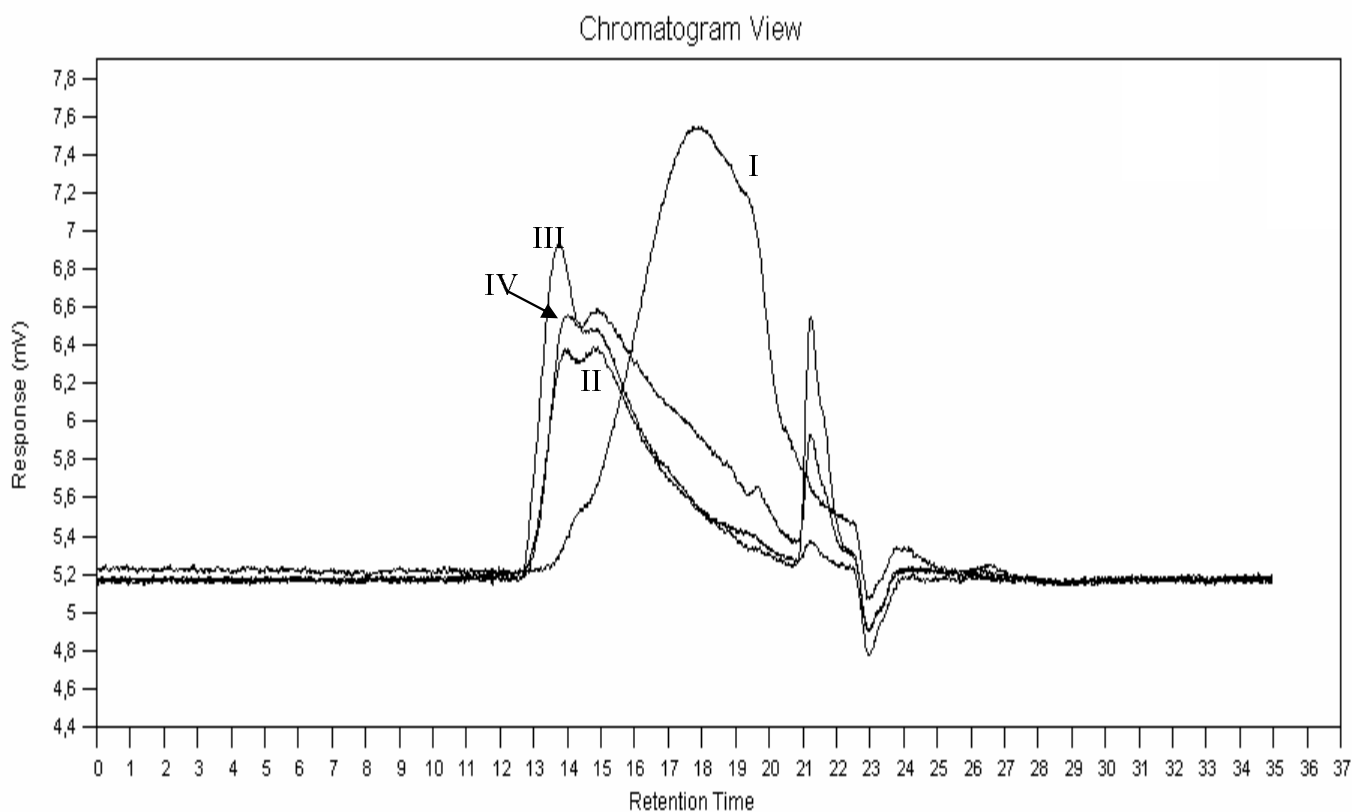


Fig. 8 SEC Chromatograms of poly(VDF-ter-HFP-ter-SF₅M) terpolymers. Terpolymer compositions of VDF/HFP/SF₅M in mol % :I -71.0/11.6/17.4 ;II- 83.8/14.1/2.1; III – 78.3/16.4/5.3; IV – 78.1/13.5/8.3

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-SF₅M) terpolymers (experiments I, II and III with ca. 8.6 mol % in feed of fluorinated SF₅ monomer) or poly(VDF-ter-HFP-ter-SF₅M) terpolymers (experiment IV), 13.6 mol % in feed of perfluorinated SF₅ 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 SF₅M 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 ¹⁹F and ¹H NMR spectra (few presence of triplet of triplets and doublet of multiplets centered at 6.1 and 5.5 ppm assigned to -CH₂CF₂H and -CF₂CF(CF₃)H, respectively. On the other hand using the same strategy of binary poly(VDF-co-SF₅MIII) copolymers, the molecular weights of terpolymers can be assessed by ¹H and ¹⁹F NMR analyses. The equation 6 can be modified as follows :

$$\overline{M}_n = N_{\text{VDF}} \times 64 + \alpha_1 N_{\text{VDF}} \times 150 + \alpha_2 N_{\text{VDF}} \times M_{\text{SF}_5\text{M}_i} + 30 \quad (9)$$

where α_1 and α_2 are the molar ratios of HFP and SF₅M_i monomer units vs. VDF and M_{SF₅M_i} are the molecular weights of SF₅MI, SF₅MII and SF₅MIII 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-SF₅) 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 (T_g) 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, T_gs were ranging from – 40 to – 50 °C without any other transitions, showing amorphous behavior. 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.

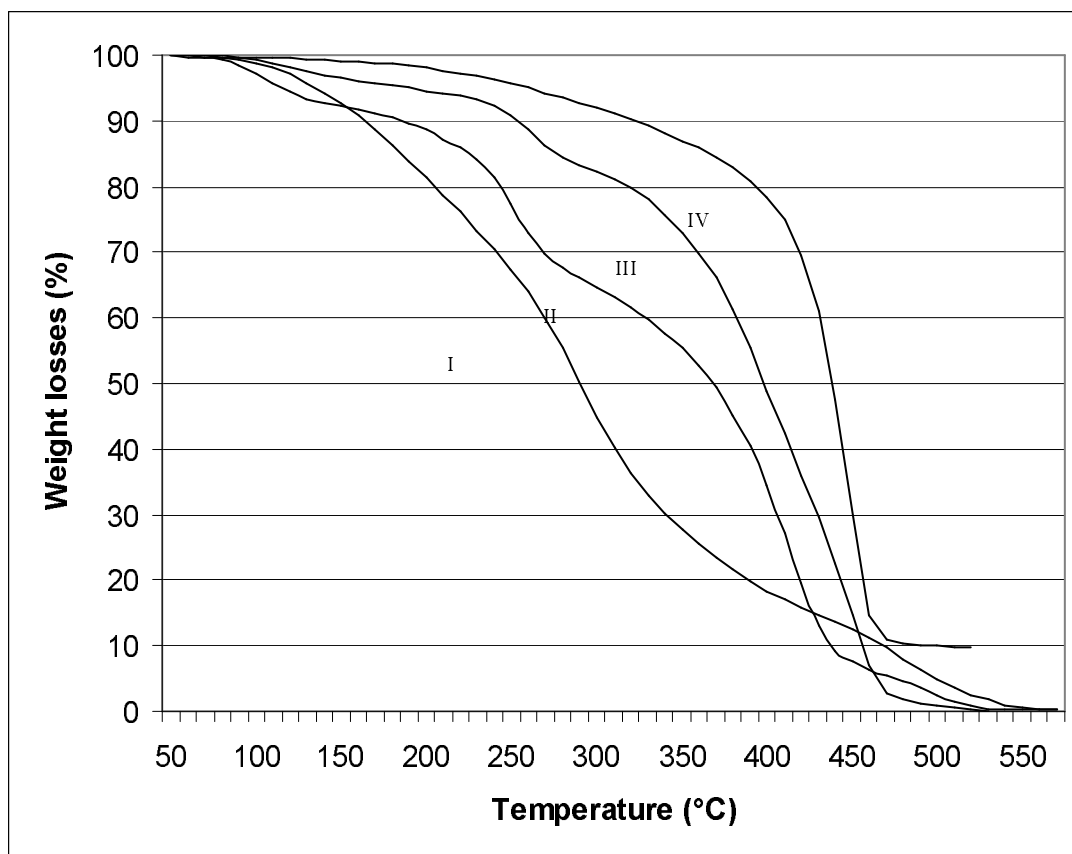
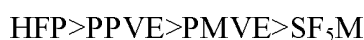


Fig.9 Thermogravimetric curves of poly(VDFter-HFP-ter-SF₅M) terpolymers in air of VDF/HFP/SF₅ terpolymers. Terpolymer compositions of VDF/HFP/SF₅M in mol % :I-71.0/11.6/17.4 ;II-83.8/14.1/2.1; III – 78.3/16.4/5.3; IV – 78.1/13.5/8.3

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.

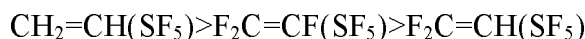
CONCLUSION

Monomers $\text{CH}_2=\text{CHSF}_5$, M-I and $\text{CF}_2=\text{CHSF}_5$, M-II were prepared by using a new Et_3B -initiation methodology to add SF_5Cl to ethylene and VDF, respectively. $\text{CF}_2=\text{CFSF}_5$, 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:



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 peroxyde 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 $\text{CH}_2=\text{CHSF}_5$ monomer was more reactive than $\text{CF}_2=\text{CHSF}_5$ and even more reactive than $\text{CF}_2=\text{CFSF}_5$.



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.

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SUPPORTING INFORMATION

NMR and FT-IR spectra, and DSC curves can be found free of charge on <http://acs.org>.

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FIGURE CAPTIONS

Fig. 1 ^{19}F NMR spectrum of VDF/ $\text{CF}_2=\text{CF}(\text{SF}_5)$ copolymer at 70/30 mol % monomer ratio in the feed

Fig. 2 ^1H NMR spectrum of VDF/ $\text{CF}_2=\text{CF}(\text{SF}_5)$ copolymer at 70/30 mol % monomer ratio in the feed

Fig. 3 Radical terpolymerizations of SF_5 monomers with VDF and HFP.

Fig. 4 ^{19}F NMR spectrum of VDF/HFP/ $\text{SF}_5(\text{M-I})$ terpolymer at initial monomer ratio in the feed =72.0/19.4/8.6 mol %

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

Fig. 6 ^{19}F NMR spectrum of VDF/HFP/ $\text{SF}_5(\text{M-III})$ terpolymer III recorded in deuterated acetone at initial monomer ratio 73.1/18.3/8.6 mol %

Fig. 7 ^1H NMR spectrum of VDF/HFP/ $\text{SF}_5(\text{M-III})$ 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_5M) terpolymers. Terpolymer compositions of VDF/HFP/ SF_5M 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

Fig. 9 Thermogravimetric curves of VDF/HFP/- SF_5M terpolymers in air of VDF/HFP/ SF_5 terpolymers. Terpolymer compositions of VDF/HFP/ SF_5M 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

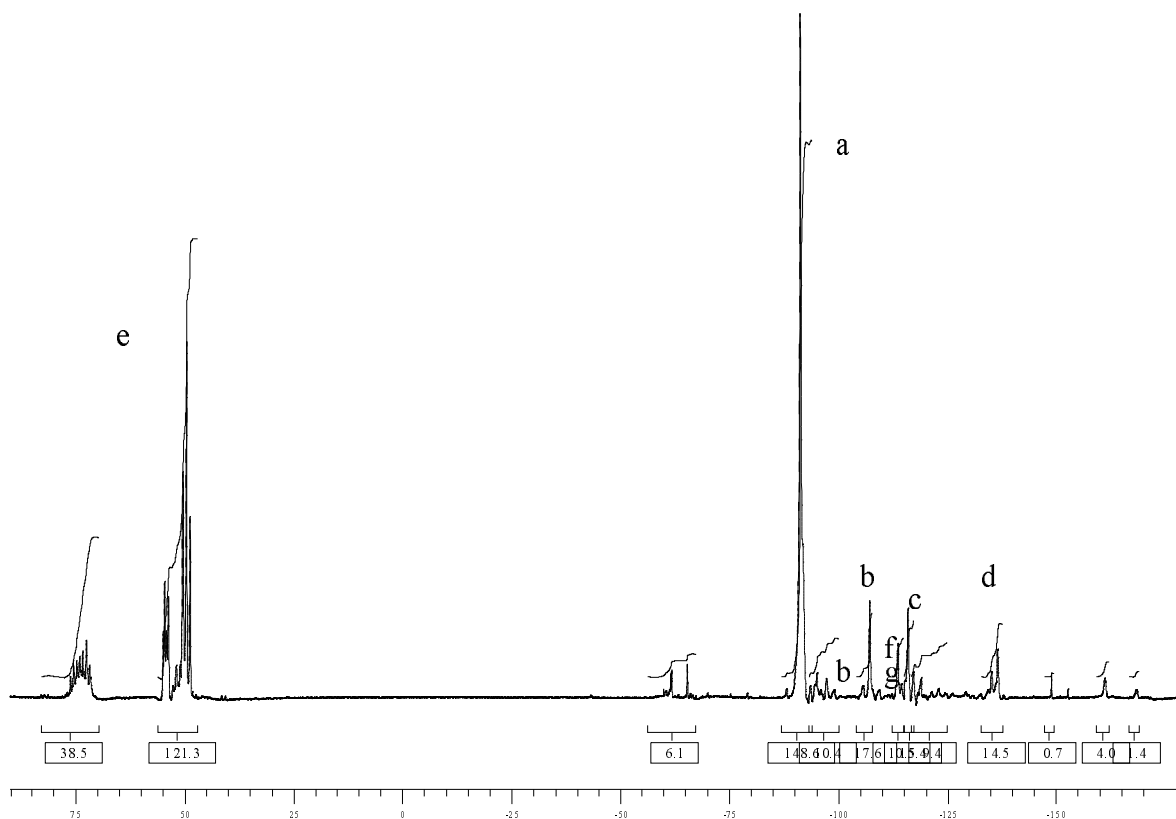
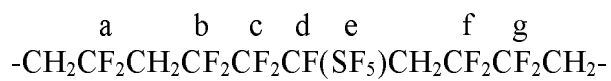


Fig. 1 ^{19}F NMR spectrum of VDF/ $\text{CF}_2=\text{CF}(\text{SF}_3)$ copolymer at 70/30 mol % monomer ratio in the feed

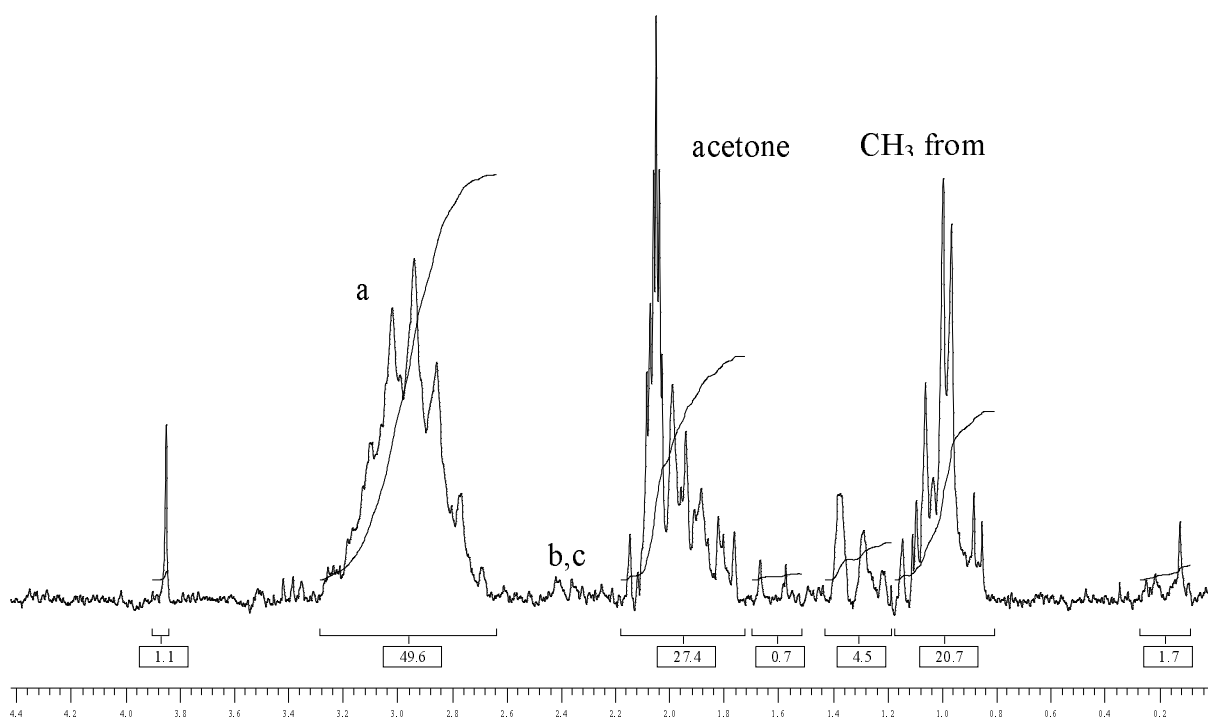
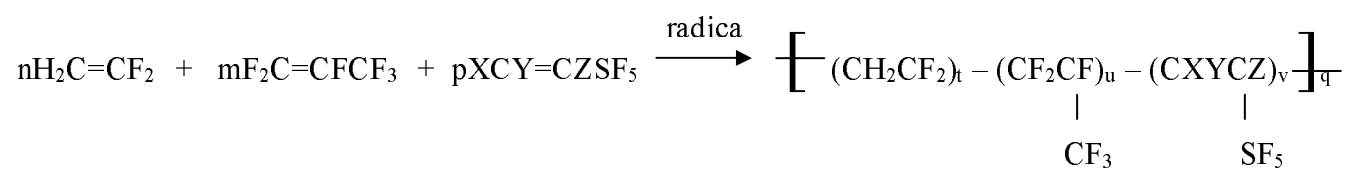


Fig. 2 ^1H NMR spectrum of VDF/ $\text{CF}_2=\text{CF}(\text{SF}_5)$ copolymer at 70/30 mol % monomer ratio in the feed

Fig. 3: Radical terpolymerization of SF₅ monomers with VDF and HFP.



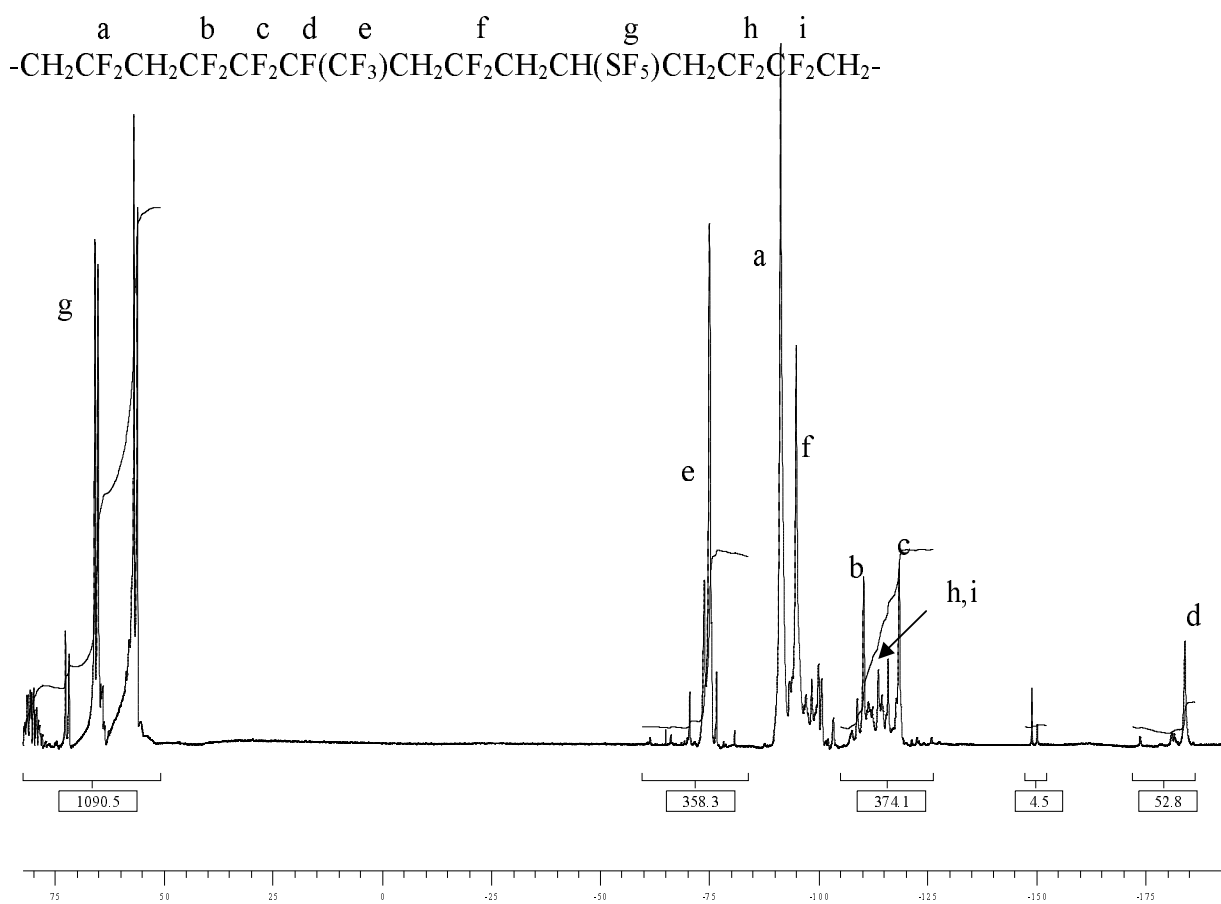


Fig. 4 ^{19}F NMR spectrum of VDF/HFP/SF₅(M-I) terpolymer I at initial monomer ratio in the feed =72.0/19.4/8.6 mol %

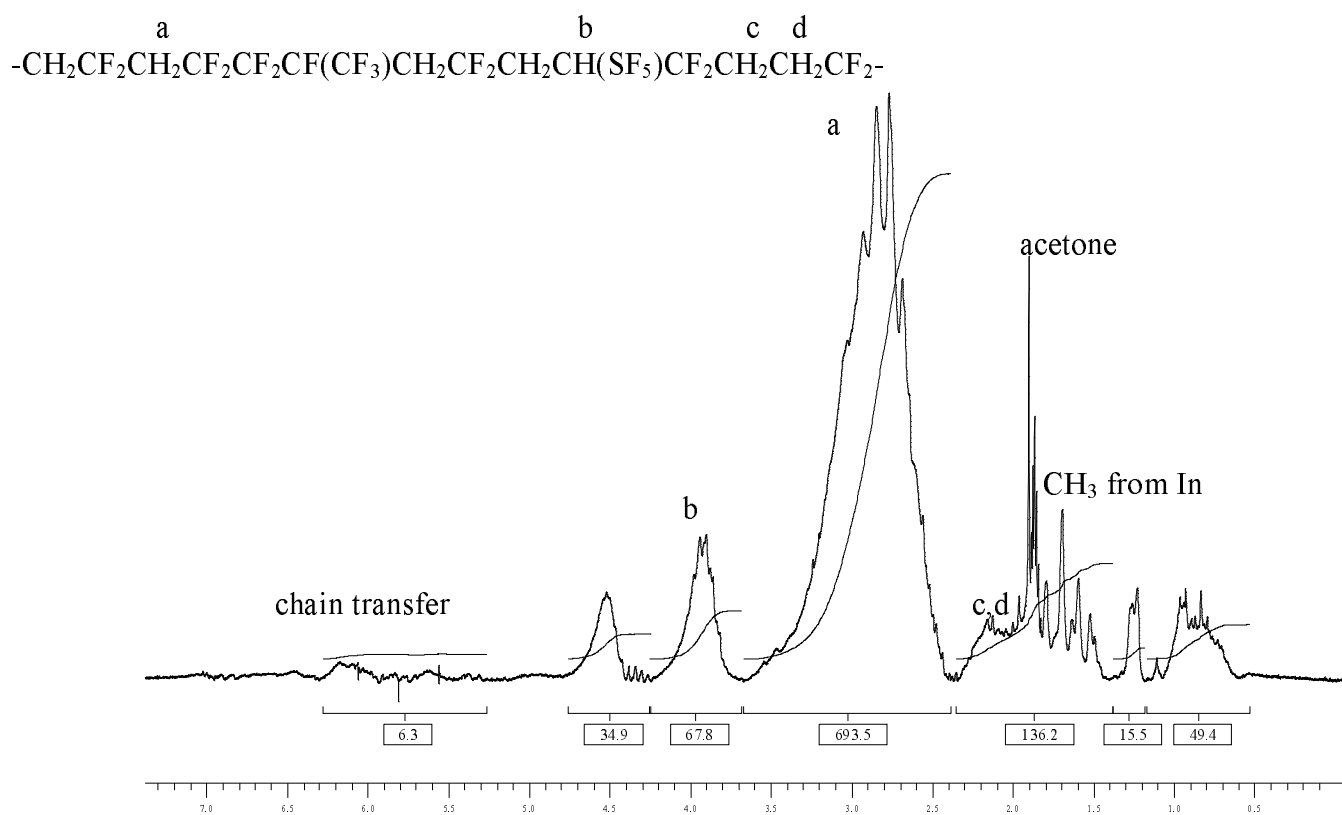


Fig. 5 ^1H NMR spectrum of VDF/HFP/SF₅(M-I) terpolymer I at initial monomer ratio in the feed =72.0/19.4/8.6 mol %

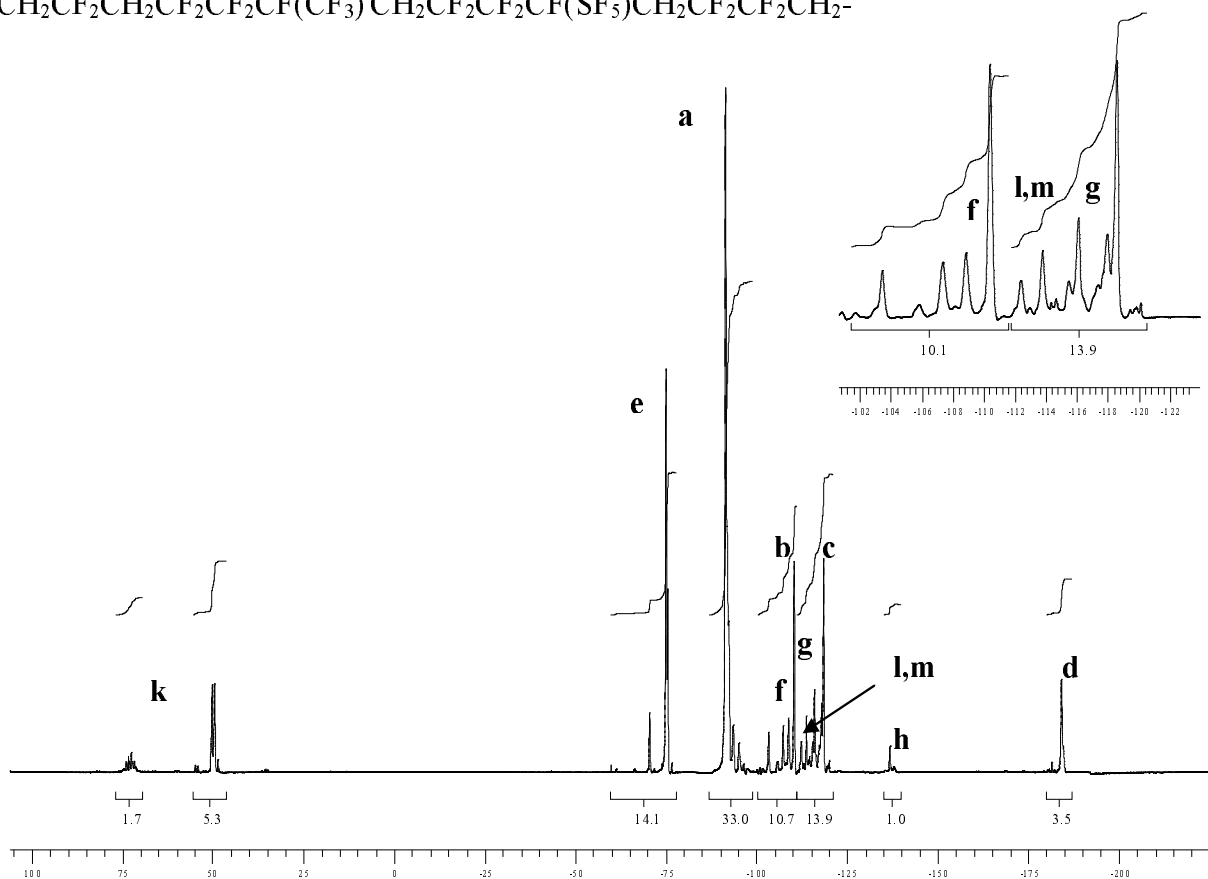


Fig. 6 ^{19}F NMR spectrum of VDF/HFP/SF₅(M-III) terpolymer III recorded in deuterated acetone at initial monomer ratio 73.1/18.3/8.6 mol %

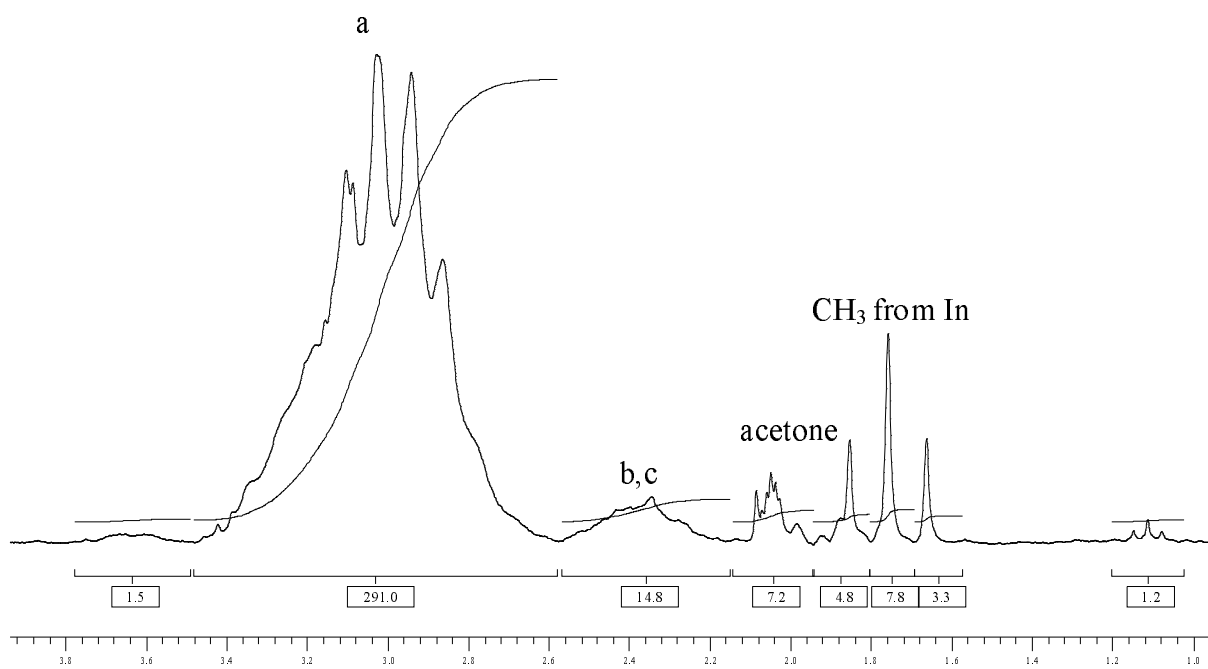


Fig.7 ¹H NMR spectrum of VDF/HFP/SF₅(M-III) terpolymer III recorded in deuterated acetone at initial monomer ratio 73.1/18.3/8.6 mol %

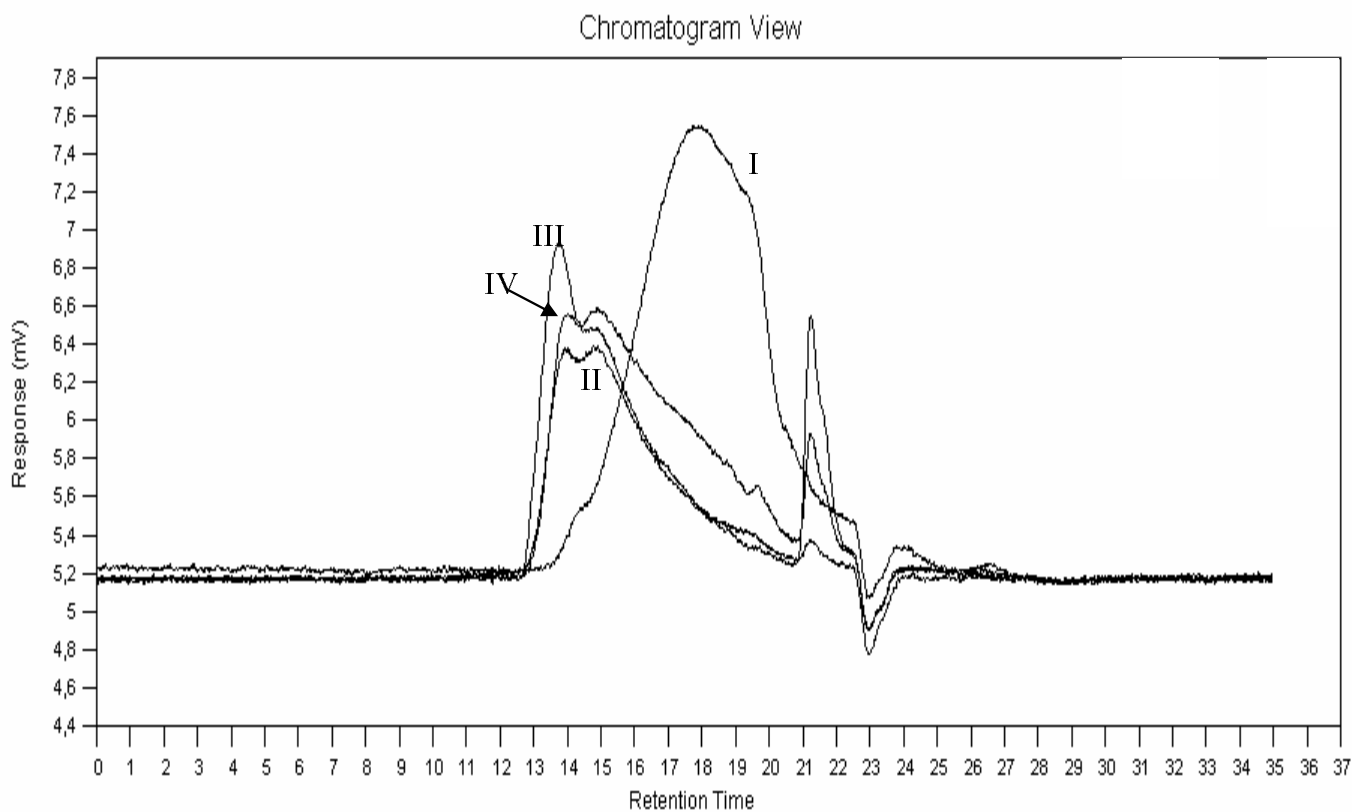


Fig. 8 SEC Chromatograms of poly(VDF-ter-HFP-ter-SF₅M) terpolymers. Terpolymer compositions of VDF/HFP/SF₅M in mol % :I -71.0/11.6/17.4 ;II- 83.8/14.1/2.1; III – 78.3/16.4/5.3; IV – 78.1/13.5/8.3

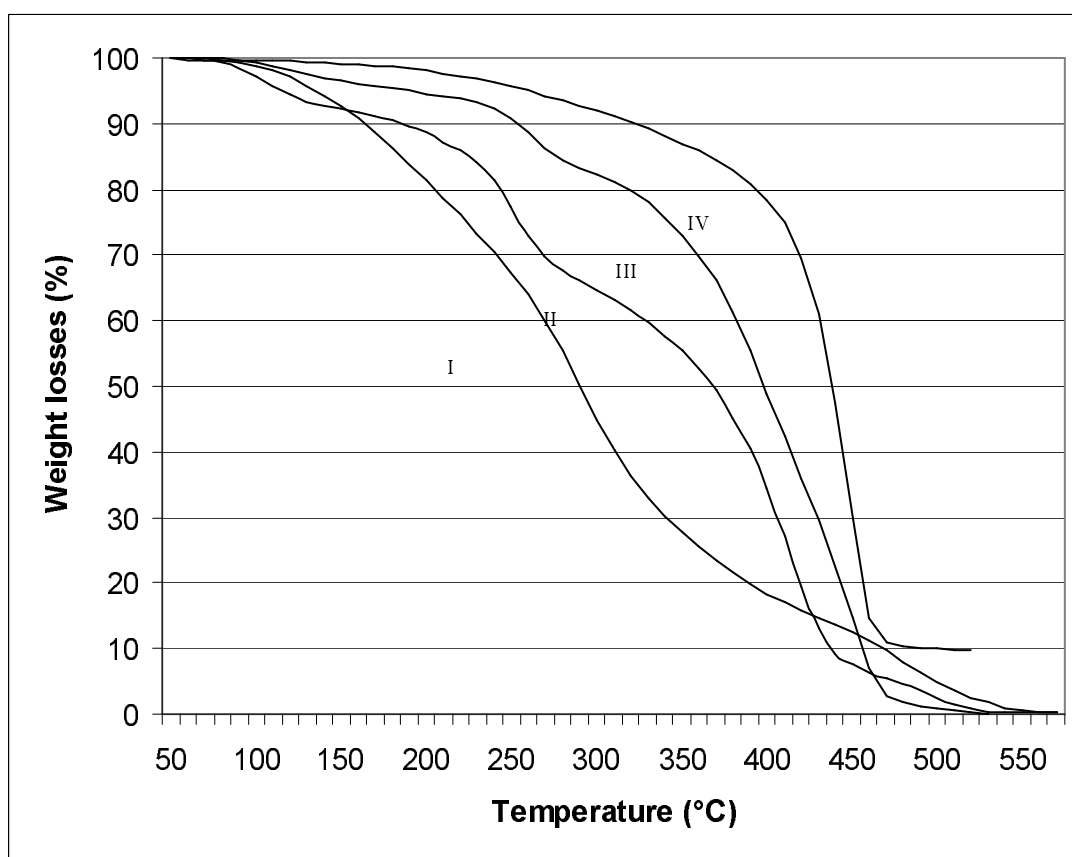


Fig.9 Thermogravimetric curves of VDF/HFP/-SF₅M terpolymers in air of VDF/HFP/SF₅ terpolymers. Terpolymer compositions of VDF/HFP/SF₅M in mol % :I -71.0/11.6/17.4 ;II- 83.8/14.1/2.1; III – 78.3/16.4/5.3; IV – 78.1/13.5/8.3

TABLE CAPTIONS

Table 1: Comparative study of different reactivities of VDF with various monomers^a :HFP, PMVE, PPVE, CF₂=CF SF₅

Table 2. ¹⁹F-NMR assignments of fluorinated groups in the poly(VDF-ter-HFP-ter- SF₅M) terpolymers recorded in deuterated acetone.

Table 3: Molecular weights of poly(VDF-co-SF₅MIII) and poly(VDF-ter-HFP-ter-SF₅Mi) copolymers assessed by ¹H and ¹⁹F NMR analyses

Table 4: Monomer – polymer compositions of poly(VDF-ter-HFP-ter-SF₅M) terpolymers and their main characteristics . Reaction conditions: initiator DTBP – 1 mol %; solvent pentafluorobutane – 70 wt % ; 143 °C ; 5 hrs.

Table 1.Comparative study of different reactivities of VDF with various monomers in radical copolymerization^a

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

a) no homopolymerization of CF₂=CF SF₅ monomer

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

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

Table 3. Molecular weights of poly(VDF-co-SF₅MIII) and poly (VDF-ter-HFP-ter-SF₅Mi) copolymers assessed by ¹H and ¹⁹F 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% SF₅MIII / mol %VDF in copolymer, α_1 =% HFP / mol %VDF in terpolymer ;
 α_2 = mol %SF₅Mi / mol % VDF in terpolymer

Table 4. Monomer – polymer compositions of poly(VDF-ter-HFP-ter-SF₅M) terpolymers and their main characteristics. Reaction conditions : initiator DTBP – 1 mol %; solvent pentafluorobutane – 70 wt % ; 143 °C ; 5 h

Exp No Monomer	Feed (mol %)			Terpo (mol%)			Y (wt %)	Mn (g/mol)	PDI	Tg (°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, C₄F₅H₅; Polymers I and II not soluble in CHCl₃ and CH₂Cl₂ whereas polymers III and IV are soluble in CH₂Cl₂ and partially in CHCl₃