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Radical terpolymerization of 1,1,2-trifluoro-2-pentafluorosulfanylene and pentafluorosulfanylene in the presence of Vinylidene Fluoride and Hexafluoropropylene by Iodine Transfer Polymerization.

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ABSTRACT

Iodine transfer terpolymerization of two monomers bearing an SF₅ group, i.e. 1,1,2-trifluoro-2-pentafluorosulfanylene (F₂C=CF₂CF₂CF₂CF₃) and pentafluorosulfanylene (H₂C=CHSF₅), with 1,1-difluoroethylene (or vinylidene fluoride, VDF) and hexafluoropropylene (HFP) is presented. These pentafluorosulfanyl monomers present a peculiar reactivity. They do not homopolymerize by conventional radical polymerization, but they co- and terpolymerize with the above fluorinated olefins. The resulting fluorinated terpolymers were characterized by ¹⁹F and ¹H NMR spectroscopies which enabled the assessment of the molar percentages of the three comonomers. Size exclusion chromatography and NMR characterizations were also used to assess the molecular weights, *M_n*, ranging between 260 and 8 400 g/mol. Interestingly, both these pentafluorosulfanyl monomers exhibit different behaviors in that radical terpolymerization in the presence of C₆F₁₃I as a degenerative chain transfer agent. Thus, F₂C=CF₂CF₂CF₂CF₃ can be terpolymerized with VDF and HFP with a good control of molecular weight leading fluoropolymers bearing SF₅ groups with low polydispersity index (PDI). Unexpectedly, only two iodide functionalities of the terpolymers namely two end-groups (-CH₂CF₂I and -CF₂CH₂I) were observed and their proportions were influenced by the number of VDF units. Indeed, -CH₂CF₂I functionality decreased when the number of VDFs per chain increased. In contrast to 1,1,2-trifluoro-2-pentafluorosulfanyl ethylene, H₂C=CHSF₅ could not be terpolymerized by ITP but led to C₆F₁₃-[(CH₂CF₂)-(CH₂CH(SF₅))]n-I alternating cooligomers of low molecular weight in poor yields (10-20%). The formation of by-product (C₆F₁₃CH=CHSF₅ monoadduct obtained by dehydrofluorination) was also observed, which corresponds to the elimination of HI from the 1:1 adduct. In the last part, the thermal properties were discussed. The presence of SF₅ group decreases the *T_g* of fluoropolymers whereas the thermal stabilities depended on the molecular weights.

KEYWORDS. Fluorinated polymers, controlled radical polymerization, iodine transfer polymerization, functional oligomers, pentafluorosulfanyl monomers.

INTRODUCTION

Fluoropolymers exhibit remarkable properties,¹⁻⁵ such as chemical inertness (to acids, bases, organic solvents), low dielectric constants and dissipation factors, hydrophobic and oleophobic properties, excellent weathering, and interesting surface properties. Hence, these high-value-added-materials can find applications in many fields of high technology: aeronautics,⁶ microelectronics,⁷ optics,^{8,9} textile finishing,^{10,11} in the nuclear industry,¹² in paints and coatings¹³ and military use.¹⁴ Improvement of the properties of the fluoropolymers can be achieved from the copolymerization or the terpolymerization of monomers bearing functional group(s) born by the co- or termonomers. Among commercially available fluoroalkenes, vinylidene fluoride (VDF) is commonly used and regarded as an attractive monomer. It possesses a reactivity close to those of tetrafluoroethylene, trifluoroethylene and chlorotrifluoroethylene, but it is much less dangerous (it is not explosive and has a low toxicity) and is a precursor of thermoplastics or elastomers^{4,5} endowed with interesting properties.

Pentafluorosulfanyl (SF_5) grouping polymers imparts original properties, such as high-performance lubricant and oil resistance properties, protective surface coatings, and insulating properties¹⁵⁻¹⁸. These interesting properties provide significant motivation to synthesize polymers bearing SF_5 , e.g. polyfluoroalkylacrylates,^{19,20} polyfluoroalkylsiloxanes,²¹ polyimides containing $\text{SF}_5(\text{CF}_2)_n$ - groups ($n = 0, 2$),²² just like polystyrene bearing the $\text{SF}_5\text{CF}_2\text{CF}_2$ - group.²³ Thus, the use of monomers which possess an SF_5 group allowed the preparation of organic superconductors,²⁴ SF_5 -organic metals/organic semiconductors,²⁵ ionic liquids,²⁶ and of liquid crystals.²⁷ In a previous study²⁸, the homopolymerization, copolymerization and terpolymerization of SF_5 containing-monomers with commercial fluoroalkenes was investigated by conventional radical polymerization. However, poor control of the molecular weights, the high polydispersity indexes (PDIs) and the presence of non-functional end-groups to achieve functional or telechelic polymers was considered to limit the use (e.g. block copolymers or thermoplastic elastomers) and the applications of these copolymers. Therefore, to overcome these drawbacks, a major goal of this work became a controlled radical copolymerization of these monomers. Indeed, the peculiar reactivity of these fluorinated olefins allows the control of the radical polymerization by iodine transfer polymerization (ITP)^{4,5,29} only. Actually, neither atom transfer radical polymerization (ATRP)³⁰, nor nitroxide mediated polymerization (NMP)³¹, nor reversible addition fragmentation transfer (RAFT)³² of fluorinated olefins has successfully been reported in the

literature. ITP is a powerful technique which allows the synthesis of monofunctional and telechelic polymers terminated by iodine atom(s)^{4,5,29}. Such end-groups can be modified to obtain polymers terminated by reactive groups. Furthermore, ITP allows the synthesis of different commercially available products, for example thermoplastic elastomers (TPE).³³⁻³⁹

The objectives of the present article concern the study of the radical terpolymerizations of VDF and hexafluoropropylene (HFP) with two different pentafluorosulfanyl monomers by iodine transfer terpolymerization in the presence of C₆F₁₃I as a degenerative chain transfer agent. The influence of the structure of both the SF₅-monomers, i.e. F₂C=CFSF₅ and H₂C=CHSF₅, on the controlled character of the ITP was investigated, i.e. the correlation between targeted and experimental average degrees of polymerization (or average molecular weights) and the polydispersity indexes. Moreover, the behaviors between both these monomers according to the technique of polymerization (i.e., conventional and controlled radical polymerization) have also been compared. Indeed, different yields and compositions have been observed between both kinds of polymerization. In addition, the effect of the incorporation of SF₅-monomer during the polymerization of VDF onto the reversed additions has also been considered and compared to the results achieved from the ITP of VDF. Lastly, the thermal properties of the resulting fluorinated terpolymers *versus* the molecular weights have been investigated, which was not reported in our previous study²⁸.

EXPERIMENTAL SECTION:

Materials

Vinylidene fluoride (or 1,1-difluoroethylene, VDF), hexafluoropropylene (HFP) and 1,1,1,3,3-pentafluorobutane were kindly donated by Solvay S.A. (Tavaux, France and Brussels, Belgium). 1-Iodoperfluorohexane ($C_6F_{13}I$, purity 95 %) was generously supplied by Atofina (now Arkema, Pierre-Benite, France). It was treated with sodium thiosulfate and then distilled prior to use. *Tert*-butylperoxypivalate (TBPPI) (purity 75 %) was a gift from Akzo, Chalons sur Marne, France used as supplied. Acetonitrile, dimethylformamide (DMF), tetrahydrofuran (THF), methanol, methylethylketone and dimethylacetamide (DMAc) of analytical grade were purchased from Aldrich Chimie, 38299 Saint Quentin-Fallavier, France.

1,1,2-trifluoro-2-pentafluorosulfanylethylene ($F_2C=CFSF_5$) was prepared as described in the literature³⁵ and the purity was checked by ^{19}F NMR and by FT-IR spectroscopies.

^{19}F NMR ($CDCl_3$, 298 K, 400 MHz, δ (ppm)): +69.7 (1F, SF_5), +59.0 (d, 4F, SF_5), -99.5 (m, $CF_2=$, 2F), -163.0 ppm (m, 1F, $=CF(SF_5)$).

FT-IR (cm^{-1}): 1782 (s, C=C), 1351 (s), 1246 (s), 1089 (m), 898 (vs), 862 (vs), 706 (m), 654 (m), 613 (s). The adsorption at 898 and 862 cm^{-1} are assigned to S-F stretching while that at 613 cm^{-1} corresponds to one of SF_5 group deformation modes.

The synthesis of pentafluorosulfanylethylene was as described in the literature^{28,36} and checked by ^{19}F and 1H NMR spectroscopies.

1H NMR ($CDCl_3$, 298 K, 400 MHz, δ (ppm)): 5.74 (m, 1H, $=CHSF_5$), 6.01 (d, $J = 15$ Hz, 1H, $CH_2=$), 6.68 (m, 1H, $CH_2=$).

^{19}F NMR ($CDCl_3$, 298 K, 400 MHz, δ (ppm)): +81.4 (AB_4 system, J_{AB} 146Hz, qi, 1F, SF_5), +59.7 (d, 4F, SF_5).

Note: Symbols s, d, t, qi and m correspond to singlet, doublet, triplet, quintet and multiplet, respectively. For IR, s, vs, m stand for strong, very strong, medium, respectively.

Analyses

The compositions and the structures of the terpolymers obtained by ITP were determined by ^{19}F and 1H NMR spectroscopies. The NMR spectra were recorded on Bruker AC 200, AC 250, 400 (200, 250 and 400 MHz) instruments, using deuterated acetone and deuterated chloroform as the solvents and tetramethylsilane (TMS) (or $CFCl_3$) as the references for 1H (or ^{19}F) nuclei. Coupling constants and chemical shifts are given in Hz and ppm, respectively. The experimental conditions for 1H (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 128), and a pulse width of 5 μs for ¹⁹F NMR.

Gel Permeation Chromatography (GPC) or Size Exclusion Chromatography (SEC) analyses were performed with a Spectra-Physics apparatus equipped with two PLgel 5μm Mixed-C columns from Polymer Laboratories and a Spectra Physics SP8430 Refractive Index detector (the signals assigned to poly(VDF-*ter*-HFP-*ter*-SF₅ monomer) terpolymers gave negative values). Tetrahydrofuran (THF) was chosen as the eluent at $T = 30$ °C, with a flow rate of 0.8 mL min⁻¹. Monodispersed poly(styrene) standards were purchased from Polymer Laboratories. Aliquots were sampled from the reactional medium. Solvent was removed by evaporation, and after aliquots were diluted in THF up to a known concentration ca. 2 wt.-%, filtered through a 200 microns PTFE chromafil membrane, and finally analyzed by SEC.

Thermal properties: The glass transition temperatures (T_g s) were determined by differential scanning calorimetry (DSC) using a Perkin Elmer Pyris 1 apparatus calibrated with indium and n-decane. The samples (about 10 mg) were initially cooled to -105 °C for 10 mins, then heated from -100 to 50 °C at a heating rate of 20 °C /min (a second recooling was done to -105 °C, and the same cycle was repeated three times). The values of T_g s reported herein correspond to the inflexion point the heat capacity jump of the glass transition. TGA analyses were performed with a Texas Instrument ATG 51-133 apparatus in air at the heating rate of 20 °C/min from room temperature up to 550 °C.

Reaction in autoclave

Iodine transfer polymerizations of VDF, HFP and SF₅-monomers were performed in the presence of 1-iodoperfluorohexane as the degenerative chain transfer agent (CTA) and initiated by *tert*-butylperoxypivalate at 75 °C. A typical experiment is reported below with molar feed (VDF/HFP/ F₂C=CFSF₅): 75.2/ 16.5/ 8.3, [C₆F₁₃I]₀ / [VDF+HFP+SF₅ monomer]₀ = 0.056, [Initiator]₀ / [VDF+HFP+SF₅ monomer]₀ = 0.01.

A 160-mL Hastelloy (HC-276) autoclave, equipped with inlet and outlet valves, a manometer and a rupture disc, was degassed and pressurized with 30 bar of nitrogen to check for eventual leaks. Then, a 20 mmHg vacuum was imposed for 30 min. Under vacuum were transferred into the autoclave 0.320 g (1.38 mmol) of *tert*-butylperoxypivalate (TBPPI), 3.430 g (7.69 mmol) of 1-iodoperfluorohexane (C₆F₁₃I), 2.363 g (0.011 mol) of 1,1,2-trifluoro-2-pentafluorosulfanylethylene (F₂C=CFSF₅) and 35.0 g of 1,1,1,3,3-pentafluorobutane. Then, by double weighing, 3.4 g (0.02 mol) of HFP and 6.4 g (0.10 mol) of VDF were introduced in

the mixture. Then, the autoclave was slowly heated to 75 °C. It was observed a low exotherm of ca. 5 °C and then a sharp drop of pressure from 10 bars to 1 bars. After 6 hr-reaction, the autoclave was placed in an ice bath for about 60 minutes and unreacted VDF, SF₅-monomers and HFP were progressively released. After opening the autoclave, about 50.0 g of a brown liquid was obtained. The solvent and traces of monomers and CTA were removed by distillation at 60 °C under reduce pressure (P = 20 mmHg), to obtain a viscous and brown product. The sample was dissolved in acetone and precipitated from pentane to eliminate the traces of initiator and of CTA (yield = 80%). The terpolymer was characterized by ¹⁹F and ¹H NMR spectroscopies, SEC, DSC and TGA analyses. The molecular weights were 1,650 g/mol and 2,100 g/mol, PDI = 1.36 with poly(styrene standard), assessed by ¹⁹F NMR and by SEC analysis, respectively.

The same process was used for the radical terpolymerization involving pentafluorosulfanylene.

RESULTS AND DISCUSSION.

The radical terpolymerizations of fluorinated monomers bearing a $-\text{SF}_5$ group such as 1,1,2-trifluoro-2-pentafluorosulfanylene (i.e. $\text{F}_2\text{C}=\text{CFSF}_5$) and pentafluorosulfanylene (i.e. $\text{H}_2\text{C}=\text{CHSF}_5$) with 1,1-difluoroethylene (vinylidene fluoride, VDF) and hexafluoropropylene (HFP) were carried out in the presence of *tert*-butylperoxypivalate (TBPPI) as the initiator, with or without $\text{C}_6\text{F}_{13}\text{I}$ as the chain transfer agent (CTA), in 1,1,1,3,3-pentafluorobutane as the solvent at $75\text{ }^\circ\text{C}$ for 14 hours (Scheme 1).

INSERT SCHEME 1

During the course of the reaction, a drop of pressure was observed, which was assigned to the incorporation of both gaseous monomers into the terpolymers. After reaction, the solvent was removed by distillation, and the resulting terpolymers were purified by precipitation from cold pentane. After separation and drying, brown rubber-like polymers were obtained.

1. Mechanistic of ITP

Iodine transfer polymerization (ITP) is a degenerative chain transfer polymerization (DT) requiring alkyl iodides⁴. ITP was developed in the late seventies by Tatemoto *et al.*^{34,37-39} at the Daikin Company, and then was confirmed by other companies, such as Dupont de Nemours (now, Dupont Performance Elastomers)⁴⁰, Ausimont⁴¹⁻⁴³ (now Solvay Solexis) and recently by Tosoh T-Tech Co.⁴⁴. The mechanism of iodine transfer polymerization (ITP) with alkyl iodide is shown in Scheme S1 in the Supporting Information.

The initiating radical, A° , generated by thermal decomposition of a conventional initiator (such as *tert*-butylperoxypivalate, TBPPI) in step a), can be added onto M monomer (minor reaction) in step b or onto R-I (to lead to R° , major reaction) in step b'), and the resulting radical propagates (step d). The exchange of iodine from the transfer agent, R-I, to the propagating radical, P_n° , results in the formation of the polymeric alkyl iodide, $\text{P}_n\text{-I}$, and a new initiating radical, R° (step c). Large differences in the stability of the reactants and products involved in step 4 could result in shifting the equilibrium overwhelmingly to the right or to the left. Therefore, the ideal case is when the structure of R closely looks like that

of the propagating radical, resulting in a thermodynamically neutral transfer step. In step d), R° , generated from the alkyl iodide, adds onto a monomer unit. The exchange process described in step 6 is thermodynamically neutral, because P_n and P_m propagating chains exhibit the same structure. As in any radical process, the termination occurs with alkyl iodides in ITP polymerization (step e)). Minimizing the termination step remains essential to keep a good control of the polymerization (step f)). Ideally, in ITP, to obtain polymer with a narrow molar mass-distribution the rate of exchange should be higher than that of the propagation. ITP allows one to control a great variety of hydrogenated monomers, such as acrylates⁴⁵, styrenics^{45,46}, methacrylates⁴⁷ (by reverse iodine transfer polymerization) and vinyl acetate⁴⁸⁻⁵⁰ and also fluorinated monomers^{4,5}, such as VDF^{29,51} or a mixture of fluoroolefins (VDF/HFP^{52,53}, VDF/HFP/TFE^{54,55}, VDF/MAF (where MAF represents α -trifluoromethacrylic acid⁴⁴)).... Finally, ITP allows the synthesis of well-defined architectures such as monofunctional and telechelic polymers^{4,5,39}, PVDF-*b*-poly(styrene) diblock copolymer⁵⁶, and PVDF-*g*-PS graft copolymer^{49,50,57}.

2. Radical terpolymerization of 1,1,2-trifluoro-2-pentafluorosulfanylethylene ($F_2C=CFSF_5$) with vinylidene fluoride (VDF) and hexafluoropropylene (HFP).

2.1. Characterizations of the poly(VDF-*ter*-HFP-*ter*-SF₅M) terpolymers by ¹H and ¹⁹F NMR spectroscopies

The microstructures of these resulting terpolymers were characterized by ¹H and ¹⁹F NMR spectroscopies. Figure 1 represents the ¹⁹F NMR of the terpolymers from an initial molar feed 74 / 18 / 8 of VDF/HFP/SF₅. This spectrum shows signals centered at -92.2 and at -92.4 ppm characteristic of the difluoromethylene groups of the head-to-tail VDF chaining (i.e. normal VDF addition) and a multiplet centered at -40.0 ppm assigned to CH₂CF₂I end-group. Moreover, it is very interesting to note the absence of a series of signals centered at -94.9, -113.7 and -115.7 ppm assigned to -CF₂- groups in -(CH₂-CF₂)-(CF₂-CH₂)-(CH₂-CF₂)-(CH₂-CF₂); -(CH₂-CF₂)-(CF₂-CH₂)-; -(CH₂-CF₂)-(CF₂-CH₂)- sequences, respectively for the low molecular weight (Figure 1)⁵⁸. These sequences correspond to the reverse VDF addition (i.e., head-to-head addition)⁵⁹⁻⁶². Moreover, the presence of -SF₅ monomer is confirmed by an AB₄ system ranging between +50 and +75 ppm. As expected, the difluoromethylene group of VDF adjacent to -CF₂-CF(SF₅)- leads to a signal centered at -109.8 ppm, while those

corresponding to CF₂ and CF are observed at -118.8 ppm and -138.0 ppm, respectively²⁸. Lastly, the signals centered at -183.5, -119.0 and from -71.2 to -76.0 ppm correspond to CF, CF₂ and CF₃ groups of hexafluoropropene (HFP)^{53,63-65}. The presence of the chain transfer agent was confirmed by the different signals centered at -82.0, -112.2, -122.5, -123.5, -124.0 and -127.0 ppm assigned to CF₃, CF₂-CH₂, -CF₂-CF₂-CH₂, -CF₂-(CF₂)₂-CH₂, -CF₂-(CF₂)₃-CH₂ and CF₃-CF₂, respectively. The CTA conversion was evidenced by the absence of signal at -60.0 ppm assigned to -CF₂CF₂I end-group. Thus, it is possible to assess the number of VDF, HFP and SF₅ monomeric units by the following equations:

$$\text{Number of VDF units} = DP_n^{\text{VDF}} = [\int \underline{\text{CF}}_2^{\text{at } -40.0 \text{ ppm}} + \int \underline{\text{CF}}_2^{\text{at } -92.0 \text{ ppm}} + \int \underline{\text{CF}}_2^{\text{at } -109.8 \text{ ppm}} + \int \underline{\text{CF}}_2^{\text{at } -113.7 \text{ ppm}} + \int \underline{\text{CF}}_2^{\text{at } -115.7 \text{ ppm}}] / 2 + (\int \underline{\text{CF}}_3^{\text{at } -82.0 \text{ ppm}} / 3). \quad (\text{Eq. 1})$$

$$\text{Number of HFP units} = DP_n^{\text{HFP}} = (\int \underline{\text{CF}}_3^{\text{from } -75.0 \text{ to } -76.0 \text{ ppm}}) / (\int \underline{\text{CF}}_3^{\text{at } -82.0 \text{ ppm}}). \quad (\text{Eq. 2})$$

$$\text{Number of SF}_5 \text{ monomers} = DP_n^{\text{SF}_5\text{M}} = (\int \underline{\text{CF}}^{\text{at } -138 \text{ ppm}}) / (\int \underline{\text{CF}}_3^{\text{at } -82.0 \text{ ppm}} / 3). \quad (\text{Eq. 3})$$

Where $\int \underline{\text{CF}}_x^{\text{at } -i \text{ ppm}}$ represents the integral of signal centered at -i ppm assigned to CF_x group.

The molecular weight, M_n , can also be calculated as follows: $M_n = DP_n^{\text{VDF}} \times 64 + DP_n^{\text{HFP}} \times 150 + DP_n^{\text{SF}_5} \times 208 + 446$. The experimental results were close to the theoretical values assessed by equation $M_n = DP_{n, \text{theoretical}}^{\text{VDF}} \times 64 + DP_{n, \text{theoretical}}^{\text{HFP}} \times 150 + DP_{n, \text{theoretical}}^{\text{SF}_5} \times 208 + 446$, with $DP_{n, \text{theoretical}}^M = \alpha \times [M]_0 / [CTA]_0$, where α , M , $[CTA]_0$ and $[M]_0$ stand for the ratio of composition in M of terpolymer on the feed in M, the monomer (for example VDF, HFP or F₂C=CFSF₅); the initial concentrations of chain transfer agent and of monomer, respectively). Taking into account that HFP⁴ and 1,1,2-trifluoro-2-pentafluorosulfanylene do not homopolymerize, their reactivity ratios worth 0.

The compositions of monomeric -CF₂-CF(SF₅), VDF and HFP units in the terpolymers were assessed by ¹⁹F NMR (e.g., Figure 1) from equations 4, 5 and 6, respectively:

$$\%SF_5 = \int \underline{\text{CF}}^{\text{at } -138 \text{ ppm}} / [(\int \underline{\text{CF}}_2^{\text{at } -40.0 \text{ ppm}} + \int \underline{\text{CF}}_2^{\text{at } -92.0 \text{ ppm}} + \int \underline{\text{CF}}_2^{\text{from } -109.0} + \int \underline{\text{CF}}_2^{\text{at } -110.8 \text{ ppm}} + \int \underline{\text{CF}}_2^{\text{at } -113.7} + \int \underline{\text{CF}}_2^{\text{at } -115.7}) / 2 + (\int \underline{\text{CF}}_3^{\text{from } -71.2 \text{ to } -76.0 \text{ ppm}}) / 3 + (\int \underline{\text{CF}}^{\text{at } -138 \text{ ppm}})]. \quad (\text{Eq. 4})$$

$$\% \text{ VDF} = (\int \underline{\text{CF}}_2^{\text{at } -40.0 \text{ ppm}} + \int \underline{\text{CF}}_2^{\text{at } -92.0 \text{ ppm}} + \int \underline{\text{CF}}_2^{\text{from } -109.0} + \int \underline{\text{CF}}_2^{\text{at } -110.8 \text{ ppm}} + \int \underline{\text{CF}}_2^{\text{at } -113.7} + \int \underline{\text{CF}}_2^{\text{at } -115.7})/2 / [(\int \underline{\text{CF}}_2^{\text{at } -40.0 \text{ ppm}} + \int \underline{\text{CF}}_2^{\text{at } -92.0 \text{ ppm}} + \int \underline{\text{CF}}_2^{\text{from } -109.0} + \int \underline{\text{CF}}_2^{\text{at } -113.7} + \int \underline{\text{CF}}_2^{\text{at } -115.7})/2 + (\int \underline{\text{CF}}_3^{\text{from } -71.2 \text{ to } -76.0 \text{ ppm}})/3 + (\int \underline{\text{CF}}^{\text{at } -138 \text{ ppm}})].$$

(Eq. 5)

$$\% \text{ HFP} = [(\int \underline{\text{CF}}_3^{\text{from } -75.0 \text{ to } 76.0 \text{ ppm}})/3] / [(\int \underline{\text{CF}}_2^{\text{at } -40.0 \text{ ppm}} + \int \underline{\text{CF}}_2^{\text{at } -92.0 \text{ ppm}} + \int \underline{\text{CF}}_2^{\text{from } -109.0} + \int \underline{\text{CF}}_2^{\text{at } -110.8 \text{ ppm}} + \int \underline{\text{CF}}_2^{\text{at } -113.7} + \int \underline{\text{CF}}_2^{\text{at } -115.7})/2 + (\int \underline{\text{CF}}_3^{\text{from } -71.2 \text{ to } -76.0 \text{ ppm}})/3 + (\int \underline{\text{CF}}^{\text{at } -138 \text{ ppm}})].$$

(Eq. 6)

with $\underline{\text{CF}}^{\text{at } -138 \text{ ppm}}$, $(\int \underline{\text{CF}}_2^{\text{at } -40.0 \text{ ppm}} + \int \underline{\text{CF}}_2^{\text{at } -92.0 \text{ ppm}} + \int \underline{\text{CF}}_2^{\text{from } -108.8 \text{ to } -115.7 \text{ ppm}})$ and $(\int \underline{\text{CF}}_3^{\text{from } -71.2 \text{ to } -76.0 \text{ ppm}})$ correspond to monomer bearing SF_5 group, VDF and HFP units.

Interestingly, in contrast to a previous study²⁸, the absence (or the weak integral) of signals assigned to $\text{CH}_2\text{CF}_2\text{-CF}_2\text{CH}_2\text{-}$ reversed VDF adducts can also evidence the controlled behavior of that terpolymerization.

The compositions of the terpolymers are given in Table 1. Whatever the concentration of the chain transfer agent, they were close (runs 2-4) to the compositions obtained by conventional radical polymerization (run 1) under the same experimental conditions. Moreover, the final molar percentages of VDF are higher than those in the feed and are in good agreement with those assessed from the conventional radical polymerization observed in our previous work²⁸.

Finally, it is noted the absence (or not detectable by ^{19}F NMR) of signal assigned to the end-group of direct initiation by radicals generated from the decomposition of the initiator, such as $(\text{CH}_3)_3\text{C-CH}_2\underline{\text{CF}}_2\text{-CH}_2\text{CF}_2\text{-}$, $\text{CH}_3\text{-CH}_2\underline{\text{CF}}_2\text{-CH}_2\text{CF}_2\text{-}$, $\text{CH}_3\underline{\text{CF}}_2\text{-CF}_2\text{CH}_2\text{-CF}_2\text{-}$ and $(\text{CH}_3)_3\text{C-}\underline{\text{CF}}_2\text{CH}_2\text{-CF}_2\text{-}$ which appears at -92.2, -95.7, -107.5, and -112.3 ppm²⁸. The absence of the direct initiation is attributed to the high transfer constant of $\text{C}_6\text{F}_{13}\text{I}$.

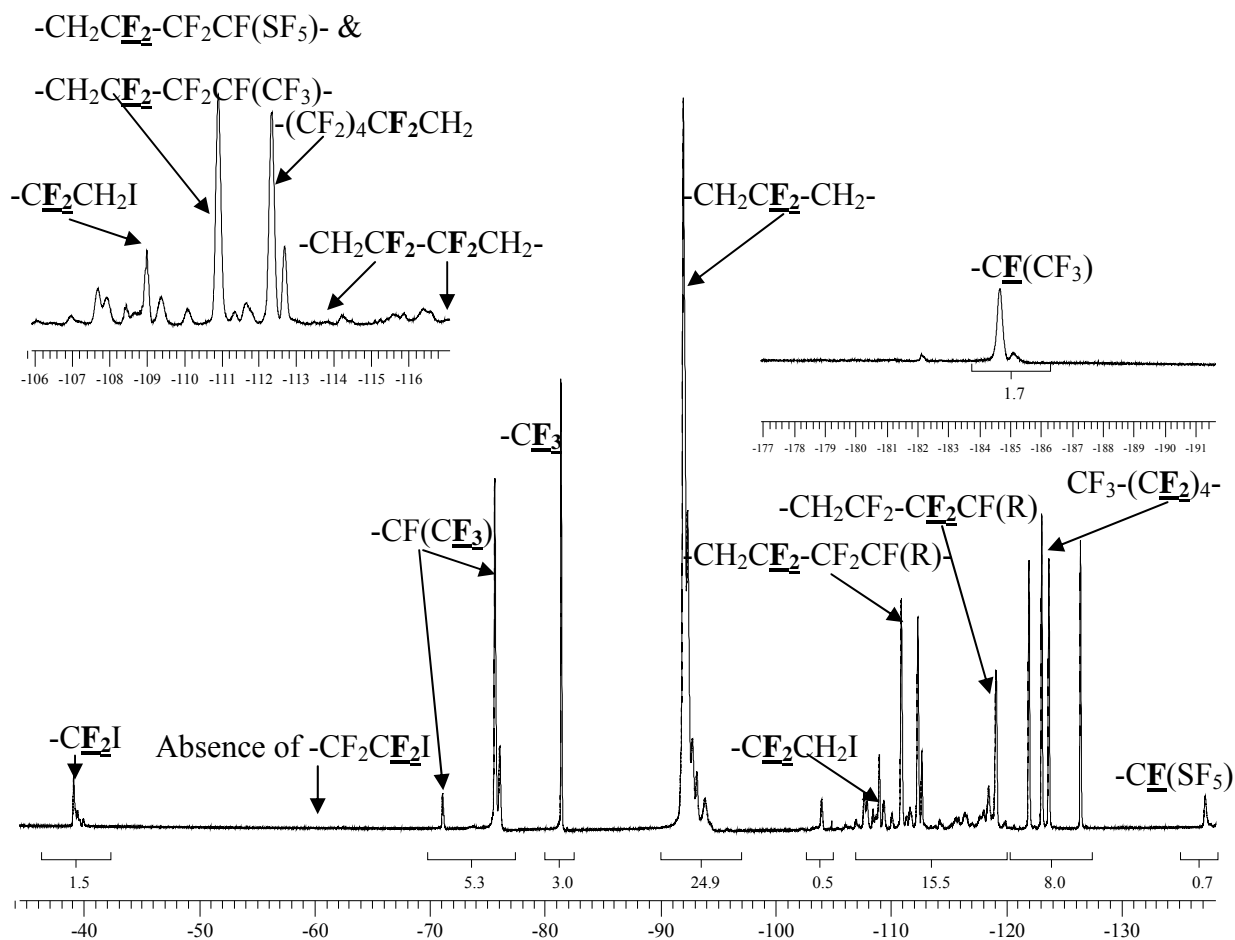


Figure 1. ^{19}F NMR spectrum of poly(VDF-*ter*-HFP-*ter*-CF₂CF(SF₅)) terpolymer obtained by ITP in the presence of C₆F₁₃I at 75 °C (molar feed VDF/HFP/CF₂CF(SF₅) ratio = 74.2/17.8/8.0, molar composition = 83.0/12.2/4.8, $M_{n, \text{exp.}}$ (^{19}F NMR)= 1,650 g/mol, -CH₂CF₂I functionality = 0.75; run #2 in Table 1 (Recorded in d₆ acetone, at 293 K, 400 MHz).

Experimental conditions [C₆F₁₃I]₀ / [VDF+HFP+SF₅ monomer]₀ = 0.05, [Initiator]₀ / [VDF+HFP+SF₅monomer]₀ = 0.01 in 1,1,1,3,3-pentafluorobutane at 75 °C for 6 hrs.

INSERT TABLE 1

The ^1H NMR spectra (Figure S5 and S6 in the Supporting Information) of poly(VDF-*ter*-HFP-*ter*-CF₂CF(SF₅)) terpolymers for two concentrations of chain transfer agent (CTA) (Table 1) shows different signals centered at 3.3 ppm, 3.8 ppm, and 4.0 ppm attributed to methylene groups of VDF, -CH₂CF₂I, and -CH₂-I, respectively. The quasi-absence of the triplet of triplets with $^2J_{\text{HF}} = 55.0$ Hz and $^3J_{\text{HH}} = 6.9$ Hz) around at 6.3 ppm⁶⁶ assigned to

HCF₂CH₂- end-group show the weak transfer to the solvent, monomer, polymer or initiator. Interestingly, the peak centered at 2.5 ppm of negligible intensity shows the *quasi*-absence of tail-to-tail addition of VDF (-CF₂-**CH₂**-**CH₂**-CF₂-) for both low and high molecular weights. This may be an evidence of the controlled radical copolymerization showing that each VDF unit is incorporated in a regioselective way in the poly(VDF-*ter*-HFP-*ter*-CF₂CF(SF₅)) terpolymers. This also indicates the high transfer constant of C₆F₁₃I and confirms previous studies^{29,51} on the iodine transfer copolymerization of VDF in the presence of C₆F₁₃I.

2.2. Assessment of the iodinated functionality in the poly(VDF-HFP-SF₅M) terpolymers:

In the course of the radical terpolymerization of VDF, HFP and SF₅ monomers in the presence of C₆F₁₃I, it is possible to obtain 6 chain-ends, i.e. -CH₂CF₂I, -CF₂CH₂I, -CF(CF₃)CF₂I, -CF₂CF(CF₃)I, -CF(SF₅)CF₂I and -CF₂CF(SF₅)I (Scheme 2). The amount of each species can be determined by ¹⁹F NMR. Indeed, these different structures should lead to different signals as summarized in Table 2^{61,67-73}. The -CH₂CF₂I and -CF₂CH₂I chain-ends correspond to the normal and the reverse addition of C-I bond onto VDF (Scheme S2 in the Supporting Information). Their corresponding signals appear at -40.0 ppm and -109.0 ppm. However, it is noted the absence of signals centered at -60.0 ppm and -145.0 ppm, which correspond to -CF(CF₃)CF₂I and -CF₂CF(CF₃)I chain-ends comprising reverse and normal addition of radical onto HFP⁷⁰, respectively (Table 2). Finally, it is also interesting to note the absence of SF₅-monomer chain-end. The great reactivity of these iodides explains the absence of such signals. Thus, when these species are formed during the reaction, they rapidly transfer. Thus, the polymeric chains terminated by (-CF₂CF(CF₃)I, -CF(CF₃)CF₂I - CF(SF₅)CF₂I and -CF₂CF(SF₅)I), are quickly consumed, while the other species (i.e. -CH₂CF₂I and -CF₂CH₂I), which present a weaker reactivity, are more slowly consumed.

INSERT SCHEME 2

INSERT TABLE 2

-CF₂CH₂I and -CH₂CF₂I functionalities were assessed by the following equations.

$$\text{Functionality in } -\text{CH}_2-\text{CF}_2\text{I} = (\int -\text{CH}_2-\text{CF}_2\text{I}^{-40.0 \text{ ppm}}/2) / (\int -\text{CF}_3^{-82.0 \text{ ppm}}/3) \quad (\text{Eq. 7})$$

$$\text{Functionality in } -\text{CF}_2-\text{CH}_2\text{I} = (\int -\text{CF}_2-\text{CH}_2\text{I}^{-109.0 \text{ ppm}}/2) / (\int -\text{CF}_3^{-82.0 \text{ ppm}}/3) \quad (\text{Eq. 8})$$

The sum of $-\text{CH}_2\text{CF}_2\text{I}$ and $-\text{CF}_2\text{CH}_2\text{I}$ functionalities worths 1, hence confirming the absence of terpolymers terminated by $-\text{CF}(\text{SF}_5)\text{CF}_2\text{I}$, $-\text{CF}_2\text{CF}(\text{SF}_5)\text{I}$; $-\text{CF}_2\text{CF}(\text{CF}_3)\text{I}$ and $-\text{CF}(\text{CF}_3)\text{CF}_2\text{I}$.

Further, according to the CTA concentration in the medium, the functionalities in $-\text{CH}_2\text{CF}_2\text{I}$ and $-\text{CF}_2\text{CH}_2\text{I}$ are different. Indeed, a decrease of CTA concentration (and hence an increase of the molecular weight) induces a decrease $-\text{CH}_2\text{CF}_2\text{I}$ functionality (from 0.7 to 0.3). The low reactivity of $-\text{CH}_2\text{I}$ explains its accumulation in the reactional medium (Table 3). This observation is in agreement with the results obtained for the ITP of VDF in the presence of CTA^{29,51}. Indeed, VDF is an unsymmetrical monomer and the produced macroradical generated in the propagation step may add onto CF_2 or CH_2 sites (Scheme 2 in Supporting Information).⁵¹ As a matter of fact, it is known that PVDF contain microstructures defects linked to the presence of reversed VDF addition since tail-to-tail, or head-to-head chainings have been observed (Figure S1-3 in the Supporting Information).^{29,51} Nevertheless, the $-\text{CF}_2\text{I}$ proportions in the terpolymers are higher than those obtained in the case of the PVDF homopolymer synthesized by ITP in the presence of VDF and of $\text{C}_6\text{F}_{13}\text{I}$, only (Figure 2). In conclusion, the addition of comonomer in the polymerization decreases the reverse addition and improves the control of ITP.

INSERT TABLE 3

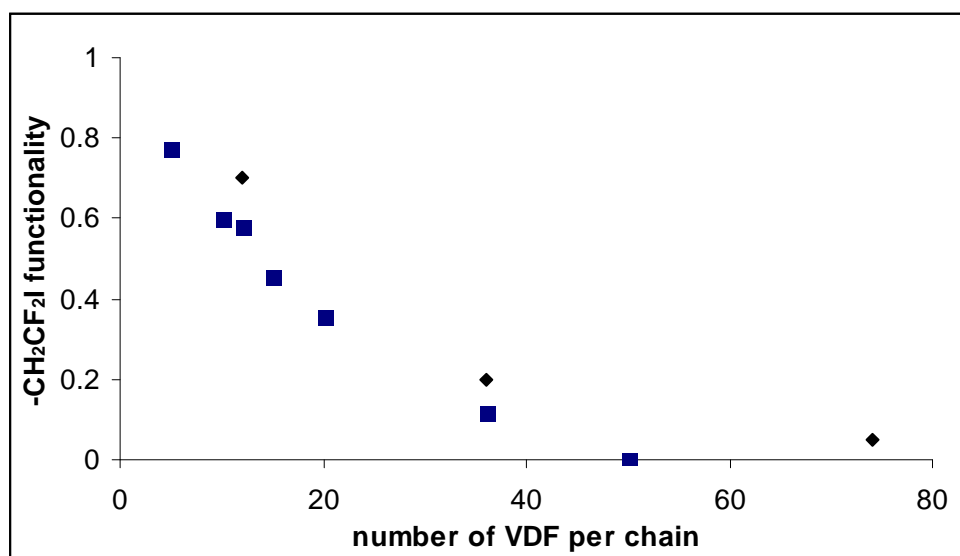
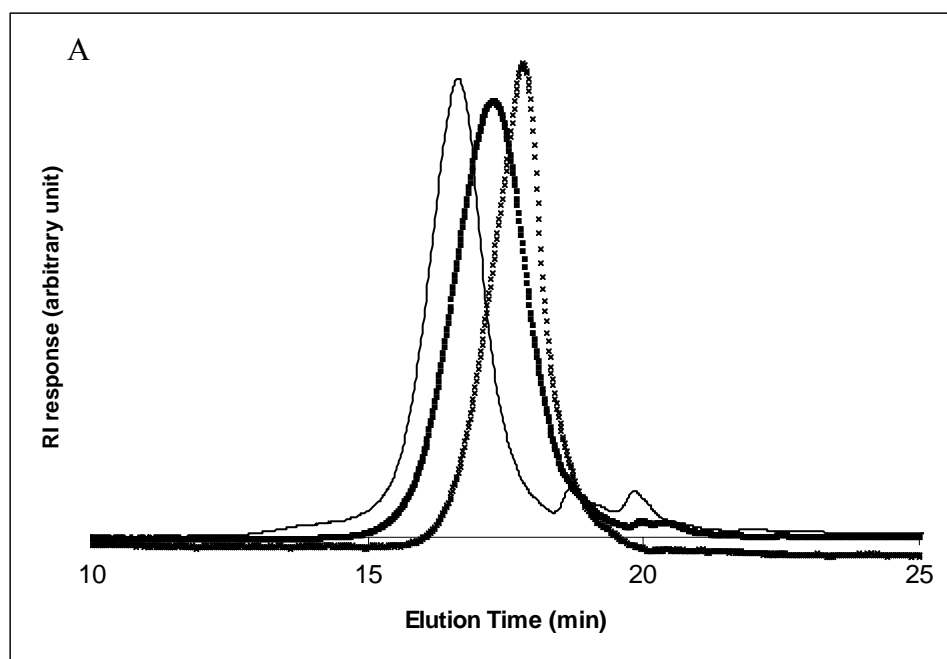


Figure 2. Evolution of $-\text{CH}_2\text{CF}_2\text{I}$ functionality *versus* the number of VDF units per chain for poly(VDF-*ter*-HFP-*ter*- $\text{CF}_2\text{CF}(\text{SF}_5)$) terpolymer (♦) and for PVDF-I homopolymer (■) obtained by iodine transfer polymerization of VDF in the presence of $\text{C}_6\text{F}_{13}\text{I}$ as the degenerative chain transfer agent, in the same following experimental conditions: $[\text{Initiator}]_0 /$

$[\text{VDF}+\text{HFP}+\text{SF}_5 \text{ monomer}]_0$ or $[\text{Initiator}]_0 / [\text{VDF}]_0 = 0.01$ in 1,1,1,3,3-pentafluorobutane at 75 °C for 6 hrs.

2.3. Influence of the CTA concentration onto the molecular weights of poly(VDF-*ter*-HFP-SF5M) terpolymers

Different reactions were carried out with the same VDF/HFP/CF₂CFSF₅ feed and in the presence of different $[\text{CTA}]_0/[\text{VDF}+\text{HFP}+\text{CF}_2\text{CF}(\text{SF}_5)]_0$ molar ratios, R_0 , ranging from 0.005 to 0.05. The molecular weights were assessed by SEC analysis (with a calibration made of polystyrene standards) and by ¹⁹F NMR. As expected, these samples are soluble in THF and their molecular weights can be characterized by SEC. Figure 3 exhibits different SEC traces of poly(VDF-*ter*-HFP-*ter*-CF₂CFSF₅) terpolymers versus different CTA concentrations.



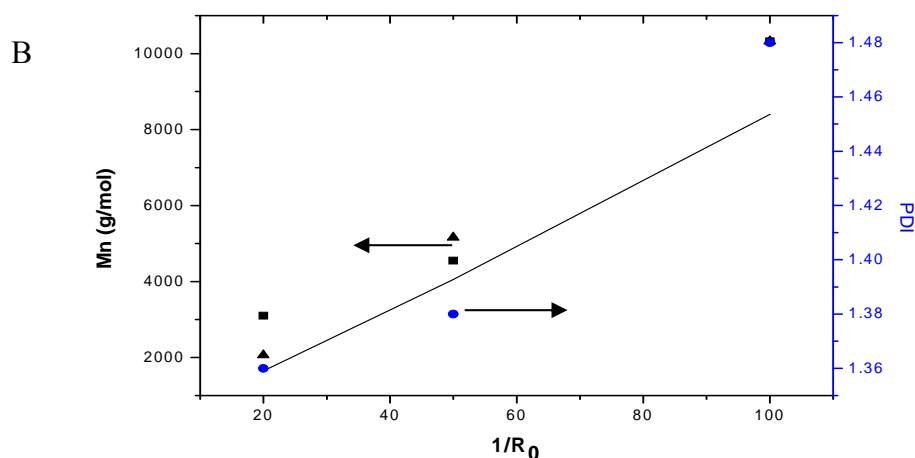
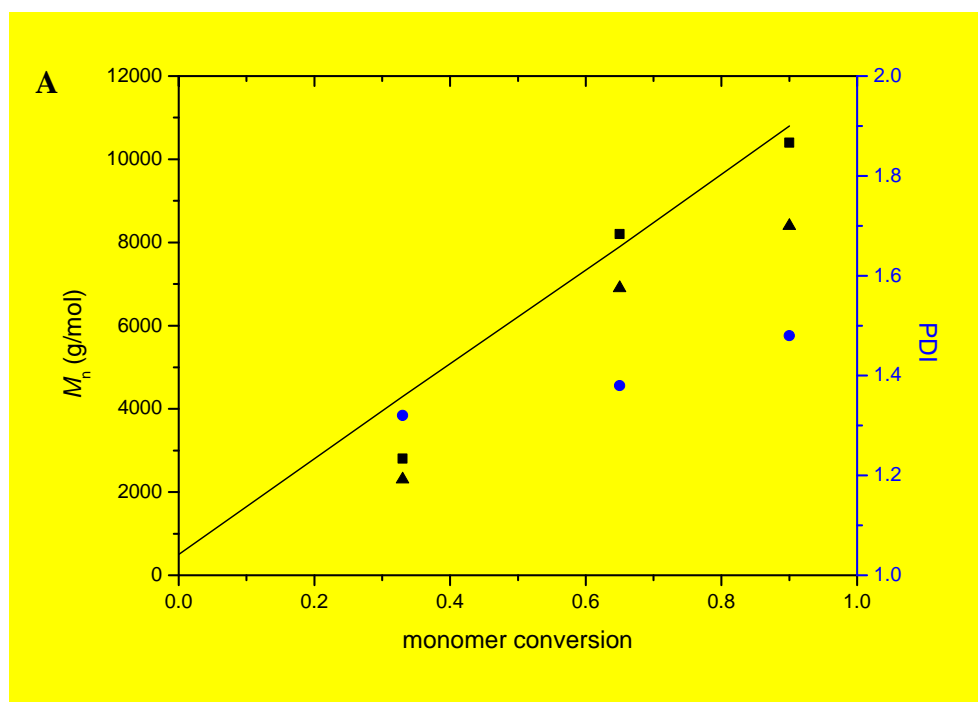


Figure 3. (A) SEC chromatograms of poly(VDF-*ter*-HFP-*ter*-SF₅-monomers) terpolymers obtained by iodine transfer polymerization of vinylidene fluoride, hexafluoropropylene and SF₅-monomers (xx) run 2 ($R_0 = 0.05$); (■) run 3 ($R_0 = 0.01$); (full line) run 4 ($R_0 = 0.005$), respectively. (B) Evolution of molecular weight (M_n , ■ and ▲ assessed by SEC and ¹⁹F NMR, and theoretical value (full line), respectively) and polydispersity index (PDI, ●) versus $1/R_0$ ($R_0 = [C_6F_{13}I]/[M]$ where M represent the monomer concentrations. Experimental conditions $[Initiator]_0 / [VDF+HFP+SF_5 \text{ monomer}]_0 = 0.01$ in the 1,1,1,3,3-pentafluorobutane at 75 °C for 6 hrs. The straight line is the theoretical curve.

Interestingly, whatever R_0 ratio, the experimental molecular weights are different (depending on the initial CTA concentration) and close to the theoretical values (Figure 3). The polydispersity index (PDI) values are relatively low, which indicates that the radical polymerization is controlled to some extent. Indeed, runs 2-4 led to PDI values of 1.36, 1.38 and 1.48, respectively, in contrast to run 1 (without any CTA) that yielded a terpolymer (PDI = 2.40). Thus, the C₆F₁₃I allows the control of the molecular weight in the presence of 1,1,2-trifluoro-2-pentafluorosulfanylene (CF₂=CF(SF₅)) with a suitable PDI value.

2.4. Evolution of the molecular weights and PDI versus monomer conversion.

Finally, the evolution of the molecular weights and of the polydispersity indexes (PDIs) versus the monomer conversion has been supplied for ITP (Figure 4). The molecular weights, as determined by SEC and by ^{19}F NMR, are in good agreement with the theoretical values. Interestingly, these molecular weights increase linearly versus the monomer conversion. PDI values are close to 1.3-1.5. The slight increase of PDI values during the polymerization can be attributed to the accumulation of the $-\text{CH}_2\text{I}$ end-group of the terpolymers due to the reverse addition of VDF and they are not able to reinitiate another chain (Figure 4-B, see Scheme S2 in the Supporting Information). Indeed, such terpolymers exhibit low transfer constant values (lower than 1) in contrast to those of the terpolymers containing a $-\text{CF}_2\text{I}$ end-group, which possess transfer constants higher than 7,^{29,51} which thus explains the increase of these PDI values. Nevertheless, it can be concluded that such a terpolymerization shows a controlled/"pseudoliving" behavior.



B

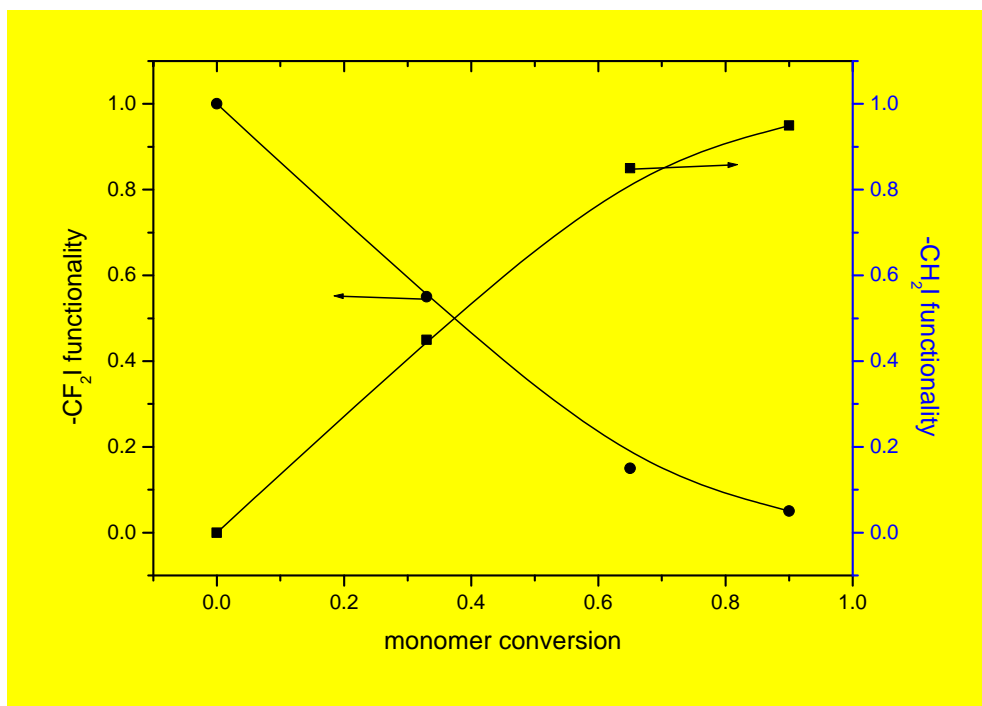


Figure 4. A- Evolution of molecular weights (▲ assessed by ¹⁹F NMR and (■) SEC, full line corresponds to theoretical value) and (●) PDI versus overall monomer conversion; B- evolution of (●) -CF₂I and (■) -CH₂I functionality versus monomer conversion.

3. Radical terpolymerization of VDF with HFP and H₂C=CHSF₅

The same above reaction was carried out in the presence of CH₂=CHSF₅ monomer instead of F₂C=CFSF₅ i.e. a similar initial molar feed of 74/17/9 was chosen for VDF/HFP/SF₅). During the course of the reaction, a slight drop of pressure (from 15 to 12 bars) was observed, which was assigned to the incorporation of the gaseous monomers into the terpolymers. After reaction and purification, the resulting terpolymer obtained in poor yield (10-20%) was characterized by ¹⁹F and ¹H NMR spectroscopy and by SEC.

Figure 5 displays the ¹⁹F NMR spectrum of poly(VDF-*ter*-SF₅-*ter*-HFP) terpolymer. First, the absence of -CF₂CF₂I signal centered at -60.0 ppm confirms the quantitative consumption of chain transfer agent (CTA). Also observed is the absence of the signals assigned to HFP units (absences of signals at -71, -75, -120 and -186 ppm), in the terpolymer and poor incorporation of VDF (the signal centered at -92.0 ppm has a small integral). Conversely to the previous monomer, the presence of the multiplet centered at -112.0 ppm was assigned to

$-\text{CF}_2-\text{CF}_2-\text{CH}_2-\text{CH}(\text{SF}_5)-$. However, the incorporation of SF_5 monomer has been confirmed by the multiplet ranging from +50 to +80 ppm characteristic of SF_5 group. It is interesting to observe that the functionality in $-\text{CH}_2\text{CF}_2\text{I}$ (signal centered at -40.0 ppm) worth 0.3, whereas the absence of $-\text{CF}_2\text{CH}_2\text{I}$ (centered at -109.0 ppm) confirms the absence of reverse addition of VDF during the polymerization. Thus, the terpolymers are terminated mainly by $-\text{CH}_2\text{CH}(\text{SF}_5)\text{I}$ though there are traces of $-\text{CH}=\text{CHSF}_5$.

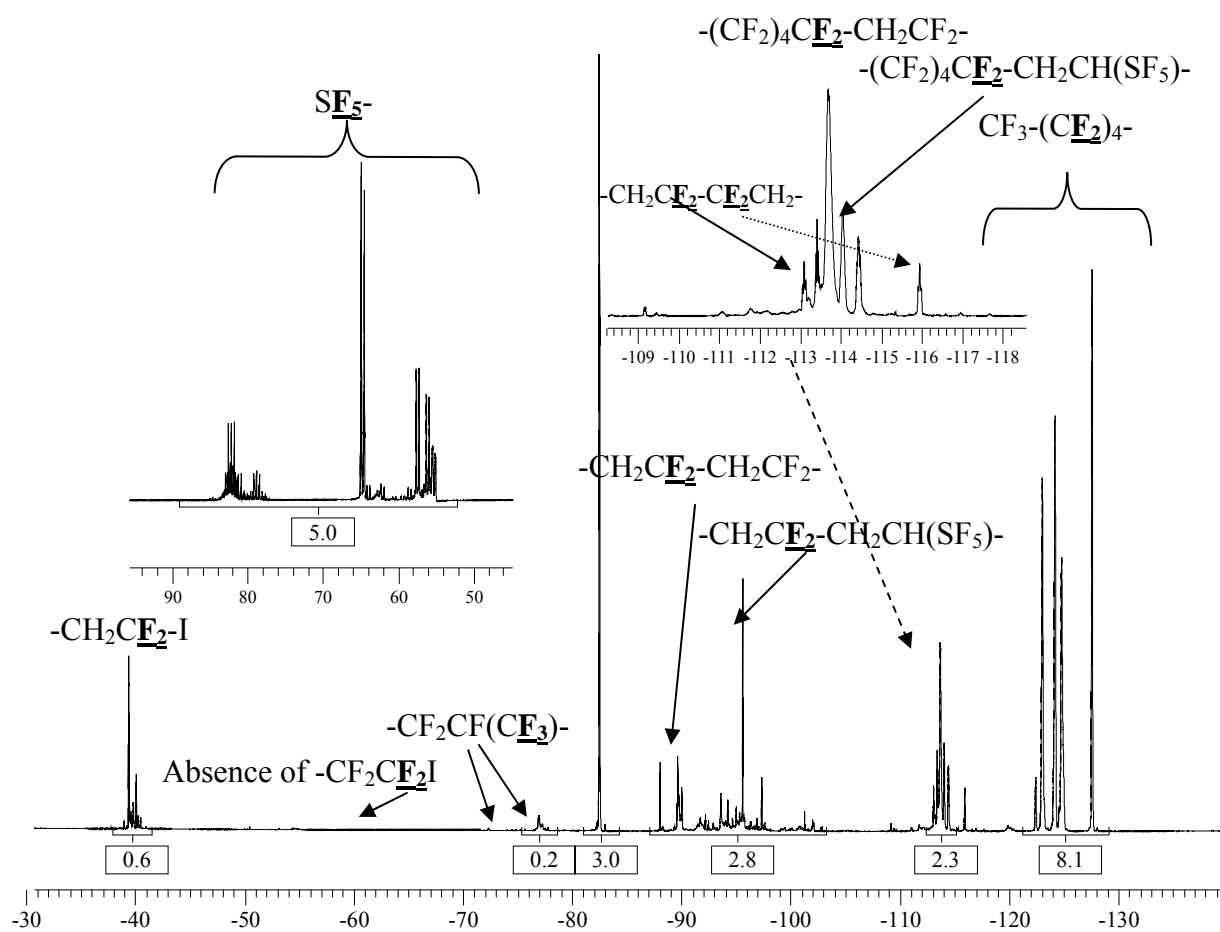


Figure 5. ^{19}F NMR spectrum of poly(VDF-*ter*-HFP-*ter*- CH_2CHSF_5) terpolymer obtained by iodine transfer polymerization in the presence of $\text{C}_6\text{F}_{13}\text{I}$ at 75 °C (molar feed VDF/HFP/ $\text{CH}_2\text{CH}(\text{SF}_5)$ = 74.0/18.0/8.0), $-\text{CH}_2\text{CF}_2\text{I}$ functionality = 0.30. (Recorded in d_6 acetone, at 293 K, 400 MHz). Experimental conditions: $[\text{C}_6\text{F}_{13}\text{I}]_0 / [\text{VDF}+\text{HFP}+\text{SF}_5 \text{ monomer}]_0 = 0.05$, $[\text{Initiator}]_0 / [\text{VDF}+\text{HFP}+\text{SF}_5 \text{ monomer}]_0 = 0.01$ in 1,1,1,3,3-pentafluorobutane at 75 °C for 6 hrs run #5 in Table1.

^1H NMR spectrum (Figure S7 in the Supporting Information) confirms this characterization by the presence of signals at 3.8 ppm and 4.4 ppm assigned to $-\text{CF}_2\text{CF}_2-$

$\text{C}\underline{\text{H}}_2\text{CH}(\text{SF}_5)\text{I}$ and $-\text{CH}_2\text{C}\underline{\text{H}}(\text{SF}_5)\text{I}$, respectively. Moreover, the low incorporation of VDF is confirmed by the low intensity of signal centered at 2.8-3.0 ppm. In contrast to the above case, it is noted the presence of $-\text{CF}_2\text{H}$ signal (6.3-6.5 ppm) arising from the transfer reaction to the polymer, the monomer or the solvent. If we compare this result with those obtained when $\text{CF}_2=\text{CF}\text{SF}_5$ was involved in the terpolymerization, $\text{CH}_2=\text{CH}\text{SF}_5$ monomer exhibits a higher transfer. Moreover, the presence of signal at 5.8-6.0 ppm can be attributed to the formation of $-\text{C}\underline{\text{H}}=\text{CH}(\text{SF}_5)$ species obtained by dehydroiodination of $-\text{CH}_2-\text{CH}(\text{SF}_5)-\text{I}$. Indeed, it can be assumed that the highly electronegative SF_5 induces the easiness of iodine living group.

In conclusion of this NMR study, we observe for the terpolymerization of VDF, HFP and $\text{H}_2\text{C}=\text{CH}\text{SF}_5$ the formation of an alternate structure, i.e. $\text{C}_6\text{F}_{13}-[\text{CH}_2\text{CF}_2-\text{CH}_2\text{CH}(\text{SF}_5)]_n-\text{I}$, of low molecular weight. This assumption was confirmed by the absence of signal centered at -92.0 ppm (assigned to the normal VDF addition $-\text{CH}_2\underline{\text{C}}\text{F}_2-\text{CH}_2\underline{\text{C}}\text{F}_2-$) attributed to VDF and the absence of $(-\text{C}\underline{\text{H}}_2\underline{\text{C}}\text{F}_2-\text{C}\underline{\text{H}}_2\underline{\text{C}}\text{F}_2-)$ in ^1H NMR is in good agreement with this assumption.

SEC analysis shows that the terpolymer obtained exhibits a low molecular weight and low polydispersity index ($M_n = 600$ g/mol and $\text{PDI} = 1.2$ (Table 1)). The experimental and targeted molecular weights are not in agreement (M_n , targeted = 2,000 g/mol and 5,000 g/mol). The same result was obtained when using different CTA concentrations. The major obtained product corresponds to the monoaddition of $\text{C}_6\text{F}_{13}\text{I}$ onto $\text{CH}_2=\text{CH}\text{SF}_5$ (to leading to $\text{C}_6\text{F}_{13}-\text{CH}_2\text{CH}(\text{SF}_5)-\text{I}$). The C-I bond of this product (i.e., $\text{C}_6\text{F}_{13}-\text{CH}_2\text{CH}(\text{SF}_5)-\text{I}$) appears to be very stable and do not react (and hence does not lead to any transfer).

In conclusion, pentafluorosulfanylene can not be terpolymerized in the presence of VDF and HFP by iodine transfer polymerization in suitable yields as for $\text{F}_2\text{C}=\text{CF}\text{SF}_5$. Indeed, after radical addition of $-\text{CF}_2\text{I}$ onto $\text{CH}_2\text{CH}(\text{SF}_5)$, the produced species $-\text{CF}_2-\text{CH}_2\text{CH}(\text{SF}_5)-\text{I}$ exhibits a low transfer constant and can not be used as a further macrotransfer agent.

4. Thermal properties.

The thermal properties of poly(VDF-*ter*-HFP-*ter*- $\text{F}_2\text{C}=\text{CF}\text{SF}_5$) and poly(VDF-*ter*-HFP-*ter*- $\text{H}_2\text{C}=\text{CH}\text{SF}_5$) terpolymers were assessed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

The TGA thermograms (Figure 6) show that even for low molecular-weight terpolymers, the poly(VDF-*ter*-HFP-*ter*- $\text{CF}_2\text{CF}(\text{SF}_5)$) terpolymers exhibit good thermal stability since their

decomposition started from 250 to 300°C. If one compares these results with those obtained from the copolymers obtained by conventional radical polymerization, poly(VDF-*ter*-HFP-*ter*-CF₂CF(SF₅)) present a **better** thermostability. Moreover, as expected, the thermal stability of this poly(VDF-*ter*-HFP-*ter*-CF₂CF(SF₅)) increases with the molecular weight (Figure 6B). In contrast, poly(VDF-*ter*-HFP-*ter*-CH₂CH(SF₅)) terpolymers exhibits a **poor thermostability** ($T_{dec} = 130-140$ °C, note T_{dec} corresponds to decomposition temperature, i.e. 10% of weight loss). Such a statement may be explained by the evaporation of the terpolymer before its degradation and may arise from the low molecular weight obtained. **Hence**, terpolymers based on hydrogenated SF₅ comonomer exhibit lower molecular weights and hence undergo **an easier** evaporation before degradation.

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 4. The T_g values of poly(VDF-*ter*-HFP-*ter*-CF₂CF(SF₅)) terpolymers were ranging from -50 to -40 °C without any other transitions (melting transition), showing an amorphous behavior and **potential use for elastomer applications**. As expected, T_g values increase *versus* molecular weights (Figure 6B) of the terpolymers and are close to T_g previously obtained (Table 4). With such T_g values, and as reported in the literature, it is known that fluoropolymers, containing VDF and HFP base units only, exhibit an average T_g of -26 °C for high M_n . The comparison of this result to those obtained with a low CTA concentration indicates that the addition of SF₅ group leads to a decrease the T_g value (decrease of ca. -20 °C).

INSERT TABLE 4

A- TGA thermograms of terpolymers.

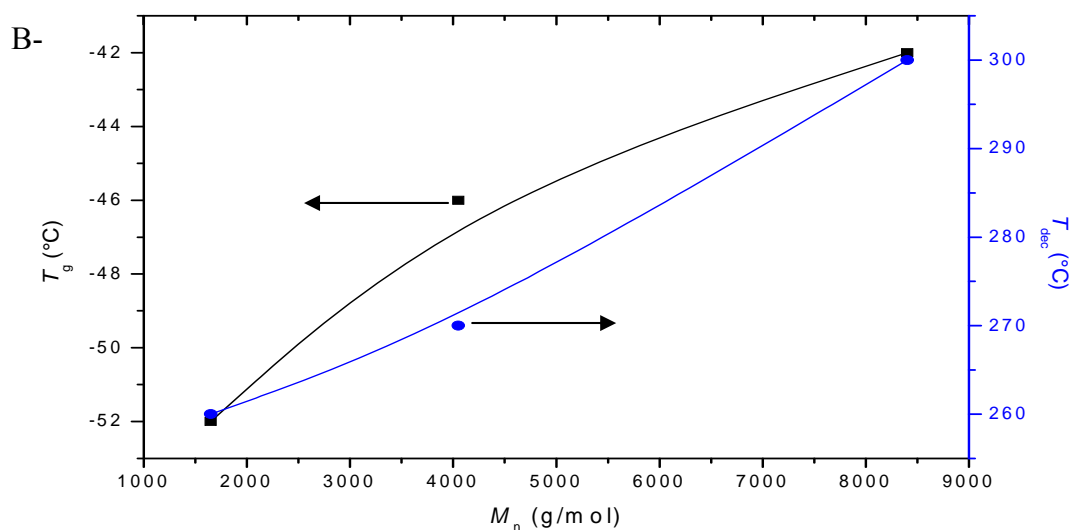
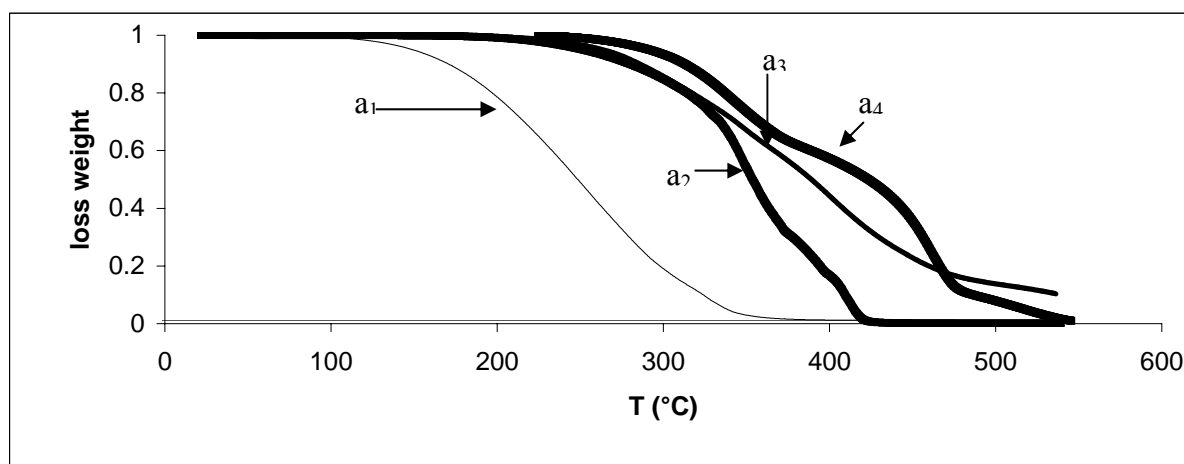


Figure 6. Thermal properties of poly(VDF-ter-HFP-ter-SF₅-monomer) terpolymers.

A- TGA thermograms of poly(VDF-ter-HFP-ter-SF₅-monomer) terpolymers, under air (10 °C/min); a₁ represents the poly(VDF-ter-HFP-ter-CH₂CH(SF₅)) (M_n = 600 g/mol, run 5, Table 1), while a₂, a₃ and a₄ correspond to poly(VDF-ter-HFP-ter-CF₂CF₂SF₅) terpolymers with M_n = 1650 (run 2, Table 1), 4050 (run 3, Table 1) and 8400 g/mol (run 4, Table 1), respectively.

B- Glass transition (T_g) and decomposition (T_{dec}) temperature values of poly(VDF-ter-HFP-ter-CH₂CHSF₅) terpolymers versus their molecular weights.

CONCLUSION

Monomers bearing a pentafluorosulfanyl group (i.e. 1,1,2-trifluoro-2-pentafluorosulfanylethylene and pentafluorosulfanylethylene) were utilized in the attempted radical terpolymerization of hexafluoropropylene (HFP) and vinylidene fluoride (VDF) by iodine transfer polymerization in the presence of 1-iodoperfluorohexane. Under the same conditions, different behaviors were observed for both SF₅ monomers. Interestingly, when using CF₂=CFSF₅, a controlled radical terpolymerization was observed as evidenced by the good control of the molecular weights, i.e. the experimental molecular weights were in good agreement with the targeted ones for the first time and in good yields (80-90%). These terpolymers contain two chain-ends (well-characterized by ¹⁹F NMR), i.e. -CH₂CF₂I and -CF₂CH₂I, while the other chain-ends (i.e. -CF₂CF(SF₅)I, -CF(SF₅)CF₂I, -CF₂CF(CF₃)I and -CF(CF₃)CF₂I) were not produced. Moreover, the functionality in -CH₂CF₂I decreases *versus* the number of VDF units, but this functionality of terpolymer remains higher than that noted for poly(VDF)-I. Indeed, VDF, HFP and F₂C=CFSF₅ were incorporated in the terpolymer by ITP in the same proportion as that observed by conventional radical polymerization. Thus, this monomer could be terpolymerized by ITP successfully. Various poly(VDF-ter-HFP-ter-SF₅M) terpolymers were produced, the thermal stability (T_g and T_{dec}) of which depend on their molecular weights. Their T_gs values, in the range of -52 to -42 °C, show that these terpolymers are original elastomers stable up to 250-300 °C. On the other hand, the latter monomer, pentafluorosulfanylethylene, behaved differently, since it does not terpolymerize under ITP conditions, the yields being poor (ca.10-20%). Furthermore, experimental and targeted molecular weights were far from each other and confirm the poor control of this terpolymerization. In addition, C₆F₁₃CH₂CHISF₅ monoadduct produced as a by-product, and could not re-initiate a further the terpolymerization. This could arise from a C-I bond that is not labile enough to enable a transfer in the radical polymerization but was not able to undergo a dehydroiodination to lead to C₆F₁₃-CH₂=CHSF₅. Furthermore, the formation of terpolymers bearing -CF₂H end-group attributed to a transfer reaction also induced a lack of control of the terpolymerization and favored short chain lengths. Further work is in progress regarding the synthesis of block copolymers based on F₂C=CFSF₅ monomer.

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Supporting Information Available. Additional data in the experimental section (schemes of ITP mechanism, ^1H and ^{19}F NMRs of poly(VDF)-I and poly(VDF-ter-HFP-ter-SF₅M) terpolymers, DSC curves, and Tables of ^1H and ^{19}F NMR assignments of poly(VDF-ter-HFP-SF₅M) terpolymers. This material is available free of charge via internet at <http://pubs.acs.org>.

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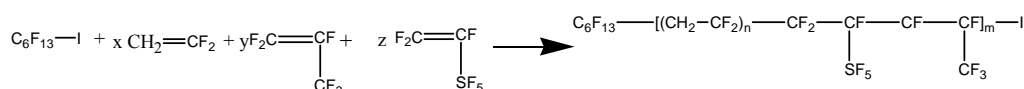
Radical terpolymerization of 1,1,2-trifluoro-2-pentafluorosulfanylethylene and pentafluorosulfanylethylene in the presence of Vinylidene Fluoride and Hexafluoropropylene by Iodine Transfer Polymerization.

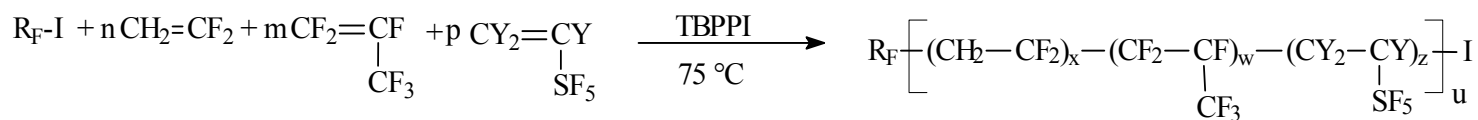
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Scheme. Radical terpolymerization of 1,1-difluoroethylene (VDF), hexafluoropropylene (HFP) and SF₅-containing monomers, i.e. 1,1,2-trifluoro-2-pentafluorosulfanylene and pentafluorosulfanylene in the presence of 1-iodoperfluorohexane (C₆F₁₃I) by iodine transfer polymerization (ITP).

Y represents either a hydrogen or a fluorine atom, and TBPPI stands for tert-butyl peroxyvalate.

Table 1. Assessment of the compositions of comonomers in the poly(VDF-ter-HFP-ter-SF₅M) terpolymers, from eq.(1)-(6), *versus* different radical terpolymerizations of vinylidene fluoride (VDF), hexafluoropropylene (HFP) and SF₅-monomers in the presence of C₆F₁₃I as the chain transfer agent at 75 °C for 6hrs.

Runs	R ₀	Feed (mol %)			Composition (mol %)			M _n theoretical	M _n (SEC) ^d	PDI ^b	M _n ¹⁹ F NMR	yield
		VDF	HFP	SF ₅	VDF	HFP	SF ₅	(g/mol)	(g/mol)		(g/mol)	(%)
1	- ^a	73.1	18.3	8.6	78.3	16.4	5.5	-	10 000	2.40	-	80
2 ^b	0.05	74.2	17.8	8.0	83.3	12.2	4.8	2060	2100	1.36	1650	85
3 ^b	0.02	74.5	18.5	7.0	80.5	16.1	3.4	5160	4550	1.38	4050	90
4 ^b	0.01	75.6	17.2	7.2	80.2	15.0	4.8	10320	10400	1.48	8400	90
5 ^c	0.05	74.0	18.0	8.0	61.8	2.0	36.2	2000	600	1.32	260	12
6 ^c	0.01	75.0	17.5	7.5	58.9	1.1	40.0	5100	600	1.35	300	5

Note: a- without any chain transfer agent; b- with F₂C=CF₃ as the comonomer; c- with H₂C=CHSF₅ as the comonomer; d- assessed from SEC using THF as the solvent with polystyrene standards.

Table 2. Chemical shifts of different compounds bearing C-I bond according the substituents.

Monomers	Compounds	δ (^{19}F NMR) (ppm)	δ (^1H NMR) (ppm)	Ref.
TFE	-CF ₂ -CF(F)I	-60.0	-	67,71
Tetrafluoroethylene	-CF ₂ -CF(F)I	-60.0	-	
TrFE	-CF ₂ -CF(H)I	-167.7	7.2	71
Trifluoroethylene	-CF(H)-CF ₂ I	-54.5	5.1	
VDF	-CH ₂ -CF(F)I	-40.0 (-39) ^a	3.6	59
1,1-Difluoroethylene	-CF ₂ -CH ₂ I	-109.0	3.8	
CTFE	-CF(Cl)-CF ₂ I	-55.0	-	68
Chlorotrifluoroethylene	-CF ₂ -CF(Cl)I	-72.4	-	
HFP	-CF ₂ -CF(CF ₃)I	-145.0	-	70
Hexafluoropropene	-CF(CF ₃)-CF ₂ I	-60.0	-	
PMVE	-CF(OCF ₃)-CF ₂ I	-60.0	-	73
Perfluoromethylvinylether	-CF ₂ -CF(OCF ₃)I	-73.0	-	
F ₂ C=CFSF ₅	-CF(SF ₅)-CF ₂ I	-63.8	-	21,72
1,1,2-trifluoro-2-pentafluorosulfanylethylene	-CF ₂ -CF(SF ₅) I	-58.8	-	
H ₂ C=CHSF ₅	-CH(SF ₅)-CH ₂ I	-	3.6	21
Pentafluorosulfanylethylene	-CH ₂ -CH(SF ₅)I	-	4.4	

Table 3. Results of the functionality obtained by iodine transfer terpolymerization of VDF, HFP and SF₅-monomers.

Runs	R ₀	Feed (mol %)			<i>functionality</i>			
		VDF	HFP	SF ₅	-CH ₂ CF ₂ I	-CF ₂ CH ₂ I	-CY(SF ₅)CY ₂ I	-CY ₂ CY(SF ₅)I
1 ^a	-	73.1	18.3	8.6	-	-	-	-
2 ^b	0.05	74.2	17.8	8.0	0.70	0.30	0	0
3 ^b	0.02	74.5	18.5	7.0	0.20	0.80	0	0
4 ^b	0.01	75.6	17.2	7.2	0.05	0.95	0	0
5 ^c	0.05	74.0	18.0	8.0	0.30	0	0	0.70
6 ^c	0.01	75.0	17.5	7.5	0.25	0	0	0.65

Note: a- without any chain transfer agent; b- with F₂C=CFSF₅ as the comonomer; c- with H₂C=CHSF₅ as the comonomer.

Table 4. Thermal properties of poly(VDF-ter-HFP-ter-SF₅ monomer) obtained by iodine transfer terpolymerization.

Runs	R ₀	M _n ^d (g/mol)	Thermal properties	
			T _g (°C)	T _{dec} (°C)
1 ^a	-	10 000	-50	280
2 ^b	0.05	1650	-52	260
3 ^b	0.02	4050	-46	270
4 ^b	0.01	8400	-42	300
5 ^c	0.05	260	-70 ^e	120
6 ^c	0.01	300	nd	130

Note: a- without any chain transfer agent; b- with F₂C=CFSF₅ as the comonomer; c- with H₂C=CHSF₅ as the comonomer, d- determined by ¹⁹F NMR, e- this T_g value is not characteristic because it corresponds to T_g of a very low molecular weight.