

# Original SF<sub>5</sub>-Containing Fluorinated Copolymers Based on Vinylidene Fluoride

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**ABSTRACT:** The radical co- and terpolymerization of fluorinated monomers bearing an SF<sub>5</sub> group, XYC=CZSF<sub>5</sub> (where X, Y, and Z represent either H or F atoms) with 1,1-difluoroethylene (vinylidene fluoride, VDF or VF<sub>2</sub>) and hexafluoropropene (HFP), is presented. Although these SF<sub>5</sub> 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 SF<sub>5</sub> side groups. NMR characterizations and yields enabled one to compare the relative reactivities of F<sub>2</sub>C=CFSF<sub>5</sub>, 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 SF<sub>5</sub> monomers had an influence on their reactivity, on their relative incorporation in the copolymers, and on the molar masses of the resulting terpolymers—the higher the fluorine in the SF<sub>5</sub> monomer, the higher molecular weight. Interestingly, the greater the degree of fluorine substitution of the SF<sub>5</sub>-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 <sup>19</sup>F and <sup>1</sup>H NMR spectroscopy. The thermal properties (thermal stability and glass transition temperature) of these resulting SF<sub>5</sub>-containing fluoropolymers were also examined.

## Introduction

Fluoropolymers are of great interest because of their unique combination of outstanding properties<sup>1</sup> 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: aeronautics,<sup>2</sup> microelectronics, engineering, chemical, and automotive industries, optics,<sup>3</sup> textile finishing,<sup>4</sup> and military use.<sup>5</sup> 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., poly(vinylidene fluoride), poly(tetrafluoroethylene), 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 cross-linking.

Among these fluorinated copolymers, those incorporating vinylidene fluoride (VDF) monomeric units are of particular interest, because they can be either thermoplastics<sup>6</sup> or elastomers<sup>7</sup> or thermoplastic elastomers.<sup>14,8</sup>

Usually, such fluoropolymers can be synthesized by radical copolymerization of VDF with other fluoroalkenes leading to statistical copolymers<sup>7,9</sup> except for copolymers prepared from hexafluoroisobutylene<sup>10</sup> (commercialized by the Allied Company under the CMX trade mark), methyl trifluoroacrylate,<sup>11</sup> and  $\alpha$ -trifluoromethyl acrylic acid,<sup>12</sup> which are unexpected alternating copolymers. In fact, VDF has been copolymerized with various fluorinated monomers with the resulting copolymers bearing functions such as: hydroxy,<sup>13</sup> acetoxy,<sup>13,14</sup> thioacetoxy,<sup>15</sup> sulfonyl fluoride,<sup>16</sup> nitrile,<sup>17</sup> bromine,<sup>18</sup> or a perfluoroalkyl group.<sup>19</sup>

Interestingly, monomers bearing the SF<sub>5</sub> 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 coatings.<sup>20–23</sup> Recent studies have prepared not only SF<sub>5</sub>-polyfluoroalkylacrylates,<sup>24</sup> SF<sub>5</sub>-polyfluoroalkylsiloxanes,<sup>25</sup> SF<sub>5</sub>-polyfluoroalkylepoxides<sup>26</sup> but also aromatic polymers that include polyimides containing the SF<sub>5</sub>(CF<sub>2</sub>)<sub>n</sub>C<sub>6</sub>H<sub>3</sub>— groups ( $n = 0, 2$ ),<sup>26,27</sup> polyacrylate, and polystyrene containing the SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>— group.<sup>28</sup> Additional properties brought about by the SF<sub>5</sub> group include low wettability, low refractive index, low surface energy, high dielectric strength, and high chemical and thermal stability. The use of SF<sub>5</sub> monomers has resulted in the preparation of the first organic superconductor with an organic anion,<sup>29</sup> the first SF<sub>5</sub>—organic metals/organic semiconductors,<sup>30</sup> the first SF<sub>5</sub>-containing ionic liquids,<sup>31</sup> and the preparation of novel liquid crystals.<sup>32</sup>

Different SF<sub>5</sub>-containing copolymers (acrylates, silicons, epoxides) exhibit nonstoichiometric enrichment of the film surface with fluorinated monomers bearing SF<sub>5</sub> groups.

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Prior to our studies, in 1969 and 1974 Banks et al.<sup>33,34</sup> reported the preparation of SF<sub>5</sub>-containing polymers with VDF and HFP in emulsion using an aqueous redox initiation system and perfluorooctanoic acid. However, no data were supplied about the copolymer compositions. In addition, the microstructure, the molecular weight, and  $T_g$  values of copolymers obtained were not described. We considered it to be worthwhile to revisit that copolymerization system and to provide characterization of the binary and ternary systems with different SF<sub>5</sub> comonomers (hydrogenated and perfluorinated).

Hence, the objective of this paper deals with the radical binary and terpolymerization of different SF<sub>5</sub> containing monomers, their reactivity with VDF and HFP, and the detailed characterization of the copolymers obtained.

## Experimental Section

**Materials.** Vinylidene fluoride (VDF), hexafluoropropene (HFP), and 1,1,1,3,3-pentafluorobutane were kindly provided by Solvay Solexis S.A., Tavaux, France, and Brussels, Belgium, di-*tert*-butyl peroxide (DTBP) was obtained from Aldrich Chimie, 38299 Saint Quentin-Fallavier, France, and triethylborane and 2-propanol were from Aldrich, Milwaukee, WI. They were used as supplied. Acetonitrile, dimethyl sulfoxide, ClSF<sub>5</sub>, BrSF<sub>5</sub> from Air Products, and methylene chloride of analytical grade (Aldrich Chimie) were distilled over calcium hydride prior to use.

**Analysis.** The compositions of the co- and terpolymers (the molar contents of VDF, HFP, and SF<sub>5</sub>-containing monomers) were determined by <sup>19</sup>F and <sup>1</sup>H NMR spectroscopy. The NMR spectra were recorded on Bruker AC 200 and AC 250 instruments, using deuterated acetone as the solvent and TMS (or CFCl<sub>3</sub>) as the references for <sup>1</sup>H (or <sup>19</sup>F) nuclei. Coupling constants and chemical shifts are given in hertz and parts per million, respectively. The experimental conditions for <sup>1</sup>H (or <sup>19</sup>F) NMR spectra were as follows: flip angle 90° (or 30°), acquisition time 4.5 s (or 0.7 s), pulse delay 2 s (or 5 s), number of scans 16 (or 64), and a pulse width of 5 μs for <sup>19</sup>F NMR.

Differential scanning calorimetry (DSC) measurements were conducted using a Perkin-Elmer Pyris 1 instrument connected to a microcomputer. The apparatus was calibrated with indium and *n*-decane. After its insertion into the DSC apparatus, the sample was initially cooled to -105 °C for 15 min. Then, the first scan was made at a heating rate of 40 °C·min<sup>-1</sup> up to 80 °C, where it remained for 2 min. It was then cooled to -105 °C at a rate of 320 °C·min<sup>-1</sup> and left for 10 min at that temperature before a second scan was started at a heating rate of 20 °C·min<sup>-1</sup>. Finally, another cycle was performed and a third scan at a heating rate of 20 °C·min<sup>-1</sup> 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 °C·min<sup>-1</sup> from room temperature up to a maximum of 600 °C.

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

**Synthesis of SF<sub>5</sub>-Containing Monomers. 1-Chloro-2-pentafluorosulfanyleneethane (ClCH<sub>2</sub>CH<sub>2</sub>SF<sub>5</sub>).** 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 5 min, after which 3.2 g (0.020 mol) of SF<sub>5</sub>Cl 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 min. 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 2.5 g (yield: 65%) of a residue that was essentially pure 1-chloro-2-pentafluorosulfanyleneethane, which was used directly in the next reaction: bp 92–93 °C; <sup>1</sup>H NMR δ 4.15–3.85 (m); <sup>19</sup>F NMR δ 81.57 (q, 1F), 64.92 (d, 4F). Another batch was carried out to get further amount with a quasi-reproducible result.

**Pentafluorosulfanyleneethene, M-I (H<sub>2</sub>C=CHSF<sub>5</sub>).** To 3.5 g of KOH in 4 mL of water was added 10.5 mL of 2-propanol 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 (0.024 mol) of the 1-chloro-2-pentafluorosulfanyleneethane 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: <sup>1</sup>H NMR δ 5.74 (m, 1H), 6.01 (d,  $J$  = 15 Hz, 1H), 6.68 (m, 1H); <sup>19</sup>F NMR AB<sub>4</sub> system, δ 81.5 (pent, 1F) and 59.7 (d, 4F),  $J_{AB}$  = 146 Hz.<sup>35</sup>

**1-Chloro-1,1-difluoro-2-pentafluorosulfanyleneethane (ClCF<sub>2</sub>CH<sub>2</sub>SF<sub>5</sub>).** To a 50 mL three-necked flask bearing a dry ice condenser and cooled to -50 °C was condensed 20 mL of ClCF<sub>2</sub>CH<sub>3</sub> (Forane 142b) and 4.4 g (4 equiv) of CF<sub>2</sub>=CH<sub>2</sub> (VDF). To this mixture was added 2.7 g (0.017 mol) of SF<sub>5</sub>Cl. Then 1.5 mL of Et<sub>3</sub>B was added to the mixture dropwise, and the mixture was stirred at -20 to -30 °C for 3 h, after which the flask was stoppered and allowed to stand at -20 °C for 3 days. Then the fluorinated solvent was evaporated, leaving 1.5 g (40% yield) of almost pure product, 1-chloro-1,1-difluoro-2-pentafluorosulfanyleneethane, which was used directly in the next reaction: bp 70 °C; <sup>1</sup>H NMR δ 4.4–4.2 (m); <sup>19</sup>F NMR δ 77.04 (q, 1F), 70.06 (d, 4F), -55.35 (s, 2F).

**1,1-Difluoro-2-pentafluorosulfanyleneethene, M-II (F<sub>2</sub>C=CHSF<sub>5</sub>).** 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 wt %). 1-Chloro-1,1-difluoro-2-pentafluorosulfanyleneethane (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 h with simultaneous collection of the product **M-II** in a cold trap, 2.1 g (13 mmol, 70% yield): bp 26 °C; <sup>1</sup>H NMR δ 5.7 (m); <sup>19</sup>F NMR δ 78.89 (m, 1F, SF<sub>5</sub>), 72.78 (d, 4F, SF<sub>5</sub>), -65.80 (m, 1F), -83.96 (m, 1F).<sup>36–38</sup>

**1,1,2-Trifluoro-2-pentafluorosulfanyleneethene, SF<sub>5</sub>CF=CF<sub>2</sub> (M-III).** **M-III** was prepared from SF<sub>5</sub>CHFCF<sub>2</sub>Br as described in the literature.<sup>38</sup> The purity of the starting material was checked via IR and NMR spectroscopy.

IR (cm<sup>-1</sup>): 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<sup>-1</sup> are due to S–F stretching while that at 613 cm<sup>-1</sup> is due to one of the SF<sub>5</sub> deformation modes.

<sup>19</sup>F NMR (CDCl<sub>3</sub>, CFCl<sub>3</sub>): 69.7 (nine-line pattern, 1F, SF<sub>5</sub>); 59.0 (d, 4F, SF<sub>5</sub>); -163 (m, 1F, CF=); -99.5 (m, 2F, =CF<sub>2</sub>).

**Copolymerization.** The batch copolymerizations of VDF with CF<sub>2</sub>=CFRf (Rf stands for CF<sub>3</sub>, OCF<sub>3</sub>, or SF<sub>5</sub>) were performed in thick borosilicate Carius tubes (length 130 mm, 10 mm i.d., thickness 2.5 mm; for a total volume of 8 cm<sup>3</sup>). 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 mmHg. To introduce the targeted VDF quantities, a previous calibration was made to link the gas pressure (bar) 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 h was chosen for carrying out the

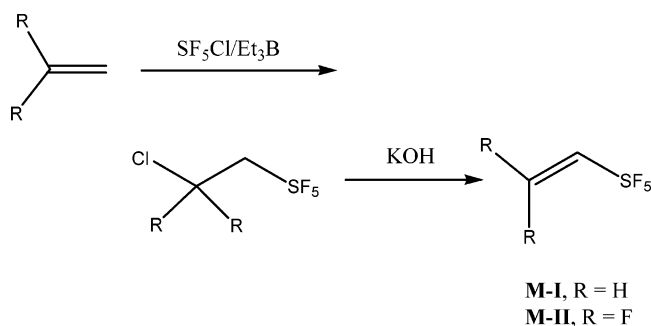
process of radical copolymerization). After reaction, the total product mixture was analyzed by  $^{19}\text{F}$  NMR and  $^1\text{H}$  NMR. Then, the copolymers were precipitated from cold pentane and dried until constant weight was reached.

Batch terpolymerizations of VDF with HFP and the  $\text{SF}_5$ -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 bar of nitrogen pressure and left closed for 20 min to test for leakage. After the pressure was released, a 20 mmHg vacuum was operated for 15 min, and then the initiator di-*tert*-butyl peroxide,  $\text{SF}_5$  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 h. After reaction, the vessel was cooled to room temperature and then put in an ice bath. The nonreacted monomers were released (from gaseous reactants) or separated and the conversion vs monomers was determined. Then, the solvent was evaporated, the terpolymer was precipitated from cold pentane, and the total product mixture was dried at 0.1 mmHg at 40 °C for 15 h (to constant weight).

Highly viscous or rubber-like polymers were obtained.

## Results and Discussion

**I. Synthesis of Monomers Containing  $\text{SF}_5$  ( $\text{SF}_5\text{M}$ ).** Monomers **M-I** and **M-II** were prepared in a manner similar to those described in the literature, but using our new  $\text{Et}_3\text{B}$ -initiation methodology<sup>39</sup> to add  $\text{SF}_5\text{-Cl}$  to ethylene and VDF, respectively.



The reaction of  $\text{SF}_5\text{Cl}$  with ethylene proceeded smoothly in dichloromethane at  $-30^\circ$  to  $-20^\circ\text{C}$  over 2 h furnishing 1-chloro-2-pentafluorosulfanylene in good yield, but the synthesis of 1-chloro-1,1-difluoro-2-pentafluorosulfanylene proved to be more difficult. As pointed out by Case et al.,<sup>40</sup> reactions of  $\text{SF}_5\text{Cl}$  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  $\text{SF}_5\text{Cl}$  in dichloromethane or pentane. On the other hand, when the reaction was carried out in  $\text{ClCF}_2\text{CH}_3$  (Forane 142B) as a solvent, it was possible to increase the yield up to 70–80%. Neat  $\text{Et}_3\text{B}$  instead of its 1 M solution in hexane was used for these reactions, which allowed us to avoid a step of solvent removal. Since the boiling point of  $\text{ClCF}_2\text{CH}_3$  is only  $-10^\circ\text{C}$ , essentially pure products were obtained by simply warming the reaction to room temperature. These chloro, pentafluorosulfanylene intermediates were used in the next step without further purification.

For the synthesis of pentafluorosulfonyl ethylene **M-I**, a method developed by Wessel et al.<sup>35</sup> was adopted. Treatment of the chloro precursor with  $\text{KOH}/\text{H}_2\text{O}/i\text{-PrOH}$  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-pentafluorosulfanylene.<sup>37</sup> 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%  $\text{KOH}$  solution.

**M-III** monomer ( $\text{F}_2\text{C}=\text{CFSF}_5$ ) was obtained from the radical addition of  $\text{BrSF}_5$  onto trifluoroethylene followed by a dehydrobromination as reported in a previous work.<sup>38,39</sup>

**II. Radical Copolymerization of  $\text{SF}_5$ -Containing Monomers with VDF and HFP. II.1. Radical Copolymerization of  $\text{F}_2\text{C}=\text{CFSF}_5$  with VDF.** Initially, the radical homopolymerization of  $\text{F}_2\text{C}=\text{CFSF}_5$  was attempted under classic conditions of homopolymerization starting from a di-*tert*-butyl peroxide  $[\text{DTBP}]_0$  to  $[\text{F}_2\text{C}=\text{CFSF}_5]_0$  molar ratio of 2 mol %, 5.0 g (0.024 mol) of  $\text{CF}_2=\text{CFSF}_5$ , solvent 1,1,1,3,3-pentafluorobutane (70 wt %), temperature 143 °C, and reaction time 5 h. It was noted that no reaction occurred, probably because of the bulky  $\text{SF}_5$  substituent which, as in the case of HFP, PPVE, PMVE, or PFP (1,1,3,3,3-pentafluoropropene) prevents these fluoromonomers from undergoing homopolymerizations.

Then, the radical copolymerization of VDF with  $\text{F}_2\text{C}=\text{CFSF}_5$  was carried out and compared to those of VDF with hexafluoropropene (HFP), VDF with perfluoromethyl vinyl ether (PMVE), and VDF with perfluoropropyl vinyl ether (PPVE). For each couple, three different copolymerizations were carried out using VDF mole percentages of ca. 20, 50, and 75% under the same batch conditions (initiator di-*tert*-butyl peroxide in 1,1,1,3,3-pentafluorobutane as the solvent). Because of the high volatilities of VDF and  $\text{SF}_5$ -containing monomers, the precise assessment of monomer conversions was difficult to obtain. Nevertheless, the monomer conversions were established to be less than 10 wt %.

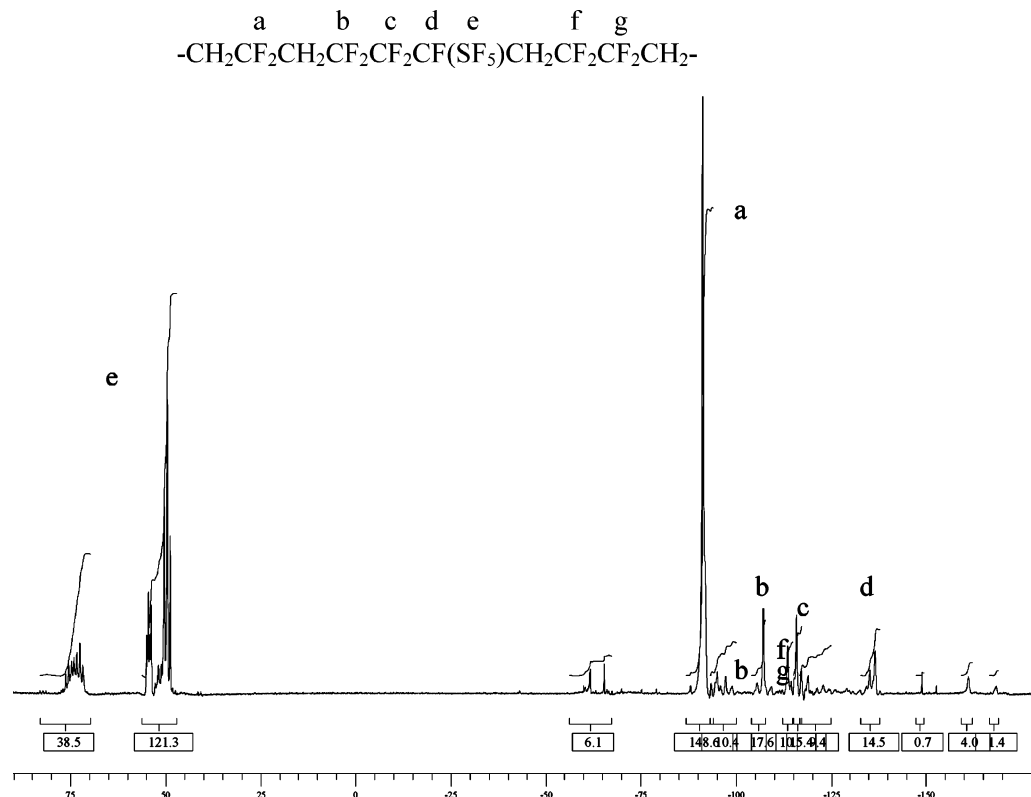
Both comonomeric units in each of the copolymers were assessed by  $^{19}\text{F}$  NMR spectroscopy.

Those of poly(VDF-*co*-HFP),<sup>41</sup> poly(VDF-*co*-PMVE),<sup>19h,42</sup> and poly(VDF-*co*-PPVE)<sup>19h,42</sup> copolymers had been previously characterized by  $^{19}\text{F}$  NMR while that of poly(VDF-*co*- $\text{SF}_5\text{M}$ ) copolymers has never been reported in the literature (Table 1). For example, Figure 1 represents the  $^{19}\text{F}$  NMR of the copolymers prepared by radical copolymerization of VDF and  $\text{SF}_5$  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  $\text{CF}_2$  groups in  $(\text{CH}_2-\text{CF}_2)-(\text{CF}_2-\text{CH}_2)-(\text{CH}_2-\text{CF}_2)-(\text{CH}_2-\text{CF}_2)-$ ;  $-(\text{CH}_2-\text{CF}_2)-(\text{CF}_2-\text{CH}_2)-(\text{CF}_2-\text{CH}_2)-$ ;  $(\text{CH}_2-\text{CF}_2)-(\text{CF}_2-\text{CH}_2)-(\text{CH}_2-\text{CF}_2)$  sequences, respectively, and correspond to the reverse VDF addition (i.e., head-to-head addition)<sup>43</sup> as noted for the chemical shifts observed for  $^{19}\text{F}$  NMR spectra of poly(VDF-*co*-HFP)<sup>41,44</sup> or poly(VDF-*co*-PVME).<sup>42</sup> The multiplet signals from  $+75$  to  $+50$  ppm are ideally an  $\text{AB}_4$  system and are assigned to the five fluorine atoms in the  $\text{SF}_5$  groups; the first one was a nine-line pattern, each line split into a triplet, and the



**Table 1. Comparative Study of Different Reactivities of VDF with Various Monomers in Radical Copolymerization<sup>a</sup>**

| run no. | mol % monomer in the feed |      |      |      |                  | mol % monomer in the copolymer |      |      |      |                  |
|---------|---------------------------|------|------|------|------------------|--------------------------------|------|------|------|------------------|
|         | VDF                       | HFP  | PMVE | PPVE | -SF <sub>5</sub> | VDF                            | HFP  | PMVE | PPVE | -SF <sub>5</sub> |
| 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             |

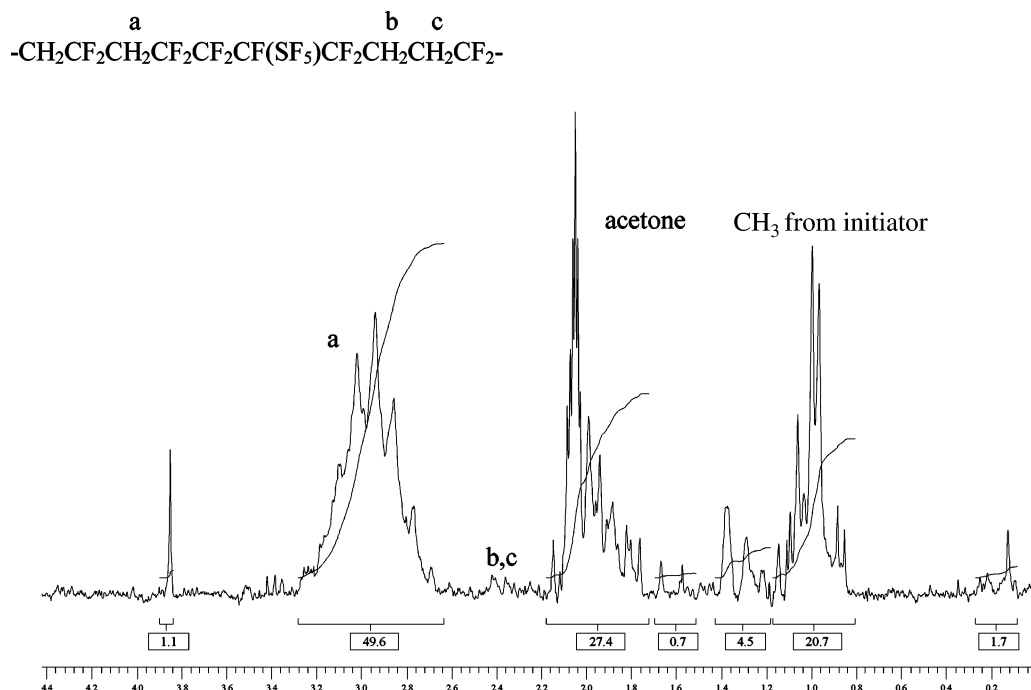
<sup>a</sup> No homopolymerization of CF<sub>2</sub>=CFSF<sub>5</sub> monomer.**Figure 1.** <sup>19</sup>F NMR spectrum of VDF/CF<sub>2</sub>=CF(SF<sub>5</sub>) copolymer at 70/30 mol % monomer ratio in the feed.

second one was a skewed doublet of a pentet. The difluoromethylene group of VDF adjacent to CF<sub>2</sub>CF(SF<sub>5</sub>) leads to a signal centered at -109.8 ppm while those centered at -118.8 and -136.7 ppm are related to the -CF<sub>2</sub> and -CF groups, respectively, deriving from the perfluorovinyl groups of the M-III monomer (Table 2). The microstructure of the copolymers was assessed by mol % SF<sub>5</sub> = (*I*<sub>+50 to +75</sub>)/5 for the multiplet centered at -135 ppm for -CF(SF<sub>5</sub>) fluorine atom. Indeed, both fluorine atoms in the difluoromethylene group adjacent to -CF(SF<sub>5</sub>) were anisochronous, hence leading to an AB system. This arises from the bulky -SF<sub>5</sub> group which stiffens the molecule as we had noted in C<sub>4</sub>F<sub>9</sub>-CF<sub>2</sub>CF(CF<sub>3</sub>)I obtained by telomerization of HFP with C<sub>4</sub>F<sub>9</sub>I.<sup>45</sup> In that monoadduct containing a bulky iodine, the central CF<sub>2</sub> group yielded an AB system. This AB system was also noted on CF<sub>2</sub> of VDF adjacent to -CF<sub>2</sub>-CF(CF<sub>3</sub>) as in the case of C<sub>3</sub>F<sub>7</sub>CF<sub>2</sub>CF(CF<sub>3</sub>)I. Because of the overlapping of different signals in that region, it was difficult to assess the mol % SF<sub>5</sub>M from δ CF<sub>2</sub> atoms. Interestingly, no doublet of multiplets centered at -114.8 ppm corresponding to the -CH<sub>2</sub>CF<sub>2</sub>H end group

**Table 2. <sup>19</sup>F NMR Assignments of Fluorinated Groups in the Poly(VDF-*ter*-HFP-*ter*-CF<sub>2</sub>=CFSF<sub>5</sub>) Terpolymers Recorded in Deuterated Acetone**

| chemical shift (ppm) | structure   | integrals in eq 1,3 |
|----------------------|---|---------------------|
| -71.2                | -CH <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF(CF <sub>3</sub> )-CF <sub>2</sub> -CH <sub>2</sub> -  | <i>I</i> -71.2      |
| -74.8                | -CH <sub>2</sub> -CF <sub>2</sub> -CF <sub>2</sub> -CF(CF <sub>3</sub> )-CH <sub>2</sub> -CF <sub>2</sub> -                                     | <i>I</i> -74.8      |
| -91.1                | -CF <sub>2</sub> -CH <sub>2</sub> -CF <sub>2</sub> -CH <sub>2</sub> -CF <sub>2</sub> -  | <i>I</i> -91.1      |
| -94.9                | (CH <sub>2</sub> -CF <sub>2</sub> )-(CF <sub>2</sub> -CH <sub>2</sub> )-(CH <sub>2</sub> -CF <sub>2</sub> )-(CH <sub>2</sub> -CF <sub>2</sub> ) | <i>I</i> -94.9      |
| -108                 | -CH <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF(SF <sub>5</sub> )-  | <i>I</i> -108       |
| -110.1               | -(CH <sub>2</sub> -CF <sub>2</sub> )CF <sub>2</sub> CF(CF <sub>3</sub> )-   | <i>I</i> -110.1     |
| -113.7               | -(CH <sub>2</sub> -CF <sub>2</sub> )-(CF <sub>2</sub> -CH <sub>2</sub> )-(CF <sub>2</sub> -CH <sub>2</sub> )-                                   | <i>I</i> -113.7     |
| -113.8               | -CF <sub>2</sub> CH <sub>2</sub> (CH <sub>2</sub> -CF <sub>2</sub> )-[CF <sub>2</sub> -CH <sub>2</sub> ]-                                       | <i>I</i> -113.8     |
| -115.7               | -(CH <sub>2</sub> -CF <sub>2</sub> )-(CF <sub>2</sub> -CH <sub>2</sub> )-(CH <sub>2</sub> -CF <sub>2</sub> )-                                   | <i>I</i> -115.7     |
| -118.8               | -CH <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF(SF <sub>5</sub> )-  | <i>I</i> -118.8     |
| -119                 | -CH <sub>2</sub> CF <sub>2</sub> -CF <sub>2</sub> CF(CF <sub>3</sub> )-   | <i>I</i> -119       |
| -136.7               | -(CH <sub>2</sub> -CF <sub>2</sub> )-[CF <sub>2</sub> -CFSF <sub>5</sub> ]-   | <i>I</i> -136.7     |
| -183.5               | -CH <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF(CF <sub>3</sub> )-  | <i>I</i> -183.5     |

was observed, proving the absence of transfer reaction.<sup>41,43-45</sup> The mole percentage of VDF in the copolymer was assessed from the following formulas taking into account that integrals of signals centered at -113



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

and  $-116$  ppm are the same with some overlapping of those centered at  $-116$  and  $-118.8$  ppm:

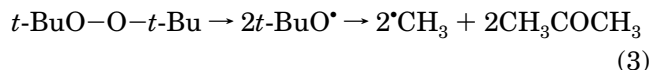
$$\text{mol \% VDF} = \frac{[I_{-91} + I_{-94} + I_{-107} + 2I_{-113.7}]/[I_{-91} + I_{-94} + I_{-107} + 2I_{-113.7}] + 2I_{-136.7}}{1} \quad (1)$$

$^1\text{H}$  NMR spectrum (Figure 2) exhibits one multiplet signal centered at  $3.0$  ppm assigned to the  $-\text{CH}_2$  protons of normal VDF units and traces of signals at  $2.3$ – $2.4$  ppm that can be related to the  $\text{CH}_2$  groups in the reverse structure of VDF (or tail to tail addition).<sup>41,43</sup> Interestingly, no triplet of triplets is seen, which would be characteristic of  $-\text{CH}_2\text{CF}_2\text{H}$  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  $\text{SF}_5$  monomer is the least reactive and the following decreasing reactivity series is suggested

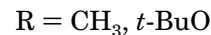


That low reactivity of  $\text{SF}_5\text{M}$  may arise from both the bulky electron-withdrawing  $\text{SF}_5$  groups and the delocalization of the electron in the radical  $\sim\text{CF}_2\text{C}^\bullet\text{F}(\text{SF}_5)$  terminal groups. This observation results in low molecular weight copolymers 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



$$T > 100^\circ\text{C}$$

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



$^1\text{H}$  NMR provides evidence of 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  $1.18$  ppm,  $(\text{CH}_3)_3\text{C}-\text{OCH}_2\text{CF}_2-$  at  $1.1$  ppm, and  $(\text{CH}_3)_3\text{C}-\text{OCF}_2\text{CH}_2-$  at  $1.15$  ppm. In addition, signals of small intensities are observed in the  $^{19}\text{F}$  NMR spectra at  $-60$  and  $-65$  ppm. They are assigned to  $\text{CF}_2$  of  $(\text{CH}_3)_3\text{C}-\text{OCF}_2\text{CH}_2-$  and confirm previous works dealing with the addition of  $t\text{-BuO}^\bullet$  onto the  $\text{CF}_2$  site of VDF<sup>43d</sup> or onto the  $\text{CF}_2$  site of PMVE.<sup>16f</sup>

Both  $^{19}\text{F}$  and  $^1\text{H}$  NMR spectra were used to assess the molecular weight of poly(VDF-*co*- $\text{SF}_5\text{M}$ -III) 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  $N_{\text{VDF}}$  is number of VDF units in copolymer and  $I_i$  values are the integrals of H signals at given ppm, assuming recombination of macroradicals as a main termination reaction.<sup>1d</sup>

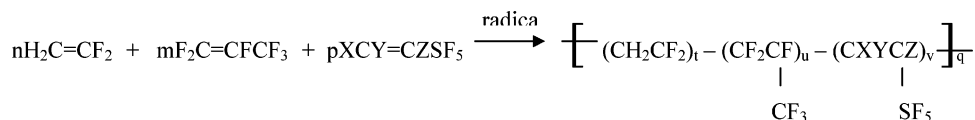
$^{19}\text{F}$  NMR spectra yield the  $\text{SF}_5/\text{VDF}$  molar ratio  $\alpha$  in the copolymer. Hence, the molecular weights can be deduced from the following equation

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

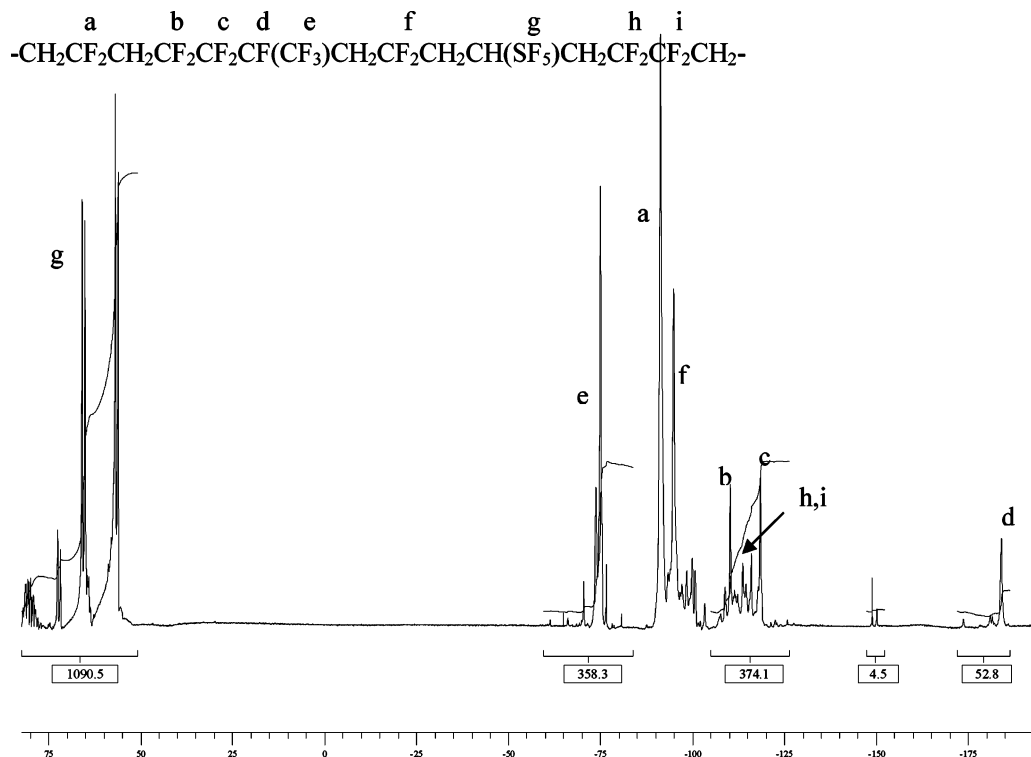
Table 3 lists the molecular weights of binary poly(VDF-*co*- $\text{SF}_5\text{M}$ -III) copolymers obtained from eq 6.

In addition the solution polymerization used leads to lower molecular weights in contrast to polymerizations carried out in aqueous media (such as emulsion, mini-emulsion, or suspension) that result in higher molecular weights (as for poly(VDF-*co*-HFP) copolymers).<sup>1,5,7c,9a</sup>

Hence, because of the difficulty to introduce an  $\text{SF}_5$  comonomer into a copolymerization, we have found it worthwhile to carry out terpolymerizations of VDF, HFP, and different  $\text{SF}_5$ -containing monomers, M-I, M-II, M-III, since it is known that the presence of HFP can



**Figure 3.** Radical terpolymerizations of SF<sub>5</sub> monomers with VDF and HFP.



**Figure 4.** <sup>19</sup>F NMR spectrum of VDF/HFP/SF<sub>5</sub>(M-I) terpolymer at initial monomer ratio in the feed 72.0/19.4/8.6 mol %.

**Table 3. Molecular Weights of Poly(VDF-co-SF<sub>5</sub>MIII) and Poly(VDF-ter-HFP-ter-SF<sub>5</sub>Mi) Copolymers Assessed by <sup>1</sup>H and <sup>19</sup>F NMR Analyses**

| exp<br>no. <sup>a</sup> | feed, mol % |                    |      |                  | molar ratio in<br>copolymers <sup>b</sup> |                |                | M <sub>n</sub><br>(g/mol) |
|-------------------------|-------------|--------------------|------|------------------|---|----------------|----------------|---------------------------|
|                         | VDF         | SF <sub>5</sub> Mi | HFP  | N <sub>VDF</sub> | α   | α <sub>1</sub> | α <sub>2</sub> |                           |
| 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                      |

<sup>a</sup> Experiments 1–3 concern runs 10–12 in Table 1. Experiments 4–7 concern experiment numbers in Table 4. <sup>b</sup> α = mol % SF<sub>5</sub>M-III/mol %VDF in copolymer, α<sub>1</sub> = mol % HFP/mol % VDF in terpolymer; α<sub>2</sub> = mol % SF<sub>5</sub>M-I/mol % VDF in terpolymer.

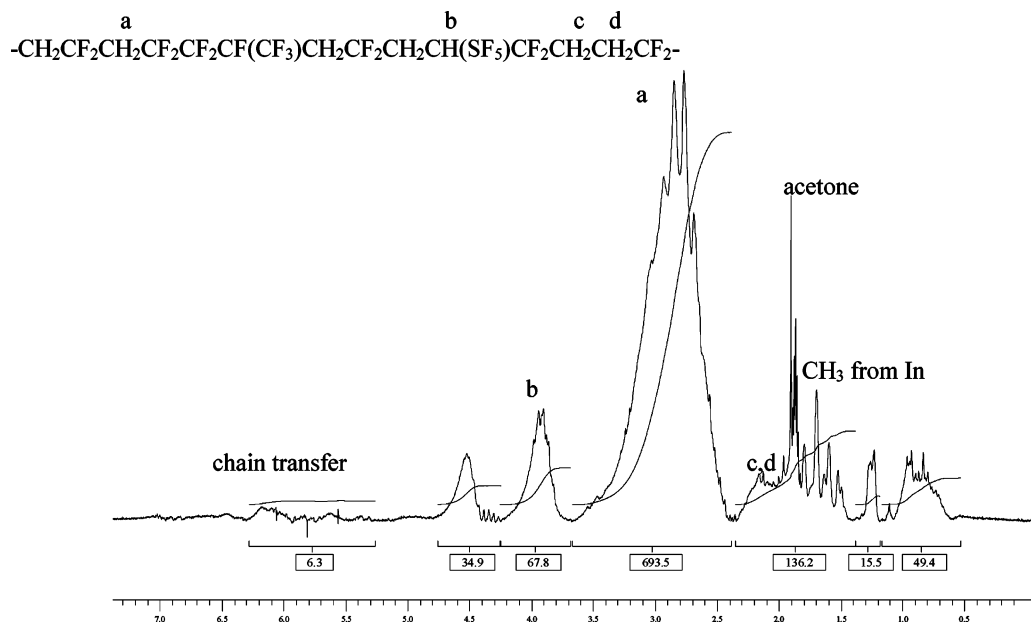
enhance the reactivity of VDF and of the comonomer as recently reported in the case of F<sub>2</sub>C=CFO-C<sub>6</sub>H<sub>4</sub>-Br.<sup>44</sup> This is the case when one reactive couple of monomers can involve the third low-reactive monomer in terpolymerization.

**II.2. Radical Terpolymerization of SF<sub>5</sub>-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 physicochemical properties of the resulting fluoropolymers.

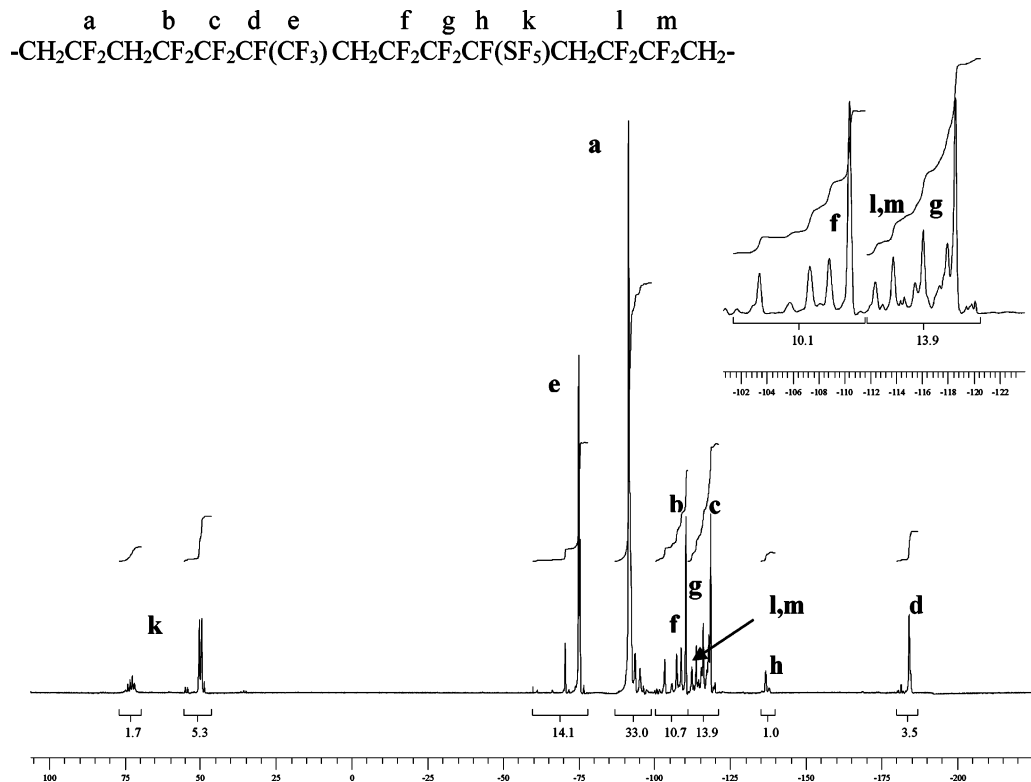
A series of terpolymerizations were performed using an initial [initiator]<sub>0</sub>/[total monomers]<sub>0</sub> molar ratio of 1%. These radical-initiated polymerizations were carried

out in a high-pressure autoclave at 143 °C for 5 h 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 <sup>1</sup>H and <sup>19</sup>F NMR spectra, which allowed characterization of the microstructures of these terpolymers. Depending on the identity of the SF<sub>5</sub>-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<sub>5</sub> monomer M-I, which bears three H atoms on the vinyl group; (b) a brown rubber-like polymer (II) when using SF<sub>5</sub> monomer (M-II); and (c) a gray 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 1,1,1,3,3-pentafluorobutane, whereas terpolymer III, based on the perfluorinated SF<sub>5</sub> monomer, was also soluble in dichloromethane and partially in chloroform. It was also noted that the higher the fluorine content of the SF<sub>5</sub> comonomer, the higher the yield of the reaction, and the higher the initiator concentration, the greater the yield (Table 4).

On the basis of such analyses, it was concluded that in all cases statistical terpolymers were obtained wherein the different monomeric units were randomly distributed in the backbone, and where microblocks of oligo-(VDF)s could be noted in the terpolymer. The relative amounts of the monomers in the terpolymers were assessed by <sup>19</sup>F NMR spectroscopy (Figures 4 and 6). In addition, all <sup>1</sup>H NMR spectra (Figures 5 and 7)



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



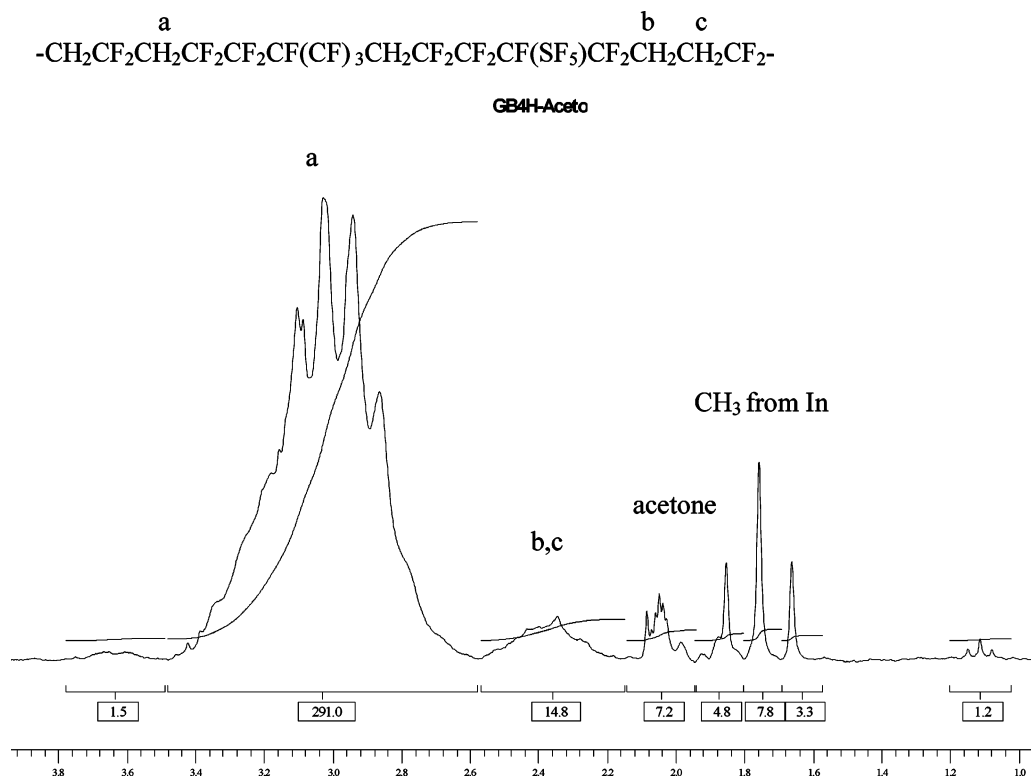
**Figure 6.**  $^{19}\text{F}$  NMR spectrum of VDF/HFP/SF<sub>5</sub>(**M-III**) terpolymer III recorded in deuterated acetone at initial monomer ratio 73.1/18.3/8.6 mol %.

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.

**II.2.1. Determination of the Terpolymer Compositions by Using  $^{19}\text{F}$  NMR Spectra.** Radical ter-

polymerizations in solution with organic initiators of SF<sub>5</sub>-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.<sup>7,16f,41,44,46</sup>

The  $^{19}\text{F}$  NMR spectra of polymers **I** and **III** (Figures 4 and 6) as well as polymer **II** exhibit the characteristic signals centered at –91, –94, –109, –110, –113.7, and –116 ppm assigned to the difluoromethylene groups of



**Figure 7.**  $^1\text{H}$  NMR spectrum of VDF/HFP/SF<sub>5</sub>(M-III) terpolymer III recorded in deuterated acetone at initial monomer ratio 73.1/18.3/8.6 mol %.

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  $-\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2-\text{CH}_2\text{CF}_2-$ ,<sup>43</sup> respectively, as observed in NMR spectra of copolymers (Table 2). The signals located at  $-109.8$  ppm (noted  $I_{-109.8}$ ) and  $-110.1$  (noted  $I_{-110.1}$ ) range are assigned to the difluoromethylene groups of the VDF unit adjacent to SF<sub>5</sub>M and HFP 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  $-\text{CH}_2-\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}(\text{CF}_3)-$  sequences and to the tertiary fluorine in  $\text{CF}_2\text{CF}(\text{CF}_3)$  of HFP,<sup>41</sup> 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<sub>5</sub>M unit in terpolymers **III** and **II**,  $-(\text{CF}_2-\text{CF}(\text{SF}_5))-$  and  $\text{CF}_2-\text{CH}(\text{SF}_5)-$ , 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  $-(\text{CF}_2-\text{CF}(\text{SF}_5))-$  monomer unit in polymer **III**. The multiplets centered at  $+55$  and  $+75$  ppm in the  $^{19}\text{F}$  NMR are consistent with the presence the SF<sub>5</sub> group. The SF<sub>5</sub> group, as found by Muller et al.,<sup>47</sup> contains four magnetically equivalent and one nonequivalent fluorine atoms (AB<sub>4</sub> system). The equatorial, A<sub>4</sub>, resonance is split into a doublet while the apex, A, resonance is grossly a pentet with a "fine structure". Cross et al.<sup>48</sup> reported that the compounds in which the SF<sub>5</sub> group is bound to aliphatic hydrocarbons, a very intense broad band centered on or about  $870\text{ cm}^{-1}$  is found. They assigned this to the S-F stretching modes. We observed the same behavior with our compounds.

The integrals in the  $^{19}\text{F}$  NMR spectra (denoted above) allow the determination of the molar fractions of VDF, HFP, and SF<sub>5</sub>M units in the terpolymers, and they are given by the following equations (eq 7):

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

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

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

where

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

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

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

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

**II.3. Characterization of the Terpolymers.** Table 4 lists the final molar percentages of each monomer and also the molecular weights and thermal properties of each terpolymer.

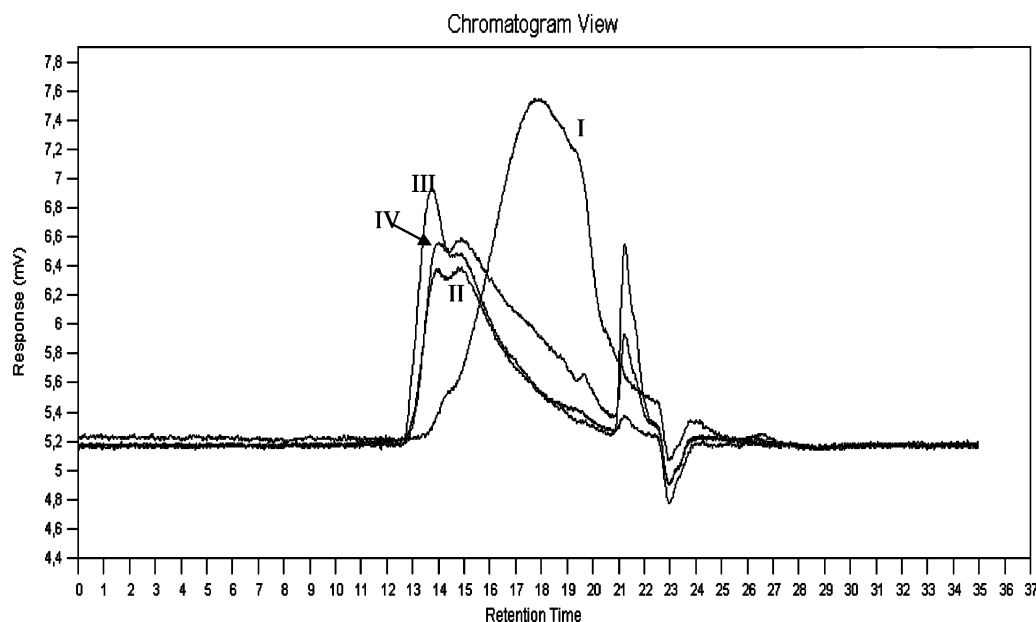
In the same experimental conditions (experiments I, II, and III: terpolymer VDF/HFP/SF<sub>5</sub>M, starting from



**Table 4.** Monomer–Polymer Compositions of Poly(VDF-*ter*-HFP-*ter*-SF<sub>5</sub>M) Terpolymers and Their Main Characteristics<sup>a</sup>

| exp no.<br>monomer  | feed (mol %) |      |                   | terpolymers<br>(mol %) |      |                   | Y<br>(wt %) | $M_n$<br>(g/mol) | PDI | $T_g$<br>(°C) |
|---|--------------|------|-------------------|------------------------|------|-------------------|-------------|------------------|-----|---------------|
|   | VDF          | HFP  | SF <sub>5</sub> M | VDF                    | HFP  | SF <sub>5</sub> M |             |                  |     |               |
| polymer I <sup>b</sup><br>H <sub>2</sub> C=CH(SF <sub>5</sub> )   | 72.0         | 19.4 | 8.6               | 71.0                   | 11.6 | 17.4              | 45.0        | 2540             | 2.0 | −50           |
| polymer II <sup>b</sup><br>F <sub>2</sub> C=CH(SF <sub>5</sub> )  | 75.2         | 16.1 | 8.7               | 83.8                   | 14.1 | 2.1               | 52.2        | 8290             | 2.3 | −41           |
| polymer III <sup>b</sup><br>F <sub>2</sub> C=CF(SF <sub>5</sub> ) | 73.1         | 18.3 | 8.6               | 78.3                   | 16.4 | 5.3               | 72.5        | 10030            | 2.4 | −40           |
| polymer IV <sup>c</sup><br>F <sub>2</sub> C=CF(SF <sub>5</sub> )  | 71.1         | 15.3 | 13.6              | 78.1                   | 13.5 | 8.3               | 91.2        | 6650             | 2.4 | −50           |

<sup>a</sup>Reaction conditions: initiator DTBP, 1 mol %; solvent pentafluorobutane, 70 wt %; 143 °C; 5 h. Polymer solubility: soluble in acetone, THF, C<sub>4</sub>F<sub>5</sub>H<sub>5</sub>; polymers I and II not soluble in CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> whereas polymers III and IV are soluble in CH<sub>2</sub>Cl<sub>2</sub> and partially in CHCl<sub>3</sub>. <sup>b</sup> DTBP concentration 1 mol %. <sup>c</sup> DTBP concentration 3 mol %.

**Figure 8.** SEC Chromatograms of poly(VDF-*ter*-HFP-*ter*-SF<sub>5</sub>M) terpolymers. Terpolymer compositions of VDF/HFP/SF<sub>5</sub>M in mol %: I, 71.0/11.6/17.4; II, 83.8/14.1/2.1; III, 78.3/16.4/5.3; IV, 78.1/13.5/8.3.

the same SF<sub>5</sub>M feed molar percentages of ca. 8.6 mol % led to copolymers containing 17.4, 2.1, and 5.3 mol %, respectively (Table 4)). The increasing mole percent of SF<sub>5</sub>M in feed makes increases in its mole percent in the terpolymer and the yield. Usually, the final molar percentages of VDF are higher than the molar percentages in feed. As a matter of fact, this result is evidence of the presence of oligo(VDF) blocks separated by one SF<sub>5</sub> monomeric unit in the terpolymer. The poor reactivity of F<sub>2</sub>C=CH(SF<sub>5</sub>) monomer is not surprising when its behavior is compared to that of F<sub>2</sub>C=CH(CF<sub>3</sub>), PFP<sup>49</sup> or F<sub>2</sub>C=CH(C<sub>6</sub>F<sub>13</sub>), HPO.<sup>50</sup> Actually, kinetics of copolymerization of both of these fluorinated monomers led to the following reactivity ratios:

$$r_{\text{PFP}} = 0.06; \quad r_{\text{VDF}} = 9.0 \quad \text{at } 40^\circ\text{C}$$

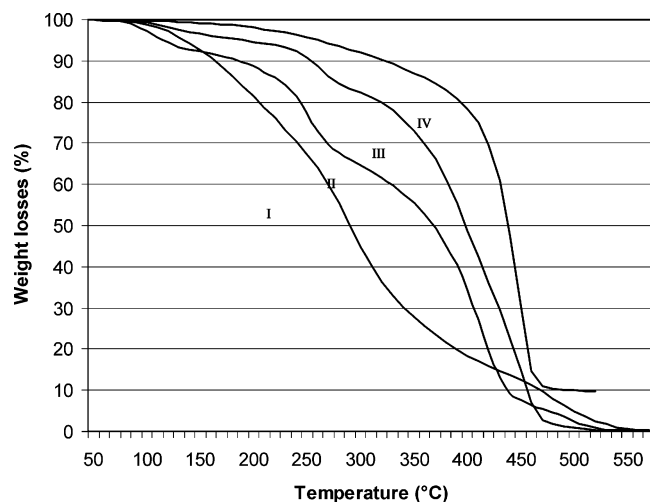
$$r_{\text{HPO}} = 0.9; \quad r_{\text{VDF}} = 12.0 \quad \text{at } 75^\circ\text{C}$$

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

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

In all cases, the SEC chromatograms (Figure 8) showed one main maximum with two shoulders. This can be surprising for terpolymers for which monomodal distribution is expected, although more detailed experiments are required to be done. The value of the average molecular weights,  $\overline{M}_n$ , of poly(VDF-*ter*-HFP-*ter*-SF<sub>5</sub>M) terpolymers (experiments I, II, and III with ca. 8.6 mol % in feed of fluorinated SF<sub>5</sub> monomer) or poly(VDF-*ter*-HFP-*ter*-SF<sub>5</sub>M) terpolymers (experiment IV), 13.6 mol % in feed of perfluorinated SF<sub>5</sub> monomer) were about 2540, 8290, 10030, and 6650 g·mol<sup>−1</sup>, 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 toward higher molecular weight with increasing of fluorine atom in SF<sub>5</sub>M for the main part of the copolymer obtained. In the case of experiments III and IV, the lower molecular weight in the latter is, as expected, due to the higher concentration of DTBP initiator (3 mol % vs 1 mol %). However, these measurements cannot be considered quite accurate because of the lack of standards for VDF polymers. The polydispersity index of terpolymers synthesized is in the range of the statistic distribution (2.0–2.4).

The transfer reaction on the macroradical appears to be quite negligible on the basis of the small presence of transfer signals in <sup>19</sup>F and <sup>1</sup>H NMR spectra (presence of triplet of triplets and doublet of multiplets centered



**Figure 9.** Thermogravimetric curves of VDF/HFP/SF<sub>5</sub>M terpolymers in air of VDF/HFP/SF<sub>5</sub> terpolymers. Terpolymer compositions of VDF/HFP/SF<sub>5</sub>M in mol %: I, 71.0/11.6/17.4; II, 83.8/14.1/2.1; III, 78.3/16.4/5.3; IV, 78.1/13.5/8.3.

at 6.1 and 5.5 ppm assigned to  $-\text{CH}_2\text{CF}_2\text{H}$  and  $-\text{CF}_2-\text{CF}(\text{CF}_3)\text{H}$ , respectively). On the other hand using the same strategy of binary poly(VDF-*co*-SF<sub>5</sub>MIII) copolymers, the molecular weights of terpolymers can be assessed by <sup>1</sup>H and <sup>19</sup>F NMR analyses. Equation 6 can be modified as follows

$$M_n = 64N_{\text{VDF}} + 150\alpha_1 N_{\text{VDF}} + \alpha_2 N_{\text{VDF}}(\text{MSF}_5\text{M}_i) + 30 \quad (9)$$

where  $\alpha_1$  and  $\alpha_2$  are the molar ratios of HFP and SF<sub>5</sub>M<sub>i</sub> monomer units vs VDF, and MSF<sub>5</sub>M<sub>i</sub> stands for the molecular weights of SF<sub>5</sub>MI, SF<sub>5</sub>MII, and SF<sub>5</sub>MIII 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 as discussed before.

Thermogravimetry curves (Figure 9) show that these terpolymers exhibit a good thermal stability since their decomposition started from 170 to 250 °C, for poly(VDF-*ter*-HFP-*ter*-SF<sub>5</sub>M) terpolymers. For example, terpolymer I (curve I) is the least thermally stable because of the entirely hydrogenated vinyl group in **M-I** and also because of its low molecular weight (hence inducing a certain evaporation of the terpolymer before its degradation). 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 4. In the poly(VDF-*ter*-HFP-*ter*-SF<sub>5</sub>M) terpolymers,  $T_g$  values were ranging from  $-40$  to  $-50$  °C without any other transitions, showing amorphous behavior. With such  $T_g$  values, and as reported in the literature,<sup>8,9a</sup> it is known that fluoropolymers, containing VDF and HFP base units only, exhibit an average  $T_g$  of  $-26$  °C and are fluoroelastomers.

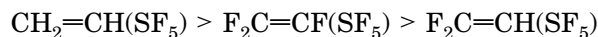
Finally, regarding the results gathered in Table 4, it appears that the hydrogenated monomer **M-I** is more reactive than **M-II** and **M-III** monomers containing two and three F- atoms in the vinyl group, respectively.

## Conclusion

Monomers CH<sub>2</sub>=CHSF<sub>5</sub> (**M-I**) and CF<sub>2</sub>=CHSF<sub>5</sub> (**M-II**) were prepared by using a new Et<sub>3</sub>B initiation

methodology to add SF<sub>5</sub>Cl to ethylene and VDF, respectively. CF<sub>2</sub>=CHSF<sub>5</sub>, (**M-III**) monomer was synthesized by radical addition of BrSF<sub>5</sub> onto trifluoroethylene followed by a dehydrobromination. It was found that **M-III** monomer does not homopolymerize but copolymerizes with VDF by free radical initiation. Its reactivity with VDF when compared to that of other fluoroalkenes (HFP, PMVE, and PPVE) gives the following decreasing series: HFP > PPVE ≥ PMVE > SF<sub>5</sub>M; i.e. the **M-III** monomer has the lowest reactivity due to the SF<sub>5</sub> bulky side groups.

The terpolymerization of SF<sub>5</sub>-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<sub>5</sub>M can be successfully performed in 1,1,1,3,3-pentafluorobutane initiated by di-*tert*-butyl peroxide. Interestingly, the terpolymerization of VDF with HFP and SF<sub>5</sub>M shows that CH<sub>2</sub>=CHSF<sub>5</sub> monomer was more reactive than CF<sub>2</sub>=CHSF<sub>5</sub> and even more reactive than CF<sub>2</sub>=CFSF<sub>5</sub>.



Both <sup>1</sup>H and <sup>19</sup>F NMR analyses enabled the calculation of molecular weights of binary and ternary SF<sub>5</sub>M copolymers.

Finally, DSC, TGA, and GPC analyses indicated that the terpolymers II and III incorporating SF<sub>5</sub> 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 Available:** NMR and FT-IR spectra and DSC curves of poly(VDF-*Co*-MIII) copolymers and poly(VDF-*ter*-HFP-*ter*-SF<sub>5</sub>M<sub>i</sub>) terpolymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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