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Telechelic Diiodopoly(VDF-*co*-PMVE) Copolymers by Iodine Transfer Copolymerization of Vinylidene Fluoride (VDF) with Perfluoromethyl Vinyl Ether (PMVE)[†]

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ABSTRACT: The synthesis and the characterization of fluoroelastomers, based on vinylidene fluoride (VDF) and perfluoromethyl vinyl ether (PMVE), poly(VDF-*co*-PMVE) copolymers, by iodine transfer copolymerization are presented. These statistic poly(VDF-*co*-PMVE) copolymers were prepared in the presence of a perfluoromonoiodo functional chain transfer agent (CTA), $C_6F_{13}I$, or telechelic diiodoperfluoroalkane CTAs, $IC_6F_{12}I$ and IC_4F_8I, using an emulsion process without any surfactant. Quasi-optimal conditions were found to lead to poly(VDF-*co*-PMVE) copolymers in satisfactory yields. The copolymer compositions, the molecular weights, and end-groups of these random-type copolymers were assessed by means of ^{19}F NMR spectroscopy. Model molecules containing only one PMVE unit were synthesized by the radical addition of different CTAs (ICl, ICF_2I, CF_3I) onto PMVE to help in the assignments by ^{19}F NMR spectroscopy of the characteristic signals of the end-group, i.e., $-CF_2CF(OCF_3)I$ and $-CF(OCF_3)CF_2I$. Indeed, only $-CH_2CF_2-I$ (major amount) and $-CF_2CH_2-I$ end-groups of these poly(VDF-*co*-PMVE) copolymers were noted, showing the high reactivity of PMVE−I in the iodine transfer polymerization of VDF. The CTA concentration enabled one to control the molecular weights of the resulting telechelic diiodopoly(VDF-*co*-PMVE) copolymers ranging from 1000 to 18 000 g mol^{-1} (assessed by ^{19}F NMR), produced for the first time. It was also noted that the higher the molar masses, the higher the amount of $-CF_2CH_2-I$ end-group. The controlled behavior of that polymerization was also evidenced by the absence of the reversed $-CH_2CF_2-CF_2CH_2-$ VDF dyads, narrow polydispersity indices (< 1.75), and the linear "molar mass versus monomer conversions" relationship. Finally, the thermal properties, i.e., the glass transition temperatures (T_g) and degradation temperatures, of these copolymers were assessed and were found to depend on the molecular weights and on the monomer composition of the copolymers. These fluoroelastomers had T_gs ranging from −63 to −35 °C according to their molecular weights and the contents of both comonomers, with decomposition temperatures greater than 250 °C under air.

Introduction

One of the most important areas for the development of fluoropolymers[1−4] is their use as elastomers.[5] Indeed, their stabilities at high temperature and their chemical inertness in a wide range of solvents allow the development of new elastomers which can be used in a wide range of temperatures (from far below −10 °C to high temperatures). The development of this type of rubber is of great interest in the aeronautics and automotive industry, for example, O-rings, gaskets, diaphragms, etc. However, the use of poly(vinylidene fluoride), PVDF, or polytetrafluoroethylene, PTFE, directly as a rubber is impossible due to the presence of a highly crystalline domain. In addition, the decrease of the glass transition temperatures (T_g) values of these polymers is a real challenge. One way to decrease the crystallinity of these polymers is the insertion of a comonomer, such as hexafluoropropylene or perfluoroalkyl vinyl ether (including perfluoromethyl vinyl ether, PMVE), yielding fluoroelastomers endowed with a low T_g and high temperature resistance (when PMVE is copolymerized with VDF).[6,7] On the other hand, the copolymerization of functional perfluoroalkyl vinyl ether with TFE leads to specific applications such as membranes, e.g. Nafion, Flemion, Hyflon (now Aquivion), Fumion, or 3M Membrane.[8,9] Regarding the elastomers, poly(VDF-*co*-PMVE) copolymers are promising materials that exhibit low T_g values. The development of these copolymers using the conventional radical polymerization has produced several commercially available products. In contrast, specific products have been reported by Worm et al.,[10] who copolymerized VDF with long perfluoroalkoxy alkyl vinyl ether(s) bearing several ether bridges leading to copolymers endowed with exceptional low T_g values (< −80 °C).

However, these pioneered works on the copolymerization of perfluoroalkyl vinyl ether and VDF were only carried out using conventional free radical polymerization.[6,7,11] Since the development of the controlled radical polymerization, the synthesis of well-defined polymers has been widely reported with a better control of molecular weights, chain-end functionalities, and chain architectures giving new properties compared to those synthesized by free radical polymerization. In the case of fluoropolymers, a few studies in the literature propose to investigate their kinetic[12]

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and to control their polymerizations[13−21] and, usually, are reported under patent forms.[22−28] Apostolo et al.[15] reported one of the first papers describing the radical copolymerization of hexafluoropropylene (HFP) and VDF (with or without addition of tetrafluoroethylene, as a comonomer) in the presence of iodoperfluoro agent in emulsion process to yield fluoroelastomer polymer. The authors showed for the first time the controlled behavior of that copolymerization. More recently, Beuermann's team[18,19,29,30] investigated similar study in supercritical carbon dioxide. However, both above groups did not provide any information on the thermal properties on the resulting copolymers. Indeed, these "exotic" monomers are relatively difficult to handle due to their low boiling point (below −20 °C) and their low solubility in water.[29,30] This present article reports for the first time the copolymerization of PMVE with VDF using a pseudo-controlled radical polymerization, i.e., iodine transfer copolymerization (ITP).[31] This is a suitable technique to control the polymerization of fluorinated olefins, while atom transfer radical polymerization (ATRP),[32−36] nitroxide-mediated polymerization,[36,37] and reversible addition−fragmentation transfer[36,38−42] failed to control the radical (co)polymerization of this type of monomer. Interestingly, Feiring et al.[43] used ATRP (or single electron transfer) to copolymerize hexafluoropropylene and tetrafluoroethylene using perfluoroalkylsulfonyl chlorides and bromides, as the initiator and hastelloy walls of the autoclave as the catalyst. However, the living character was neither claimed nor demonstrated. ITP (also called "degenerative transfer") enables the controlled polymerization of different monomers, i.e., acrylic,[44−50] methacrylic,[51] styrenic,[44,52,53] vinyl chloride,[46,50,54] and also fluorinated olefins.[13−30,55] The synthesis of different commercially available products such as thermoplastic elastomers pioneered by the Daikin Co. in 1979[56] (which nowadays produces Daiel TPE),[22] then studied by DuPont (now Dupont Performance Elastomers),[23,24,28] and developed later by Ausimont (now Solvay Solexis) under the Tecnoflon trade name[25−27] have been reported. In addition, the presence of the iodine end-atom (halogen atom) potentially enables chemical modification to prepare various functional polymers.[5,53,57−59]

Hence, the objectives of this research concern the preparation of new fluorinated elastomers based on VDF and PMVE in emulsion process using iodine transfer polymerization. This article follows the recent patent filed by Dupont Performance Elastomers,[28] and this is the first study that reports the investigation of the copolymerization of both these monomers using a pseudo-controlled radical technique, such as ITP. Finally, the thermal properties (glass transition and decomposition temperatures) were investigated. The addition of PMVE unit in the copolymer chains results in the synthesis of polymers having T_g values lower than −40 °C with a satisfactory thermostability.

Experimental Part

Materials. Vinylidene fluoride (or 1,1-difluoroethylene, VDF), perfluoromethyl vinyl ether (PMVE), and 1,4-diiodoperfluorobutane were kindly offered by Dupont Performance Elastomer. 1-Iodoperfluorohexane or perfluorohexyl iodide (purity 99%) was a gift from Elf Atochem while 1,6-diiodoperfluorohexane was purchased from Aldrich Chimie (Saint Quentin-Fallavier, France). The (di)iodinated reactants were worked up with sodium thiosulfate, dried over magnesium sulfate, and then distilled prior to use. *tert*-Butyl peroxypivalate, TBPPI (purity 75%), was a gift from Akzo while di-*tert*-butyl peroxide, DTBP, and sodium persulfate, $Na_2S_2O_8$ (purity 99%), were purchased from Aldrich. They were used as supplied. Methyl ethyl ketone (MEK), dimethylformamide (DMF), tetrahydrofuran (THF), methanol, and pentane of analytical grade were purchased from Aldrich Chimie.

Analyses. The microstructures (i.e., the compositions and the end-group functionalities) of the oligomers obtained by ITP were determined by ^{19}F and ^{1}H NMR spectroscopy. The NMR spectra were recorded on Bruker AC 250 or 400 (250 or 400 MHz) instruments, using deuterated acetone as solvent and tetramethylsilane (TMS) (or $CFCl_3$) as the references for ^{1}H (or ^{19}F) nuclei. Coupling constants and chemical shifts are given in Hz and ppm, respectively. The experimental conditions for ^{1}H (or ^{19}F) NMR spectra were the following: flip angle 90° (or 30°), acquisition time 4.5 s (or 0.7 s), pulse delay 2 s (or 5 s), number of scans 16 (or 64), and a pulse width of 5 μs for ^{19}F NMR.

Size exclusion chromatography (SEC) analyses were performed with a Spectra-Physics apparatus equipped with two PLgel 5 μm Mixed-C columns from Polymer Laboratories and a Spectra-Physics SP8430 refractive index (RI) detector (the signals assigned to PVDF-Is gave negative values). Dimethylformamide (DMF) was chosen as the eluent at $T = 70$ °C, with a flow rate of 0.8 mL min^{-1}. Standards were monodisperse poly(styrene), purchased from Polymer Laboratories.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectra were performed with an "ULTRAFLEX Bruker" (Université Montpellier II) in reflectron mode (accelerating potential of 20 kV) on a Bruker apparatus equipped with a nitrogen laser (337 nm). Pentafluorocinnamic acid (PFCA) and sodium iodide (NaI) were used as the matrix and the cationizing agent, respectively. The concentrations of sample and matrix solutions were 10 g L^{-1} in dimethylformamide, and the analyte/matrix ratio was 1/10 v/v. The mixture (1 μL) was deposited on a stainless steel target, air-dried, and introduced in the spectrometer under vacuum.

Differential scanning calorimetry (DSC) analyses were conducted using a Perkin-Elmer Pyris 1 DSC instrument calibrated with *n*-octane and *n*-octadecane, while the enthalphy change was calibrated using indium. In a typical procedure, the sample was first cooled to −100 °C where it stayed for about 5 min and was then heated at 40 °C min^{-1} up to 120 °C, where it stayed for about 3 min. Then, it was cooled to −100 at 320 °C min^{-1} before a second scan recorded at a heating rate of 20 °C min^{-1} up to 50 °C. The T_g was assessed as the inflection point in the heat capacity jump, confirmed by a third run.

Thermal gravimetry analysis (TGA) analyses were performed with a Texas Instrument ATG 51-133 apparatus in air at the heating rate of 20 °C min^{-1} from room temperature up to a maximum of 550 °C.

Reaction in Autoclave. Iodine transfer copolymerization of VDF and PMVE was performed in the presence of either perfluorohexyl iodide ($C_6F_{13}I$), 1,4-diodoperfluorobutane (IC_4F_8I), or 1,6-diiodoperfluorohexane ($IC_6F_{12}I$) as chain transfer agents (CTA) and initiated by *tert*-butyl peroxypivalate at 75 °C or $Na_2S_2O_8$ at 80 °C, detailed below.

a. Synthesis of Model Compounds

Addition of Diiodoperfluoromethane (CF_2I_2) onto Perfluoromethyl Vinyl Ether. A 160 mL hastelloy (HC-276) autoclave, equipped with inlet and outlet valves, a manometer, and a rupture disk, was degassed and pressurized with 30 bar (430 psi) of nitrogen to check eventual leaks. Then, a 20 mmHg vacuum was operated for 30 min. Under vacuum, CF_2I_2 (0.01 mol, 3.0 g) and 1,1,1,3,3-pentafluorobutane (50.0 g) used as the solvent were transferred into the autoclave. Then, by double weighing, PMVE (0.016 mol, 3.5 g) was introduced in the mixture. After this addition, the autoclave was progressively heated to 165 °C by carrying out various plateaus at 50, 80, 100, 130, and 150 °C for 2 min to reach a pressure of ca. 20 bar. After 3 h reaction (a drop of 10 bar of pressure was observed), the autoclave was placed in an ice bath for about 60 min and unreacted PMVE was progressively released. After opening the autoclave, about 50 g of a pink liquid was obtained. The solvent was removed under vacuum, and the product was distilled (yield 75%; bp: 87−89 °C/50 mmHg). The ^{19}F NMR spectrum (Figure S1 in the Supporting Information) indicated a

Table 1. Results of the Addition of 1-Iodoperfluoromethane (or Hexane), ICl, and ICF_2I onto Perfluoromethyl Vinyl Ether (PMVE) in the Presence of Different Initiators (TBPPI: *tert*-Butyl Peroxypivalate; DTBP: Di-*tert*-butyl Peroxide) in $C_4F_5H_5$

runs	ratios [PMVE]/[CTA]	CTAs	*T* (°C)	initiator	yield (%)
1	1.2	$C_6F_{13}I$	75	TBPPI	< 10
2	2.0	CF_3I	75	TBPPI	< 10
3	2.0	CF_3I	140	DTBP	< 10
4	1.5	CF_3I	165	thermal	< 10
5	1.2	ICl	75	TBPPI	< 10
6	2.0	ICl	75	TBPPI	< 10
7	2.0	ICl	140	DTBP	< 10
8	1.5	ICl	165	thermal	< 10
9	1.5	ICF_2I	165	thermal	85

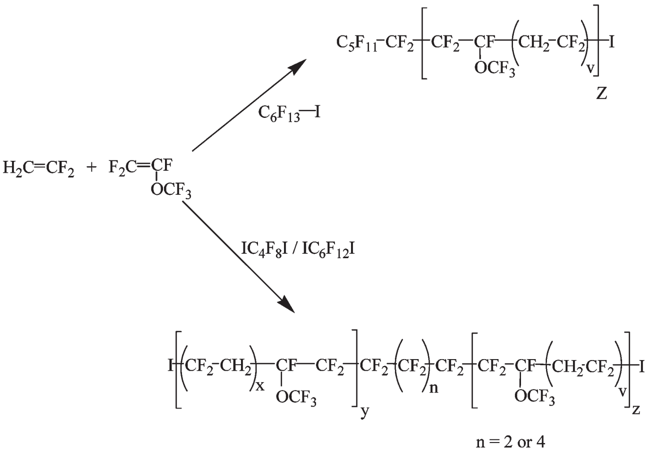
mixture $ICF_2-CF_2(CFOCF_3)-I$ and $ICF_2CF(OCF_3)CF_2-I$ in a ratio of 12:1. ^{19}F NMR for $ICF_2-CF_2(CFOCF_3)I$: −55.0 (m, 3F, OCF_3), −58.1 (d, A part of AB system, $J_{FAFB} = 11.3$ Hz, 3F), −63.4 (ddm, B part of AB system J_{FBFA} = 26.4 Hz, 1F, ICF_2CF_2), −73.0 (m, 1F, $CFI(OCF_3)$), −102.6 (dt, $J = 7.7$ Hz, 1F, A′ part of A′B′ system central in CF_2), −104.2 (dt, B′ part of A′B′ system $J = 276.4$ Hz, $J = 7.2$ Hz, 1F, central CF_2); for $ICF_2-CF(OCF_3)CF_2-I$, −51.7 (m, 3F), −53.9 (m, 4F, both CF_2), −124.2 (m, 1F, central CF).

Reactions with Other CTA Using Thermal or Radical Initiation. A similar process was used with other CTAs (ICl, $C_6F_{13}I$, CF_3I, and $(CF_3)_2CF-I$). The autoclave was prepared according to the process described above. CTA (0.05 mol, i.e., 8.1 g of ICl, 22.3 g of $C_6F_{13}I$, 14.2 g of $(CF_3)_2CF-I$, or 10.0 g of CF_3I) and 1,1,1,3,3-pentafluorobutane (50 g) used as the solvent were inserted into the autoclave. PMVE (0.06 mol, 10 g) was finally added into the autoclave. The reaction was carried out at 165 °C for 5 h. Other combinations of $[PMVE]_0/[CTA]_0$ initial molar ratios were also polymerized and the results are reported in Table 1. A similar reaction was carried out as above with the addition of an initiator, such as *tert*-butyl peroxypivalate (TBPPI) or di-*tert*-butyl peroxide (DTBP), to improve the yield ($[initiator]_0/[CTA]_0$ initial molar ratio = 1/5). Accordingly, two different temperatures were tested, 75 and 140 °C for TBPPI and DTBP, respectively.

b. Example of Emulsion Polymerization. A 160 mL Hastelloy (HC-276) autoclave, equipped with inlet and outlet valves, a manometer, and a rupture disk, was degassed and pressurized with 30 bar of nitrogen to check for leaks. Then, a 20 mmHg vacuum was operated for 30 min. Under vacuum, $Na_2S_2O_8$ (0.001 mol, 0.230 g), perfluorohexyl iodide ($C_6F_{13}I$, 0.0067 mol, 3.0 g), and deionized water (80.0 g) were transferred into the autoclave. By double weighing, PMVE (0.10 mol, 16.6 g) and then VDF (0.10 mol, 6.4 g) were introduced into the mixture. Then, the autoclave was progressively heated to 80 °C, by carrying out a heating profile that included 2 min equilibrium at 50, 60, and 70 °C. A low exotherm of ca. 5 °C (leading to a maximum pressure, P_{max} = 45 bar) was observed, after which the pressure dropped slowly to 40 bar. After 6 h reaction, the autoclave was placed in an ice bath for about 60 min (P_{min} = 5−10 bar), and unreacted VDF and PMVE (4 g) were progressively released (yield 75%). After opening the autoclave, about 100 g of a liquid was obtained. The product was solution extracted with water/methyl ethyl ketone (MEK), and after solvent removal a viscous product was obtained (yield = 80%). The sample was characterized by ^{19}F and ^{1}H NMR spectroscopy, SEC analysis, and MALDI-TOF spectroscopy. The poly(PMVE-*co*-VDF) copolymers were soluble in different polar solvents, such as acetone, DMF, THF, MEK, and DMSO.

Kinetics of Iodine Transfer Polymerization of VDF and PMVE. Aliquots were periodically taken from the autoclave (by means of a probe) in the course of the copolymerization of VDF to monitor both: (i) the conversions of both monomers and the CTA and (ii) the evolution of the molar masses. The collected samples were quenched in liquid nitrogen to stop the polymerization reaction, then diluted in dimethylformamide (DMF), and were characterized by SEC and NMR spectroscopy.

Scheme 1. Radical Copolymerization of Perfluoromethyl Vinyl Ether (PMVE) and Vinylidene Fluoride (VDF) Performed in the Presence of Either Monofunctional or Difunctional Fluoroiodinated Chain Transfer Agents (CTAs)



Results and Discussion

The radical copolymerizations of vinylidene fluoride (VDF) and perfluoromethyl vinyl ether (PMVE) were carried out in aqueous solution using iodine transfer polymerization (ITP), initiated by sodium persulfate ($Na_2S_2O_8$) at 80 °C (Scheme 1), without any surfactant. The reaction was performed in an autoclave. The pressure increased to reach a maximum around 40−45 bar during the heating process and then decreased to 5−10 bar as evidence of the consumption of both gaseous comonomers and of the success of the polymerization. After reaction and purification, the copolymers were characterized by ^{1}H and ^{19}F NMR spectroscopy, size exclusion chromatography, and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) analysis.

1. Characterization of the Microstructures of Copolymers by ^{1}H and ^{19}F NMR Spectroscopy. The ^{1}H NMR spectrum of poly(PMVE-*co*-VDF) copolymers obtained from $C_6F_{13}I$, IC_4F_8I, or $IC_6F_{12}I$ as the CTAs (as displayed in Figure 1) exhibits different signals centered at 3.3, 3.6, and 3.8 ppm attributed to $-CH_2CF_2-$ in normal VDF−VDF dyads, $C_4F_8-CH_2CF_2-$, and $-CF_2CH_2-I$,[4,5,60] respectively. The negligible intensity of the triplet of triplets centered at 6.3 ppm, assigned to HCF_2 end-group, indicates the absence of any transfer to VDF, to water, or to the copolymers. Interestingly, the absence of signal centered at 2.5 ppm shows the absence of tail-to-tail addition of VDF for low molecular weights and is in agreement with previous works[16,17,20] that evidence a controlled copolymerization, while that multiplet is noted for higher-molecular-weight copolymers.

^{19}F NMR spectra of the poly(VDF-*co*-PMVE) copolymers produced from an initial $[VDF]_0/[PMVE]_0$ molar ratio of 50/50 in the presence $C_6F_{13}I$ as the CTA are shown in Figure 2A. It shows various features: (i) the absence of signal at −60 ppm that confirms the total CTA consumption; (ii) the characteristic signals centered at −91, −110, −82, and from −121.8 to −126.0 ppm assigned to the difluoromethylene groups of "normal" VDF−VDF dyads, to VDF unit adjacent to a PMVE in VDF−PMVE dyad, to CF_3 end-group and to the C_4F_8 inner group of the C_6F_{13} end-group, respectively; (iii) signals centered at −39 and −108 ppm attributed to $-CH_2-CF_2-I$ and $-CF_2-CH_2-I$ end-groups, respectively; (iv) interestingly, that spectrum does not show any signal assigned to the reverse head-to-head

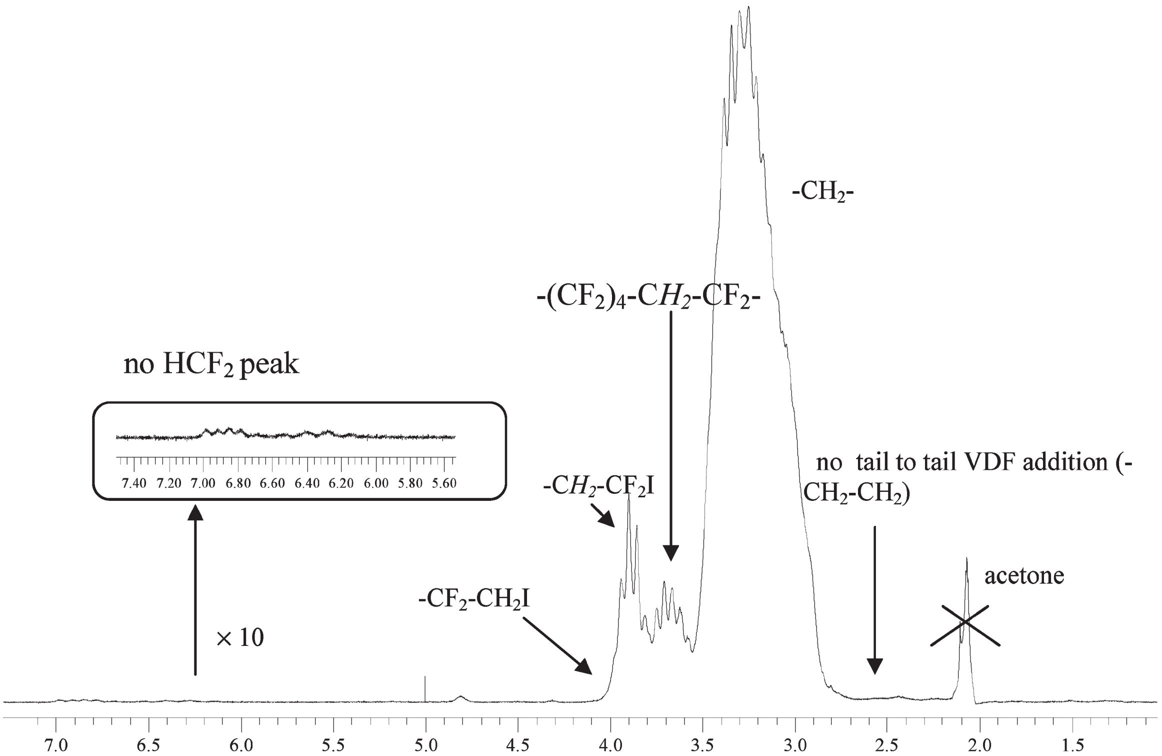


Figure 1. Typical ^{1}H NMR spectrum (recorded in deuterated acetone) of poly(VDF-*co*-PMVE) copolymer obtained by iodine transfer copolymerization of vinylidene fluoride (VDF) and perfluoromethyl vinyl ether (PMVE) in the presence of $IC_6F_{12}I$. VDF/PMVE mol %/mol % feed is 70/30 while it is 74/26 in the copolymer. M_n (assessed by ^{19}F NMR) = 4000 g mol^{-1} (run 21 of Table 3).

addition VDF units (i.e., $-CH_2-CF_2-CF_2-CH_2$) usually observed at −113.7 and −115.7 ppm[5,12,16,60] and thus confirms the lack of tail-to-tail VDF addition reported above; (v) the characteristic signal centered at −52 ppm is assigned to the $-OCF_3$ of PMVE.[7,11] The other signals of PMVE are located at −122.5 and −126.8 ppm[7,11] and are attributed to the $-CF_2-$ and $-CF-$ groups, respectively; (vi) and finally, the signal at −146.0 ppm corresponds to $-CF(OCF_3)-$ of PMVE unit adjacent to a reversed VDF unit.

Figure 2B represents the ^{19}F NMR spectrum of poly(VDF-*co*-PMVE) copolymers synthesized using an initial $[VDF]_0/[PMVE]_0$ molar feed ratio of 69/31 in the presence of 1,4-diiodoperfluorobutane. Similar signals are observed except those assigned to the fluorinated groups arising from the CTAs (i.e., those centered at −125.0 ppm attributed to $-CF_2(CF_2)_nCF_2-$).

Figures S2, S3, and S4 in the Supporting Information exhibit the NMR spectra of several poly(VDF-*co*-PMVE) copolymers synthesized in this study in the presence of different CTAs. For example, Figure S3 shows the ^{19}F NMR spectrum of poly(VDF-*co*-PMVE) obtained using an initial $[VDF]_0/[PMVE]_0$ molar feed ratio 40/60, yielding a copolymer with a molar composition 54/46 in VDF/PMVE. The presence of short PVDF microblocks is revealed by the low intensity of signals centered at −92.0 ppm. The absence of oligo(PMVE) block arises from the nonhomopolymerizability of this monomer (i.e., $r_{PMVE} = 0$ at 74 or 80 °C) as demonstrated in previous publications.[7,11]

2. Study of the Chain Extremities of Poly(VDF-*co*-PMVE) Copolymers Obtained by Iodine Transfer Copolymerization. ^{19}F NMR analysis also allows to determine the different end-group functionalities (Scheme 2) of the copolymers (Figures S2 and S3 in the Supporting Information). According to Figures 1 and 3, two different signals attributed to end-groups, i.e., $-CH_2CF_2I$ and $-CF_2CH_2I$, are noted at −40.0 and −109.0 ppm.[16] Surprisingly, the signals attributed to a copolymer terminated by a PMVE unit, i.e., $-CF(OCF_3)-I$ and $CF(OCF_3)-CF_2-I$, were not observed whatever the $[PMVE]_0/[VDF]_0$ molar feed ratio (Scheme 2) and the initial feed ratio and the nature of CTA used (Figures S2, S3, and S4). Indeed, the addition of PMVE onto VDF radical is not regioselective and occurs via two possible pathways: either the normal addition, i.e., the addition of the radical onto CH_2 of VDF leading to $-CF_2CF(OCF_3)-CH_2CF_2-$ dyad (73%) or the reverse addition, i.e., the addition of the radical onto CF_2 of VDF yielding $-CF_2CF(OCF_3)-CF_2CH_2-$ dyad (27%)[7] (see Scheme 2B), followed by the transfer onto CTA.

However, the absence of these signals may be simply due to their overlapping with other fluorine signals of the copolymers. To determine accurately the chemical shift of both these signals, the synthesis of model compounds was investigated using the radical addition of iodo compounds onto PMVE. These monoadditions gave low yields (<10%) (Table 1) and byproduct for most iodo compounds, except for ICF_2I. Although a similar result was reported by Yang,[61] no clear explanation can be suggested on this unexpected behavior. Fortunately, in the case of ICF_2I, a satisfactory yield was obtained (ca. 75%) and two isomers were isolated (Figure S1 in the Supporting Information). The ^{19}F NMR spectrum reveals that normal $ICF_2CF_2CF(OCF_3)I$:reverse $ICF_2CF(OCF_3)CF_2I$ ratio was 88:12.

The model study reveals that the signatures of CF and CF_2 in $-CF(OCF_3)-I$ and $CF(OCF_3)-CF_2-I$ groups are observed at −73.0 and −59.0 ppm, respectively. These regions in the ^{19}F NMR spectrum are clear and both of these end-groups are absent in the resulting poly(VDF-*co*-PMVE) copolymers.

Figure 3 exhibits the evolution of the functionality in $-CH_2CF_2I$ and $-CF_2CH_2I$ versus the number of VDF units in the copolymer. The $-CH_2CF_2I$ end-group decreases with the increase of the VDF units in the copolymer. This drop of

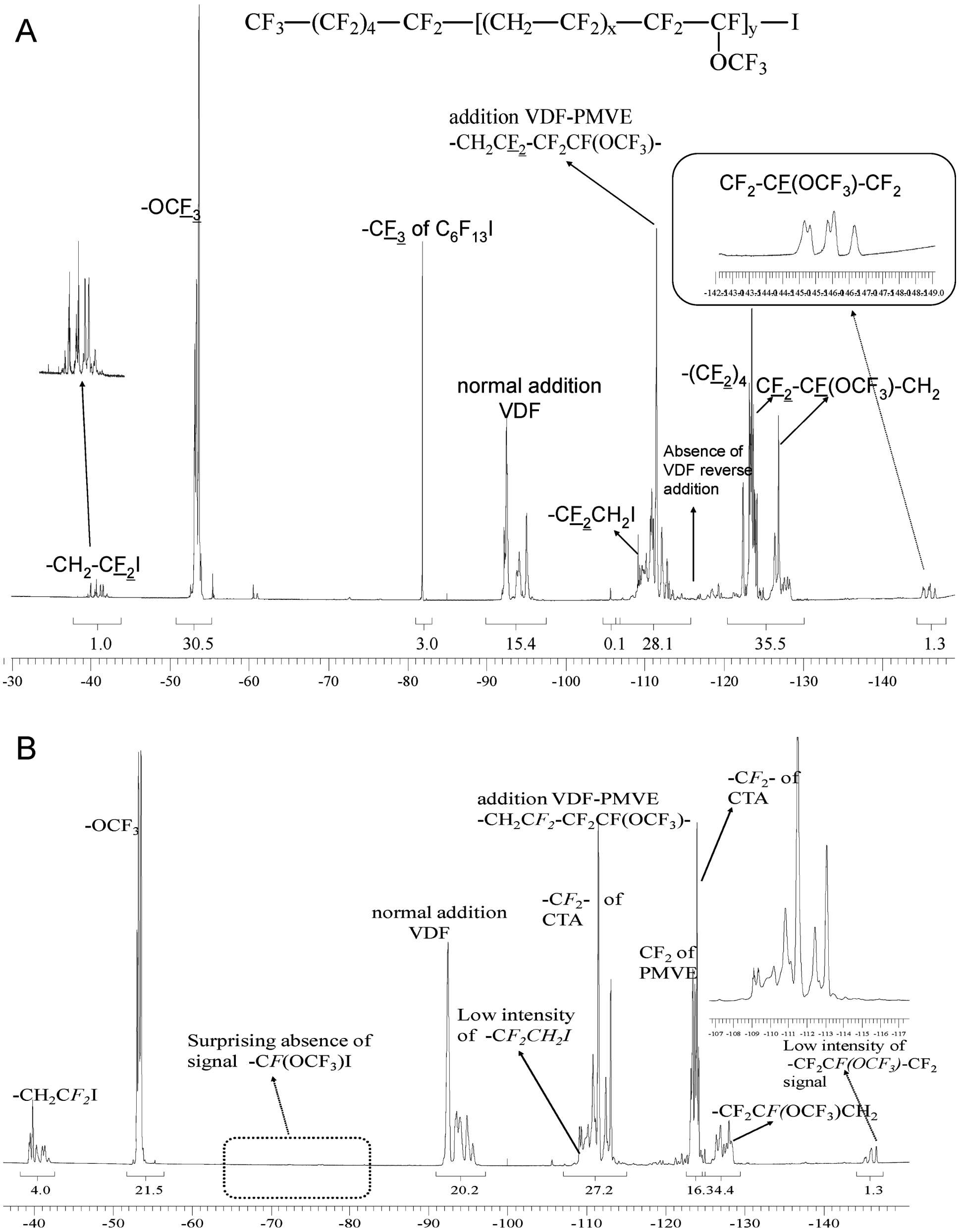


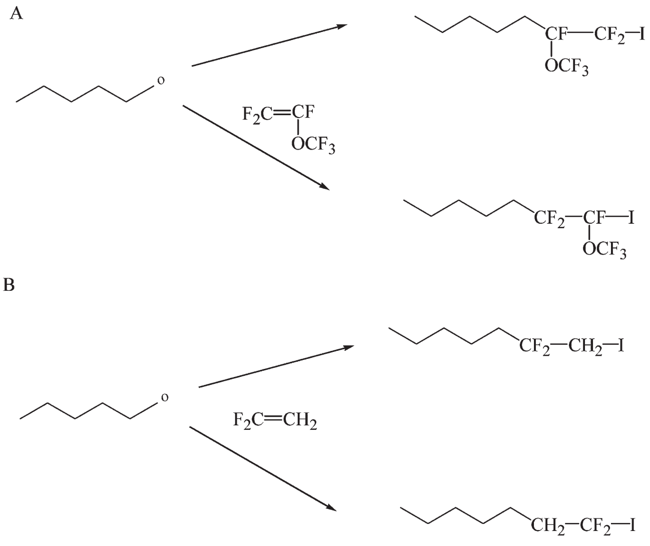
Figure 2. ^{19}F NMR spectra (recorded in deuterated acetone at 298 K) of poly(VDF-*co*-PMVE) copolymers obtained by iodine transfer copolymerization of vinylidene fluoride (VDF) and perfluoromethyl vinyl ether (PMVE): (A) in the presence of $C_6F_{13}I$ as the chain transfer agent, experimental part: VDF/PMVE molar feed ratio = 50/50 (mol %), composition = 60/40, M_n by ^{19}F NMR = 3000 g mol^{-1}, run 18 in Table 3); (B) in the presence of IC_4F_8I, experimental part: VDF/PMVE molar feed ratio = 65/35, composition = 70/30, M_n (assessed by NMR) = 1800 g mol^{-1} and M_n (assessed by SEC) = 2200 g mol^{-1}, run 27 of Table 3) at 80 °C with $Na_2S_2O_8$ as the initiator.

functionality is due to the inversion of VDF and the accumulation of $-CF_2CH_2I$ in the course of the polymerization. It is possible to simulate the evolution of the functionality versus the number of VDF units in the copolymers using the equation for a monofunctional CTA: $-CF_2I$ functionality = δ^{y-1}, where y and δ represent the number of VDF units centered at −92 ppm and the rate of normal addition, respectively. This equation assumes that the difference of reactivity between a $-CH_2I$ and a $-CF_2I$ (and also $-CF_2CF(OCF_3)I$ and $-CF(OCF_3)CF_2I$) is high. The second assumption concerns the regioselectivity of the first monoaddition of monomer onto the CTA. These assumptions were demonstrated experimentally in a previous work that reports the homopolymerization of VDF.[16,55] Interestingly, the incorporation of PMVE does not affect the decrease of $-CH_2CF_2I$ functionality (Figure 3).

Finally, the nature of CTA was also investigated. As observed in the case of monofunctional CTA, the functionality in $-CH_2CF_2I$ decreases with the increase of VDF in the polymer chain for the polymer obtained with difunctional CTAs.

3. Characterization of Copolymers by MALDI-TOF. The structures of the copolymers obtained by iodine transfer polymerization (ITP) of VDF with PMVE in the presence of $C_6F_{13}I$ were also characterized by MALDI-TOF analysis. Figure 4 gives an example for a copolymer ($M_{n,SEC}$ = 2200 g mol^{-1}, PDI = 1.41, 83/17 mol % in VDF/PMVE)). This technique was previously used for the characterization of VDF telomers obtained by free radical telomerization[62] and by ITP.[55] To the best of our knowledge, it is the first time that the characterization of poly(VDF-*co*-PMVE) copolymers has been carried out by MALDI-TOF. Figure 4 shows the

Scheme 2. Possible Chain End-Groups Obtained by Iodine Transfer Polymerization: (A) Terminated by Perfluoromethyl Vinyl Ether (PMVE) Unit and (B) Terminated by Vinylidene Fluoride (VDF) Unit



spectrum for $C_6F_{13}-[(VDF)_x-PMVE]_y-I$ copolymers. The different populations of the peak series separated by 166 Da corresponds to the molecular weight of one PMVE unit (Table 2). In each peak series, different peaks separated by 64 Da (molecular weight of VDF) are observed. All of these populations can be attributed to the expected $C_6F_{13}-[(VDF)_x-PMVE]_y-I$ due to a good agreement with the theoretical and experimental molecular weight assessed by MALDI-TOF. Thus, MALDI-TOF analysis confirms (i) the presence of chain transfer agent (CTA), i.e., $C_6F_{13}I$ and the insertion of PMVE into the copolymer, and (ii) the absences of the population generated by the direct initiation, i.e., $NaSO_4-[(VDF)_x-PMVE]_y-I$ and of the VDF homopolymers, such as $NaSO_4-(VDF)_n-I$ or $C_6F_{13}-(VDF)_n-I$ (see Table 2). These results suggest a good reactivity of PMVE with VDF in aqueous solution.

4. Influence of the CTA. *4.1. Determination of the Transfer Constant (C_T) for VDF Polymerizations.* As reported in the above section, $CF(OCF_3)-I$ and $CF(OCF_3)-CF_2I$ end-groups were not observed. To understand this phenomenon, it was of interest to assess the chain transfer constant ($C_T = k_{tr}/k_p$ ratio, where k_{tr} and k_p stand for the transfer rate and the propagation rate, respectively) for a series of CTAs. Four CTAs, i.e., $C_6F_{13}CH_2CF_2I$, $HCF_2CF_2CH_2I$, $CF_3CF(OCF_3)I$, and $CF_3(CF_2)_4CF_2I$, were used as models of poly(PMVE-*co*-VDF)−I copolymers to mimic both possible end-groups generated during the ITP of VDF and PMVE (Scheme 2). $C_6F_{13}CH_2CF_2I$ and $HCF_2CF_2CH_2I$ mimic a VDF terminated copolymers, i.e., normal addition and reverse addition, respectively, while $CF_3CF(OCF_3)I$ and $CF_3(CF_2)_4CF_2I$ represent a PMVE-terminated polymer. Two other CTAs, CF_3CF_2I and $(CF_3)_2CFI$, were included in this study to give a better comparison on their relative reactivities.[16,55]

To simplify the C_T assessment, ITP reaction was carried out in the presence of VDF without any PMVE and stopped at low conversion (< 30%). The CTA and VDF consumptions were monitored using previously reported techniques.[55] Briefly, CTA consumption was determined by the decrease of the intensity of signal centered at −60.0 ppm for the polymerization. Then, the slope of ln $[CTA]/[CTA]_0$ versus ln $[M]/[M]_0$ gives the transfer constant value. A rapid consumption of CTAs ($CF_3CF(OCF_3)I$, CF_3CF_2I, $C_6F_{13}I$, or $C_6F_{13}CH_2CF_2I$) was observed, while in the case of $HCF_2CF_2CH_2I$, a faster VDF consumption than that of CTA was noted. The transfer constant was assessed from O'Brien and Gornick's method.[63] Figure 5 represents the evolution of $\ln([CTA]_0/[CTA])$ consumption versus $\ln([VDF]_0/[VDF])$. Thus, the following decreasing order of reactivity of these CTAs was established: $CF_3CF(CF_3)I$ (C_T = 13.1) > $CF_3CF(OCF_3)I$ (11.3) > CF_3CF_2I (7.4) ~ $C_6F_{13}I$ (7.1) ~ $C_6F_{13}CH_2CF_2I$ (7.0) ≫ $HCF_2CF_2CH_2I$ (0.4) at 75 °C.

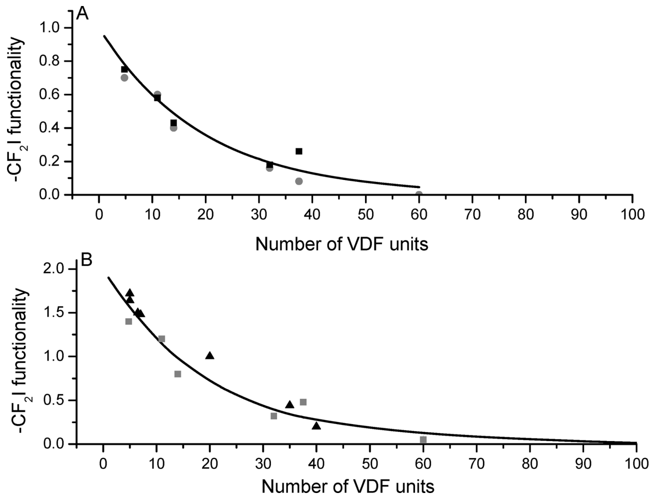


Figure 3. Evolution of $-CH_2CF_2I$ functionality by polymeric chain versus number of VDF units (y) in the copolymer (VDF units centered at −92 ppm, calculated by $y = \int -92\ \text{ppm}/2$) in the case of iodine transfer copolymerization of vinylidene fluoride (VDF) and perfluoromethyl vinyl ether (PMVE): (A) In the presence of $C_6F_{13}I$ as the chain transfer agent; full line represents the theoretical line calculated by the following equation: $f^{CF_2I} = 0.95^{y-1}$, where y corresponds to VDF centered at −92 ppm (micro-PVDF domain): (●, gray) homopolymerization of VDF[55] and (■, black) for copolymerization with PMVE. (B) In the presence of (▲, black) IC_4F_8I and (■, gray) $IC_6F_{12}I$. (Full line represents the theoretical line calculated by following equation: $f^{CF_2I} = 2 \times 0.95^{y-1}$).

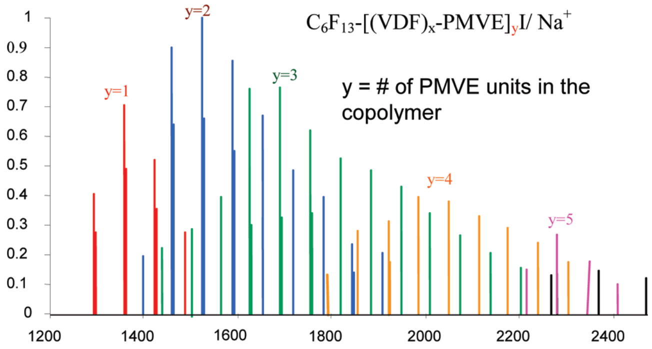


Figure 4. Assignments of the different populations characterized by MALDI-TOF analysis for a poly(VDF-*co*-PMVE) copolymer obtained by iodine transfer polymerization, of composition 83/17 mol %, VDF/PMVE (run 11 of Table 3, M_n by ^{19}F NMR = 2200 g mol^{-1}). Note: y represents the number of PMVE in poly(VDF-*co*-PMVE) copolymers. Note: the MALDI-TOF spectrum was modified to help the reader to identify the different populations present in this sample.

Using this technique, two different groups could be identified: the first one (i.e., CF_3CF_2I, $CF_3CF(OCF_3)I$, and $CF_3CF(CF_3)I$) presents a C_T value greater than 1, in agreement with the fast consumption of the transfer agent, while the second group ($HCF_2CF_2CH_2I$) exhibits a low transfer constant (lower than 1). The low reactivity of $-CH_2I$ can be attributed to higher stability of $-C-I$ bond compared to that in $-CF_2-I$. This arises from the presence of both

Table 2. Assignment of the Peaks in the MALDI-TOF Spectrum of a Copolymer Sample ($M_{\mathrm{n\ targeted}}$ = 2500 g mol^{-1}, $M_{\mathrm{n,SEC}}$ = 2200 g mol^{-1}, PDI = 1.41, of Composition 83/17 mol % in VDF/PMVE) Synthesized by Iodine Transfer Copolymerization Using $Na_2S_2O_8$ as the Initiator and $C_6F_{13}I$ as the Chain Transfer Agent

populations	series	structures
$y = 1$	1294.81; 1358.82; 1422.85; 1486.86; 1550.88	C_6F_{13}−(VDF)$_x$−(PMVE)$_y$−I, with x = 12−16
$y = 2$	1396.35; 1396.35 + n × 64; 1846.01	C_6F_{13}−(VDF)$_x$−(PMVE)$_y$−I, with x = 11−18, y = 2
$y = 3$	1562.78; 1562 + n × 64; 2010.82	C_6F_{13}−(VDF)$_x$−(PMVE)$_y$−I, with x = 11−15, y = 3
$y = 4$	1792.78; 1792 + n × 64; 1984.80	C_6F_{13}−(VDF)$_x$−(PMVE)$_y$−I, with x = 12−15, y = 4
$y = 5$	2214.8; 2214.8 + n × 64; 2343.40	C_6F_{13}−(VDF)$_x$−(PMVE)$_y$−I, with x = 15−18, y = 5

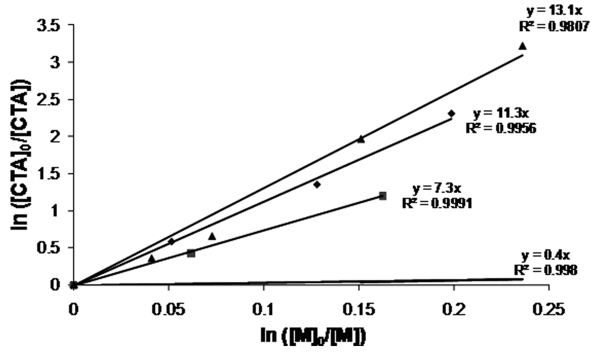


Figure 5. Determination of the transfer constants for different chain transfer agents using the O'Brien and Gornick method ((■) CF_3CF_2I, (◆) $CF_3CF(OCF_3)I$, (▲) $CF_3CF(CF_3)I$, and (—) $HCF_2CF_2CH_2I$) from the slope of ln ([CTA]$_0$/[CTA]) versus ln ([M]$_0$/[M]). Experimental conditions: the reaction was stopped at low monomer conversion (< 30%).

fluorine atoms as substituents in $-CF_2-I$ and thus a better stabilization of $CF_2^{\bullet}$ radical. The greater reactivity of $-CF_2CF(OCF_3)I$ end-group induces the absence of the ^{19}F NMR signal assigned to $-CF(OCF_3)I$. Indeed, when produced, this species tends to transfer, resulting in a propagating polymeric chain. The low reactivity of $-CH_2I$ is in agreement with its accumulation in the polymerization medium and also confirms previous work.[16]

4.2. Influence of the CTA Concentration on the Molecular Weights of the Poly(VDF-co-PMVE) Copolymers. Table 3 exhibits the evolution of the molecular weights of the copolymers versus the concentration of CTAs. The initial molar ratio of VDF and PMVE comonomers over CTA controls the targeted average degree of polymerization ($DP_{\mathrm{n,targeted}}$) and then the molecular weight: $M_{\mathrm{n,targeted}} = [[\mathrm{VDF}]_0 \times \mathrm{MW_{VDF}} + [\mathrm{PMVE}]_0 \times \mathrm{MW_{PMVE}}]/([\mathrm{CTA}]_0) + \mathrm{MW_{CTA}}$, where $\mathrm{MW_{VDF}}$ and $\mathrm{MW_{VDF}}$ represent the molecular weights of VDF and PMVE, respectively. This equation can be used for a monomer conversion close to 100%. In addition, dead chains generated from the excess of initiator used in the polymerization are neglected. Using ^{19}F NMR spectroscopy (Figure 2), the experimental molecular weights can be assessed from the following equation: $M_{\mathrm{n}} = [{}^{3}/_{2}(\int CF_2{}^{-39\,\mathrm{ppm}} + \int CF_2{}^{-91\,\mathrm{ppm}} + \int CF_2{}^{-108\,\mathrm{ppm}} + \int CF_2{}^{-112\,\mathrm{ppm}})/\int CF_3{}^{-82\,\mathrm{ppm}}] \times \mathrm{MW_{VDF}} + [{}^{3}/_{2}\int CF_3{}^{-53\,\mathrm{ppm}}/\int CF_2{}^{-82\,\mathrm{ppm}}] \times \mathrm{MW_{PMVE}} + \mathrm{MW_{CTA}}$ where $\int CF_x{}^{-i\,\mathrm{ppm}}$ stands for the integral of the chemical shift centered at $-i$ ppm assigned to CF_x group. It is noted that the experimental and the targeted molecular weights are in good agreement. The slight difference between the values assessed from SEC and ^{19}F NMR are attributed to the SEC calibration (involving polystyrene standards and not well-defined poly(VDF-*co*-PMVE) copolymers; Figure S4 in the Supporting Information). However, these results indicate a satisfactory control of the copolymerization in emulsion, in agreement with a relatively low PDI.

To demonstrate the controlled behavior of this copolymerization, the kinetics of iodine transfer polymerization (ITP) of VDF and PMVE was determined in the presence of $IC_6F_{12}I$ as the CTA and with different molar feed ratios of PMVE/VDF. The reaction was monitored by sampling in the autoclave. Targeted $\overline{DP}_{\mathrm{n}}$ values were chosen low enough to allow the formation of soluble oligomers which are suitable for both size exclusion chromatography (SEC in DMF or THF) and ^{19}F NMR spectroscopy (using deuterated acetone as the solvent). The former technique enabled us to access the relative molecular weights and PDI of the synthesized polymers, while the latter one gave information on the conversions of monomer (α_{VDF} and α_{PMVE}), consumption of CTA, the average number degree of polymerization ($\overline{DP}_{\mathrm{n}}$), and also allowed to identify the end-groups.

VDF conversion (α_{VDF}) was determined by ^{19}F NMR taking into account the signals previously described in the ^{19}F NMR section spectroscopy and using a previous work on ITP of VDF.[16] As the initial amount of VDF, PMVE, and CTA are known, VDF conversion can be assessed by the following equation:

$$\alpha_{\mathrm{VDF}} = \frac{(\int CF_2{}^{-39.0\,\mathrm{ppm}} + \int CF_2{}^{-92.0\,\mathrm{ppm}} + \int CF_2{}^{-110\,\mathrm{ppm}} + \int CF_2{}^{-108.0\,\mathrm{ppm}} + \int CF_2{}^{-113\,\mathrm{ppm}} + \int CF_2{}^{-116\,\mathrm{ppm}})_t/2}{[(\int CF_2{}^{-123.0\,\mathrm{ppm}} + \int CF_2{}^{-124.0\,\mathrm{ppm}})_t - 2/3 \times ((\int CF_3{}^{-53\,\mathrm{ppm}})_t)]/8} \times \frac{[\mathrm{CTA}]_0}{[\mathrm{VDF}]_0} \quad (1)$$

where $\int CF_x{}^{-i\,\mathrm{ppm}}$, [CTA]$_0$, and [VDF]$_0$ represent the integral of the signal assigned to CF_x group centered at $-i$ ppm and the initial concentrations of CTA and VDF, respectively.

PMVE consumption was assessed by using the signal of CF_3O- side group of PMVE centered at −53 ppm and the characteristic signals of CTA at −121 and −122 ppm, used as the reference.

$$\alpha_{\mathrm{PMVE}} = \frac{(\int CF_3O{}^{-53\,\mathrm{ppm}})_t/3}{[(\int CF_2{}^{-123.0\,\mathrm{ppm}} + \int CF_2{}^{-124.0\,\mathrm{ppm}})_t - 2/3 \times ((\int CF_3{}^{-53\,\mathrm{ppm}})_t)]/8} \times \frac{[\mathrm{CTA}]_0}{[\mathrm{PMVE}]_0} \quad (2)$$

where $\int CF_x{}^{-i\,\mathrm{ppm}}$, [CTA]$_0$, and [PMVE]$_0$ represent the integral of the signal assigned to CF_x group centered at $-i$ ppm and the concentrations of CTA and PMVE at t = 0, respectively.

$IC_6F_{12}I$ conversion ($\alpha_{IC_6F_{12}I}$) can also be calculated from ^{19}F NMR analysis by monitoring the decrease of the integral of the signal centered at −121.0 ppm (characteristic of $-CF_2-CF_2I$ in $IC_6F_{12}I$). This signal is shifted from −121.0 to −122.0 ppm attributed to $-CF_2-$ in adjacent position to $-CF_2-$ (eq 3).

$$\alpha_{IC_6F_{12}I} = \frac{(\int CF_2{}^{-60.0\,\mathrm{ppm}})_t/2}{(\int CF_2{}^{-121.0\,\mathrm{ppm}})_t/2 + (\int CF_2{}^{-122.0\,\mathrm{ppm}})_t/2} \quad (3)$$

Table 3. Poly(VDF-*co*-PMVE) Copolymers Synthesized by Iodine Transfer Copolymerization of Vinylidene Fluoride (VDF) and Perfluoromethyl Vinyl Ether (PMVE) in the Presence of $C_6F_{13}I$, IC_4F_8I, or $IC_6F_{12}I$ Used as Chain Transfer Agents at 80 °C without Any Surfactant, Using $Na_2S_2O_8$ as the Initiator[a]

		feed molar ratio (mol %)		composition of copolymer (mol %)					M_n (g mol^{-1})				
runs	CTA	% VDF	% PMVE	% VDF	% PMVE	time (h)	yield (%)	$M_{n,\text{targeted}}$ (g mol^{-1})	SEC[b]	^{19}F NMR	PDI (SEC)[b]	T_g (DSC)	T_d (TGA)$^{10\%}$
10	$C_6F_{13}I$	90	10	90	10	8	85	3300	4100	3200	1.38	−40	305
11	$C_6F_{13}I$	74	26	83	17	6	80	2500	2600	2200	1.41	−54	220
12	$C_6F_{13}I$	74	26	82	18	6	85	1900	2200	1700	1.36	−57	205
13	$C_6F_{13}I$	70	30	79	21	8	85	3900	4200	3800	1.40	−52	295
14	$C_6F_{13}I$	65	35	69	31	8	80	2900	3500	2800	1.36	−50	280
15	$C_6F_{13}I$	65	35	69	31	8	80	3200	4000	3200	1.38	−48	285
16	$C_6F_{13}I$	60	40	65	35	8	75	2900	2700	2500	1.40		
17	$C_6F_{13}I$	51	49	61	39	8	75	5500	5200	4450	1.41	−43	260
18	$C_6F_{13}I$	50	50	62	38	8	75	3300	3350	3200	1.40	−45	250
19	$C_6F_{13}I$	40	60	54	46	8	65	3300	2700	2200	1.35	−45	260
20	$IC_6F_{12}I$	80	20	83	17	8	90	3400	3300	3900	1.75	−48	250
21	$IC_6F_{12}I$	70	30	74	26	8	85	6000	4500	4000	1.70		
22	$IC_6F_{12}I$	54	46	65	35	8	70	12400	9500	8600	1.72	−42	280
23	$IC_6F_{12}I$	50	50	60	40	8	65	5000	3800	3400	1.75		
24	$IC_6F_{12}I$	48	52	60	40	8	67	12000	10000	10800	1.75	−40	300
25	IC_4F_8I	95	05	92	08	8	90	4900	5900	4500	1.40		
26	IC_4F_8I	74	26	82	18	8	90	3400	3900	3300	1.40		
27	IC_4F_8I	65	35	70	30	8	85	2100	2200	1800	1.38	−66	220
28	IC_4F_8I	60	40	65	35	8	75	1250	1600	1300	1.27	−55	240
29	IC_4F_8I	50	50	60	40	8	70	1300	1700	1200	1.47	−58	210
30	IC_4F_8I	45	55	60	40	8	70	7700	6900	5700	1.39	−48	330
31	IC_4F_8I	29	71	55	45	8	65	2700	2700	2300	1.35	−49	280
32	IC_4F_8I	45	55	60	40	8	75	24000	21400	18000	1.35	−38	280

[a] Experimental conditions: Co = $[\text{initiator}]_0/[\text{monomer}]_0$ = 1%. $M_{n,\text{targeted}} = ([\text{VDF}]_0 + [\text{PMVE}]_0)/[C_6F_{13}I]_0$, measured by SEC analysis (polystyrene standards); $T_d^{10\%}$ stands for the thermal temperature when the poly(VDF-*co*-PMVE) copolymer has lost 10 wt %. [b] SEC analysis (DMF or THF according the molecular weights of copolymer, DMF used for $M_n > 5000$ g mol^{-1}).

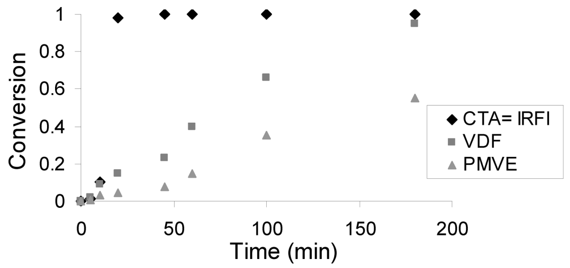


Figure 6. Conversion profiles of $IC_6F_{12}I$ as the chain transfer agent, vinylidene fluoride (VDF), and perfluoromethyl vinyl ether (PMVE) versus time assessed by ^{19}F NMR for the iodine transfer copolymerization of VDF and PMVE performed at 80 °C from 54/46 (mol %) feed of VDF/PMVE initiated by $Na_2S_2O_8$ (run 22 of Table 3).

VDF and PMVE conversions increase with time (Figure 6). It is noted that, at 75 °C after 15 min only, $IC_6F_{12}I$ was totally consumed. This behavior is characteristic of a CTA that has a high transfer constant.[64]

Figure 7 represents the evolution of M_n versus the VDF and PMVE conversions showing that the molecular weight increases with α_{VDF}. Interestingly, it is noted that experimental M_n increases linearly with monomer conversion. This figure clearly demonstrates the controlled or "pseudo-living" character[65] of iodine transfer copolymerization (ITP) of VDF with PMVE. This is the first time that this behavior is reported in the literature for these monomers.

This controlled character was also confirmed from SEC chromatograms of the sampled reaction mixtures. As expected, the SEC signals assigned to poly(VDF-*co*-PMVE)−I were negative (because of the detection by refractometer) due to the high content of fluorine atoms. The SEC chromatograms were shifted toward lower elution volumes, i.e., to higher molecular weights (Figure 7A) versus the conversion of fluoroalkenes. This observation is supported by Figure 7B in which a linear increase of the molecular weights versus VDF conversion is observed for experiments performed with $IC_6F_{12}I$. This behavior is typical of a living character and

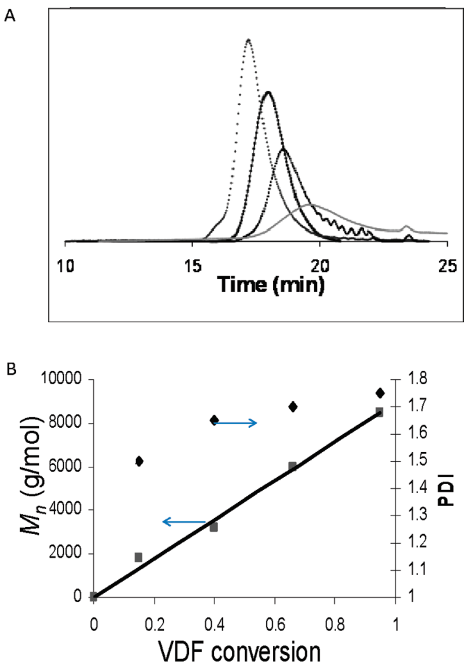


Figure 7. (A) Evolution of SEC traces for different conversions (right to left: 18%, 38%, 63%, and 95% of VDF conversion) for the iodine transfer copolymerization of vinylidene fluoride (VDF) and perfluoromethyl vinyl ether (PMVE) using $IC_6F_{12}I$ as the chain transfer agent (54/46 in molar feed ratio in VDF/PMVE, composition of copolymer 65/35 mol % of VDF/PMVE, run 22 of Table 3). (B) Evolution of molar masses, M_n (■), and polydispersity indices, PDI (◆), versus VDF conversion (the straight line corresponds to the theoretical curve).

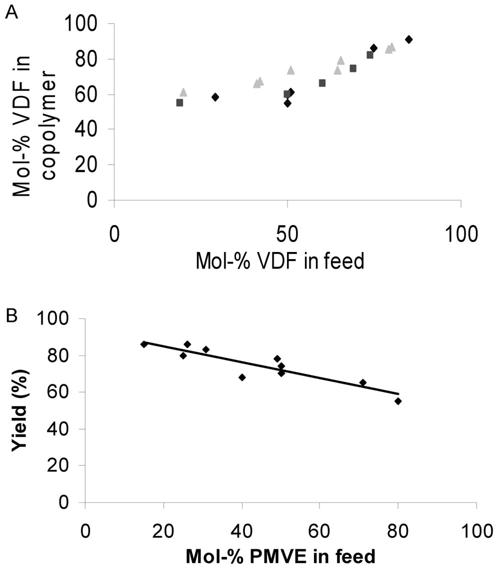


Figure 8. (A) Evolution of the copolymer composition (mol % in vinylidene fluoride, VDF) versus molar VDF feed ratio (■, black) in emulsion using iodine transfer copolymerization (ITP) and $C_6F_{13}I$ as the chain transfer agent (◆, black) in solution (conventional radical polymerization (TBPPI: *tert*-butyl peroxypivalate as the initiator) (▲, gray) in emulsion (ITP, IC_4F_8I). (B) Evolution of yield versus mol % PMVE in feed in the case of the ITP of VDF and PMVE.

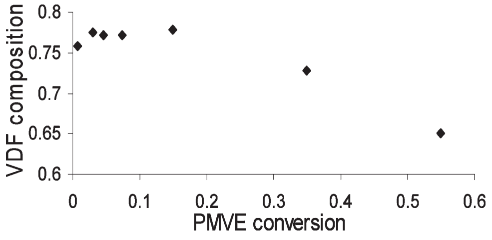


Figure 9. Evolution of vinylidene fluoride (VDF) composition (mol % of VDF in the copolymer) versus perfluoromethyl vinyl ether (PMVE) conversion for the iodine transfer copolymerization of VDF and PMVE performed from 54/46 (mol %) feed of VDF/PMVE in the presence of $IC_6F_{12}I$ initiated by $Na_2S_2O_8$ (run 22 of Table 3).

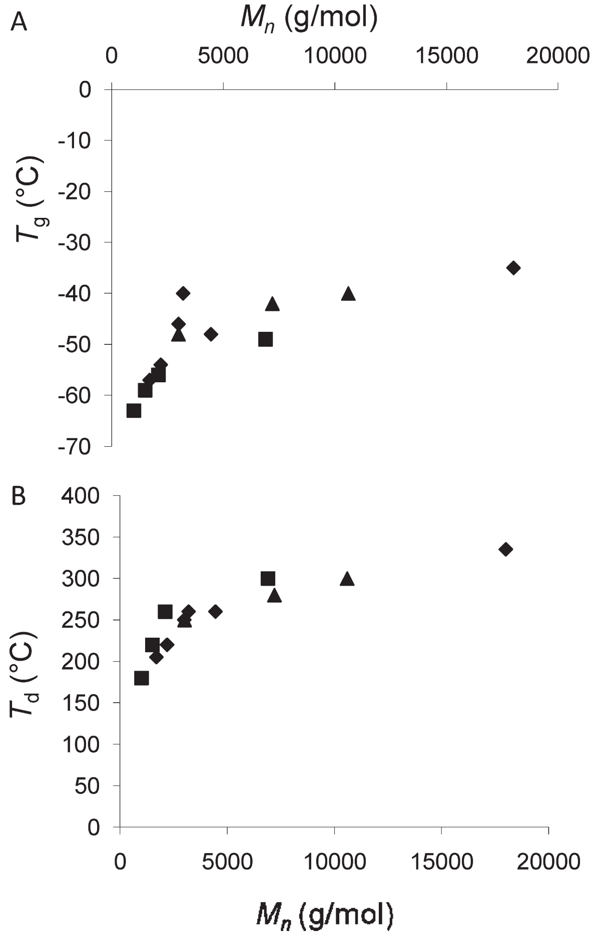


Figure 10. Thermal properties of poly(PMVE-*co*-VDF) copolymers obtained by iodine transfer copolymerization of vinylidene fluoride (VDF) and perfluoromethyl vinyl ether (PMVE) in emulsion at 80 °C: (A) Glass transition temperature, T_g, values versus molecular weights, M_n, assessed by ^{19}F NMR for different chain transfer agents: (◆) IC_4F_8I, (▲) $IC_6F_{12}I$, and (■) $C_6F_{13}I$ (composition of copolymers close to 60/40 in mol % VDF/PMVE). (B) Influence of M_n (assessed by ^{19}F NMR) on the decomposition temperature, T_d, values for different chain transfer agents: (◆) IC_4F_8I, (▲) $IC_6F_{12}I$, and (■) $C_6F_{13}I$ (composition of copolymers close to 60/40 in mol % VDF/PMVE).

also corresponds to a high chain transfer constant value of the diiodinated CTAs.[66,67]

5. Composition of the Copolymers. The VDF composition of the copolymers was monitored versus the feed ratio composition of VDF for different copolymerizations using iodine transfer radical polymerization (ITP) and conventional radical polymerization. It was observed that there is a concomitant increase in VDF composition as the feed ratio in VDF also increased (Figure 8A). This is in good agreement with previous studies[7,11] which report a satisfactory copolymerization of VDF with PMVE. However, the overall yield polymer (Figure 8B) decreases slowly with the increase of PMVE, as in the case of radical copolymerization of VDF with hexafluoropropylene (HFP). This is attributed to the absence of homopolymerization of PMVE[7,11] or HFP. In addition, the structure of CTA does not influence the reactivity of PMVE and VDF. Finally, as expected, the results obtained by conventional radical polymerization (in solution) and by ITP give similar VDF and PMVE compositions in the copolymers. In conclusion, the nature of the solvent (i.e., acetonitrile[7] or water in the present case) and the type of polymerization (solution[7] or emulsion) did not affect the reactivity of these monomers and the final compositions of these copolymers.

The consumptions of VDF and PMVE (and thus the composition of these copolymers) during the polymerization reaction were assessed. Figure 9 shows the mol % of VDF in the copolymer (assessed by ^{19}F NMR) versus the PMVE conversion. The composition in VDF decreases with the PMVE conversion. This behavior is a consequence of the low reactivity of PMVE and yielded a gradient copolymer with a relative increase of PMVE units in the copolymers as its conversion proceeds. As expected, the consumption of PMVE is not quantitative and stops when the VDF concentration in the feed is low, since PMVE does not homopolymerize.[11] Jaack or Macret's methods[68,69] enabled us to assess the reactivity ratios, r_1 and r_2. Both these methods require a large excess of one monomer with respect to the second one and can be successfully used in the case of large difference in monomer reactivity and in monomer amount. In this present case, PMVE ($r_{PMVE} = 0$ at 74 °C) confirms Schmiegel's results,[11] and then a good estimation of r_{VDF} in this copolymerization is possible. The reactivity ratio of VDF, r_{VDF}, can be determined by plotting ln([VDF]/[VDF]$_0$) versus ln([PMVE]/[PMVE]$_0$). r_{VDF} is given by the value of the slope of the straight line ($r_{VDF} = 2.5$ at 80 °C) (Figure S5 in the Supporting Information). This value is in good agreement with the observation that VDF mol % in the copolymer is always higher than that of PMVE. However, this value is lower than that found when the copolymerization was carried out in organic media ($r_{VDF} = 3.40$ and $r_{PMVE} = 0$ in acetonitrile at 74 °C).[7] No clear explanation was found for this difference.

6. Thermal Properties of Poly(PMVE-*co*-VDF) Copolymers. *6.1. Determination of the Glass Transition Temperatures (T_gs) of Poly(VDF-co-PMVE) Copolymers.* PVDF homopolymer is composed of both amorphous (30−60%) and crystalline (40−70%) regions, with a glass transition (T_g) and a melting (T_m) temperatures in the range of −45 to −30 and 155−170 °C, respectively, depending on the sample (e.g., the molecular weight and the amount of chain defects) and the testing method used.[5] The addition of a comonomer bearing a side group in PVDF results in a decrease of the crystalline part (and hence the decrease of the T_m value) and thus an increase of the T_g value. This is well evidenced by copolymers resulting from the copolymerization of VDF with hexafluoropropylene.[5,12] However, inserting comonomers bearing perfluoropolyethers as claimed by Worm[10] led to copolymers that have very low T_gs (ca. −90 °C). Nevertheless, PMVE is an interesting comonomer with a special influence on the resulting copolymers since its oxygen atom induces softness though OCF_3 is bulky. This present study displays the effect of the insertion of PMVE on the T_g of these copolymers.

T_g values were assessed by differential scanning calorimetric (DSC). (Figure S6 in the Supporting Information displays several DSC thermograms obtained for different poly(VDF-*co*-PMVE) copolymers.) Samples of poly(VDF-*co*-PMVE) copolymers having the same composition in VDF and PMVE (VDF/PMVE 60/40 mol %) were analyzed to determine the influence of the molecular weights on the T_g values. As expected, the copolymer with the low molecular weight showed a lower T_g (ca. −60 °C). T_g value was found to increase when the molecular weights of copolymer increased until reaching a plateau (T_g at −40 °C) for M_n > 5000−6000 g mol^{-1}. In addition, the effect of the nature of CTAs was also investigated. It was found that the CTAs (difunctional or monofunctional) did not affect the T_g significantly (Figure 10). Finally, an increase of PMVE in the copolymer induces a slight increase of T_g due to a T_g higher than that of PVDF, in agreement with a previous work.[7]

6.2. Determination of Decomposition Temperature (T_d) of Poly(PMVE-co-VDF) Copolymers. The thermal stabilities of poly(VDF-*co*-PMVE) copolymers were also assessed by thermogravimetric analysis (TGA) (Figure S7 in the Supporting Information). The TGA thermograms show that these copolymers of low molecular weights exhibit a low thermal stability (Figure 10) due to the evaporation of the copolymer during the heating treatment. This is not surprising since highly fluorinated low-molecular-weight molecules are known to be volatile. To confirm this statement, the evolution of molecular weights and polydispersity indices (PDIs) were investigated by SEC and by ^{19}F NMR analysis during the TGA analysis. SEC analysis (Figure S9 and Table S2 in the Supporting Information) shows a decrease of PDI

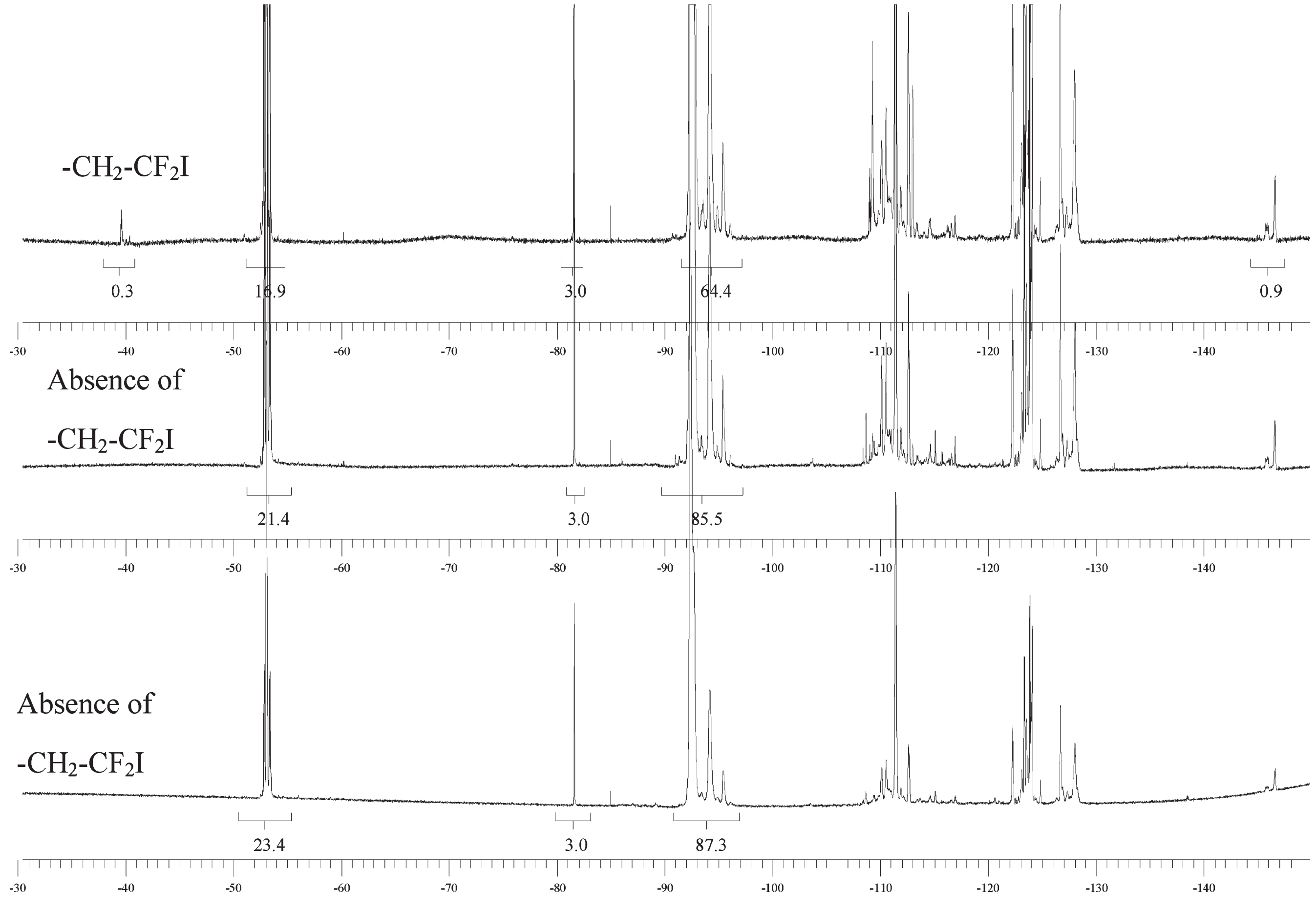


Figure 11. ^{19}F NMR spectra (recorded in acetone-d_6) of poly(VDF-*co*-PMVE) copolymers obtained by iodine transfer copolymerization of vinylidene fluoride (VDF) and perfluoromethyl vinyl ether (PMVE) in the presence of $C_6F_{13}I$ as chain transfer agent at 80 °C after heating for 1 h at 200 °C (upper spectrum), 300 °C (middle spectrum), and 350 °C (lower spectrum). Experimental conditions: VDF/PMVE composition: 65/35 in mol %, run 16 of Table 3.

and an evaporation of low-molecular-weight copolymers (vanishing of low molar mass copolymer) while the ^{19}F NMR spectrum (Figure 11) revealed the absence of $-CH_2-CF_2I$ groups and the simplification of the signal patterns which confirms the absence of lower-molecular-weight copolymers. No other differences were observed either by ^{19}F NMR or by SEC analyses. The effect of the polymer composition of VDF and PMVE was also investigated (Table 3). Interestingly, the incorporation of PMVE did not affect significantly the thermal stability of PVDF. Indeed, for high molecular weights, a copolymer containing a high ratio of PMVE shows a similar decomposition temperature as that of PVDF.

Finally, the thermal stability of these copolymers was also investigated versus time. For example, Figure S8 in the Supporting Information gives the evolution of weight loss versus time at 300 °C for a poly(VDF-*co*-PMVE) copolymer with a composition 60/40 mol % VDF/PMVE and M_n = 6900 g mol^{-1} under air. The copolymer exhibits a satisfactory stability with time for several hours.

Conclusion

For the first time, the synthesis of new fluoroelastomers based on VDF and PMVE using a controlled radical copolymerization (iodine transfer copolymerization) process is described. The microstructures of these materials were characterized by ^{19}F and ^{1}H NMR spectroscopy and by MALDI-TOF. A high incorporation of PMVE was noted though the absence of consecutive PMVE units confirms that PMVE does not homopolymerize. The increase of PMVE in the feed ratio induced a decrease in the copolymer yield. In addition, the end-groups of the copolymers were also carefully characterized using model compounds. Interestingly, the absence of two different end-groups ($-CF_2CF(OCF_3)I$ and $CF(OCF_3)CF_2I$) were attributed to their higher reactivity compared to the other chain end-groups formed by transfers, i.e., $-CF_2CH_2I$ and $-CH_2CF_2I$. This result was confirmed by the transfer constant assessed for different CTA models which mimic the different possible end-groups. In addition, it was also found an accumulation of $-CF_2CH_2I$ in the medium with an increase of the conversion and the molecular weight. The thermal properties of these copolymers were also examined with both the assessment of the glass transition (T_g) and the decomposition temperature. An increase in the molecular weights of the copolymers resulted in a higher thermal stability (300 °C) but also in an increase of the T_g value. For low-molecular-weight (2000 g mol^{-1}) materials, a T_g close to −65 °C was found. That ITP process reported in this article presents a simplification and a reduction of cost for the production of fluorinated elastomers. Finally, these copolymers present interesting properties for the production of original elastomers due to the presence of $-CF_2I$ or $-CH_2I$ end-groups, offering further modification and functionalization to yield original telechelic compounds,[70,71] under investigation.

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Supporting Information Available: ^{19}F NMR spectra for different copolymers, SEC traces, TGA and DSC curves, Tables S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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