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Random and Sequential Radical Cotelomerizations of 3,3,3-Trifluoropropene (TFP, $\text{H}_2\text{C}=\text{CHCF}_3$) with Vinylidene Fluoride (VDF, $\text{F}_2\text{C}=\text{CH}_2$).

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ABSTRACT

The synthesis of original co-telomers based on 3,3,3-trifluoropropene (TFP) and vinylidene fluoride (VDF) with a general formula: $\text{R}_F\text{-}[\text{CH}_2\text{-CF}_2]_n\text{-}[\text{CH}_2\text{-CH}(\text{CF}_3)]_m\text{-I}$ (where $n=1\text{-}63$, $m=2\text{-}640$, and $\text{R}_F=(\text{CF}_3)_2\text{CF}$) was achieved by sequential and random cotelomerizations in the presence of R_FI . The radical cotelomerizations were initiated by thermal decomposition of different peroxide and persulfate initiators either in bulk, in solution (in the presence of acetonitrile or 1,1,1,3,3-pentafluorobutane as the solvents), and in aqueous process (emulsion). Different adducts were obtained in good yield (50-70 wt%) with a relative

proportion of each adduct depending on (i) the $R_0 = [R_{FI}]_0 / ([TFP]_0 + [VDF]_0)$ initial molar ratio, (ii) the reaction temperature, and (iii) $C_0 = [In]_0 / ([TFP]_0 + [VDF]_0)$. Random cotelomerization gave higher yields than those obtained from the sequential cotelomerization. When the concentration of the chain transfer agent increased, the molecular weights of the resulting poly(VDF-*co*-TFP) cotelomers decreased and showed that the R_0 ratio targeted the molecular weights (~ 700 - $66,000$ g.mol⁻¹). Some of the obtained molecular weights were exceptionally high for a (co)telomerization. The kinetics of the radical cotelomerization of VDF and TFP led to the determination of the reactivity ratios of both comonomers ($r_{VDF} = 0.28 \pm 0.07$ and $r_{TFP} = 2.35 \pm 0.26$ at 75 °C).

KEY WORDS

Vinylidene fluoride, 3,3,3-trifluoropropene, chain-transfer agent, radical cotelomerization, ¹H and ¹⁹F NMR spectroscopy, copolymerization, reactivity ratios.

1 INTRODUCTION

3,3,3-Trifluoropropene (TFP), prepared for the first time by Hazeldine¹ by dehydroiodination of CF₃-CH₂-CH₂-I, is the precursor of commercially available fluorinated silicones manufactured by Dow Corning under the Silastic® trademark.² This polymer preserves interesting properties (inertness, fair surface tension, chain mobility) at low and quite high temperatures.³ Interestingly, this fluoroalkene is quite reactive in contrast to longer perfluorinated chain vinyl-type monomers (e.g. C_nF_{2n+1}-CH=CH₂ with

n>1). The telomerization of TFP with various chain-transfer agents (especially CF₃I) was pioneered in 1952, initiated thermally or photochemically, leading to both (CF₃)₂CHCH₂I and CF₃CH₂CHI(CF₃) isomers in 60/40 mol%, the photochemical initiation being more selective.^{4,5} In the mid 70ies, Low et al.⁶ also investigated this reaction under UV radiation, and obtained a mixture of both normal and reverse monoadducts. In the 80ies, Russian teams studied the telomerization of TFP with non-fluorinated telogens such as alcohols, esters, tetrachloromethane, tribromomethane, benzyl chloride, under redox complexes (e.g. Fe(CO)₅), UV or gamma rays initiations.⁷⁻¹⁹ In addition, Vasil'eva's team¹³ even proposed mechanisms of formation of unexpected telomers and determined various chain transfer constants of telogens showing that, in some cases, the transfer to the telogen is more efficient than the radical chain growth.^{10,16,17} Other transfer agents have been used such as silanes, phosphonates, disulfides or hydrogen bromide yielding the monoadduct.³ Recently, the Great Lakes/Chemtura Company has patented the telomerization of TFP with either perfluoroalkyl iodides²⁰ or other non-fluorinated chain-transfer agents²¹ and their further chemical modifications to get useful surfactants, coating materials, or block copolymers.²²⁻

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On the other hand, vinylidene fluoride (VDF) is a non-toxic, non-explosive, and environmentally friendly gas (it does not contain any Cl or Br atoms). It can easily polymerize under radical²⁵ or ionic²⁶ conditions. Poly(VDF) is an attractive polymer endowed with remarkable properties (it is a piezo- and pyroelectric, resistant to acids, solvents, and to nuclear radiation, and is a gas barrier polymer). It has found numerous applications just like its copolymers which have been marketed by most major companies.^{3,25-30} The telomerization of VDF has been investigated by many authors and

reviewed.³ Almost all kinds of chain transfer agents have been used with a suitable initiation (thermal, photochemical, by redox systems or by radical initiators). Regarding the thermal initiation, Hauptschein et al.^{31,32} demonstrated the possible telomerization of VDF with both brominated and iodinated compounds. Other surveys have been reported especially by Apsey et al.³³, Balagué et al.^{34,35} or Chen et al.³⁶. Successful telomerizations where the initiator generates a CF_3^\bullet radical have also been reported.³⁷⁻³⁹ Possible direct initiation was demonstrated using alcohols as poorly efficient telogens.⁴⁰ In the case of C-I cleavable telogens, it was observed that the telomerization yields mainly to the monoadduct and the addition of R_F^\bullet radical occurs exclusively onto the CH_2 side of VDF,^{3,33-35,39} though one study showed that this addition could also occur onto the CF_2 side of VDF.⁴¹ The literature also reports the telomerization using C-Cl cleavage.⁴² In contrast to only one patent⁴³ on the radical copolymerization of VDF with TFP, there are no references in the literature regarding the cotelomers based on TFP with VDF. Hence, it was worth investigating the radical cotelomerization of TFP with VDF. These cotelomers can be used as models for the copolymerization of TFP with VDF or other olefins. These cotelomers and their derivatives are interesting precursors of various fluoropolymers, such as telechelics⁴⁴ or block copolymers⁴⁵, and have found potential applications such as fluorinated surfactants.⁴⁶⁻⁴⁸ The durability and the common use of perfluorinated surfactants such as perfluorooctanoic acid (PFOA)⁴⁹ or perfluorooctane sulfonic acid (PFOS)⁵⁰ is a major environmental and health issue^{51,52} (besides their toxicity and persistency, both these surfactants are bioaccumulable in the human and animal species) and major companies such as Arkema, Asahi Glass, Chemtura, Daikin, DuPont, 3M/Dyneon, Merck, Solvay

Solexis are facing to find out new fluorinated alternatives. Advantageously, the methylene groups in the TFP and VDF units are interesting weak sites for chain cleavage which allows possible biodegradability or metabolic decomposition of these new fluorinated surfactants. The synthesis of fluorinated polymers having sites for biodegradation and functional end-group is of importance as initial block in the production of new fluorinated surfactants.⁴⁸ Hence, the objectives of this present article deal with the synthesis of original poly(VDF-*co*-TFP) cotelomers bearing an *iso*-heptafluoropropyl end-group as precursors of original surfactants with potential biodegradability.

2 EXPERIMENTAL

2.1 Materials

All reagents were used as received unless stated otherwise.

3,3,3-Trifluoropropene ($\text{CH}_2=\text{CH}-\text{CF}_3$, TFP) and 2-iodoperfluoropropane ($(\text{CF}_3)_2\text{CF}-\text{I}$) were kindly supplied by the Chemtura Company (West Lafayette, USA). The 2-Iodoperfluoropropane was treated with sodium thiosulfate and then distilled prior to use to remove impurities and molecular iodine. 1,1-Difluoroethylene (vinylidene fluoride, $\text{CH}_2=\text{CF}_2$, VDF) and 1,1,1,3,3-pentafluorobutane (Solkane® 365mfc, $\text{CF}_3-\text{CH}_2-\text{CF}_2-\text{CH}_3$) were kindly supplied by Solvay S.A. (Tavaux, France). *tert*-Butylperoxypivalate in solution of isododecane (Trigonox® 25-C75, $\text{tBuOOC}(\text{O})\text{tBu}$, TBPPi) (purity 75 wt.%) and di-*tert*-butyl peroxide (Trigonox® B, DTBP) (purity 99%) were gifts from Akzo (Chalons sur Marne, France).

Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) and sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) were purchased from Sigma-Aldrich (Saint Quentin-Fallavier, France). *Tert*-butanol, 2-butanone, pentane of analytical grade were purchased from SDS (France). Deuterated acetone d_6 was purchased from Euroiso-top (Grenoble, France) (purity>99.8%).

2.2 Characterizations.

2.2.1 GC

Gas chromatograms (GC) were obtained using a Delsi apparatus (model 330) equipped with a SE 30 column 2 m x 0.30 mm (inner diameter). The nitrogen pressure at the entrance of the column was maintained at 1 bar and the detector (FID) and injector temperature were 240 °C and 235 °C, respectively. The temperature ramp was defined from 50 °C to 200 °C at a heating rate of 10 °C/min. The GC apparatus was connected to a Hewlett Packard integrator (model 3390). The sensitivity of the apparatus and the resolution of the chromatogram limit the detection of telomers to the sixth adduct.

2.2.2 NMR

The NMR spectra were recorded on Bruker AC 400 instruments, using deuterated acetone, as the solvent and tetramethylsilane (TMS) (or CFCl_3) as the references for ^1H (or ^{19}F) nuclei. Coupling constants and chemical shifts are given in hertz (Hz) and part per million (ppm), respectively. The experimental conditions for recording ^1H [or ^{19}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 2 s], number of scans 128 [or 512], and a pulse width of 5 μs for ^{19}F NMR.

2.3 Autoclave

The radical (co)telomerizations were performed in a 160 mL, 300 mL or 2 L Hastelloy Parr autoclave systems (HC 276) equipped with a manometer, a mechanical Hastelloy anchor, a rupture disk (3000 PSI), inlet and outlet valves. An electronic device regulated and controlled both the stirring and heating of the autoclave. Prior to reaction, the autoclave was pressurized with 30 bars of nitrogen to check for leaks. The autoclave was then conditioned for the reaction with several nitrogen/vacuum cycles (10^{-2} mbar) to remove any trace of oxygen. The liquid and dissolved solid phases were introduced via a funnel and then the gases (TFP and/or VDF) were introduced by double weighing (i.e. the difference of weight before and after filling the autoclave with the gas).

2.4 Sequential cotelomerization

2.4.1 Example of telomerization of vinylidene fluoride (VDF) with $(CF_3)_2CF-I$ (Run #6 in Table 1)

To the 300 mL degassed autoclave under vacuum were added via a funnel *tert*-butylperoxypivalate (TBPPi) (2.9 g, 0.0125 mol), *ditert*-butylperoxide (DTBP) (1.87 g, 0.125 mol), and $(CF_3)_2CF-I$ (130.0 g, 0.439 mol). To that mixture, VDF (40.0 g, 0.625 mol) was added by double weighing to form the reaction mixture that was progressively heated to 75 °C whereupon an exotherm of about 10 °C and an increase of pressure from 14.6 bars up to 35.8 bars were noted. Then a drop of pressure down to 8.4 bars in 9 hours was

observed. The autoclave was then placed in an ice bath for about 60 minutes and 12.4 grams of non-reacted VDF was progressively released (the conversion of VDF was 69 wt.%). The autoclave was opened and about 236.9 grams of a brown liquid was obtained. That mixture, assessed by GC, was observed to comprise of 19 % of non-reacted $(\text{CF}_3)_2\text{CF-I}$ (b.p. = 40 °C at atmospheric pressure), 59 % of VDF monoadduct, 8 % diadduct, and 1% triadduct. The double distillation yielded the monoadduct that was characterized by ^{19}F and ^1H NMR spectroscopy ($Y_d = 59$ wt.%, b.p. = 100-101 °C at atmospheric pressure). The residue consisted mainly of diadducts (b.p. = 164 °C at atmospheric pressure).

^1H NMR (acetone d6, ppm) δ : 3.85 (q, $^3J_{\text{HF}}=15$ Hz, $-\text{CH}_2\text{CF}_2\text{I}$, 2H); 3.2 (q, $^3J_{\text{HF}}=18$ Hz, $-\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{I}$ diadduct, 2H); 2.8 (s, $^3J_{\text{HF}}=17$ Hz, $-\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_2\text{I}$ diadduct, 2H).

^{19}F NMR (acetone d6, ppm) δ : -39 (s, $-\text{CH}_2\text{CF}_2\text{I}$, 2F); -76.4 (s, $(\text{CF}_3)_2\text{CF-}$, 6F); -94.2 (s, $(\text{CF}_3)_2\text{CF-}[\text{CF}_2\text{CH}_2]_2\text{I}$, diadduct 2F); -184.5 (s, $(\text{CF}_3)_2\text{CF-}$, 1F)

Elemental Analysis

Monoadduct: %C = 16.68, %H = 0.56, %F = 47.50, %I = 35.26

Diadduct: %C = 19.83, %H = 0.95, %F = 49.29, %I = 29.93

2.4.2 Example of sequential cotelomerization of 3,3,3-trifluoropropene (TFP) with $(\text{CF}_3)_2\text{CF-CH}_2\text{CF}_2\text{-I}$ (Runs #7-11 in Tables 2 and 3).

Ditert-butylperoxide (DTBP) (0.73 g, 5.10^{-3} mol) and $(\text{CF}_3)_2\text{CF-CH}_2\text{CF}_2\text{-I}$ (obtained by the above reaction) (80 g, 0.232 mol) were added, via a funnel, to the 160 mL degassed autoclave maintained under vacuum. To that mixture, TFP (16.0 g, 0.166 mol) was added by double weighing to form the reaction mixture that was progressively heated to about 142 °C. An exotherm of about 10 °C and an increase of pressure from 7 to 15 bars followed by

a decrease of pressure to 10 bars over a period of about 10 hours were observed. The autoclave was then placed in an ice bath for about 60 minutes and 5 grams of non-reacted TFP were progressively released (the conversion of TFP was 68 wt %). Opening the autoclave to afford about 80.4 grams of the reaction mixture, in what can be observed as a brown liquid, was collected and analyzed by gas chromatography (GC). The total product mixture contained (assessed by GC): 41 % of non-reacted $(\text{CF}_3)_2\text{CFCH}_2\text{CF}_2\text{I}$ (retention time RT=1.3 min, b.p. = 100-101 °C/atm), 23 % of VDF/TFP monoadduct $(\text{CF}_3)_2\text{CFCH}_2\text{CF}_2\text{CH}_2\text{CHICF}_3$ (RT=3.3-3.8 min and b.p. = 28-30 °C at 3 mm Hg) and 13 % diadduct (RT = 6.4 min). Double distillation was performed and yielded $Y_d = 38$ wt % of monoadduct (purity 85 %) that was characterized by ^{19}F and ^1H NMR spectroscopy and the molar ratio of VDF/TFP in the cotelomer was found to be about 50/50 mole %.

^1H NMR (acetone d6, ppm) δ : 4.8 (quint. AB-X system, $^3J_{\text{HF}} = ^3J_{\text{HHA}} = 15$ Hz, $^3J_{\text{HHB}} = 7$ Hz, $(\text{CF}_3)_2\text{CFCH}_2\text{CF}_2\text{C}^*\text{H}(\text{CF}_3)\text{CH}_2\text{I}$, 1H); 4.7-5.0 (m, $(\text{CF}_3)_2\text{CFCH}_2\text{CF}_2\text{CH}_2\text{C}^*\text{H}(\text{CF}_3)\text{I}$, 1H); 3.4 – 2.65 (centr. 2.9m, H_A, H_B in AB system $(\text{CF}_3)_2\text{CFCH}_2\text{CF}_2-$, 2H); 3.1 (m, $(\text{CF}_3)_2\text{CFCH}_2\text{CF}_2\text{C}^*\text{H}(\text{CF}_3)\text{CH}_2\text{I}$; 2H); 2.8 (m, $(\text{CF}_3)_2\text{CFCH}_2\text{CF}_2\text{CH}_2\text{C}^*\text{H}(\text{CF}_3)\text{I}$, 2H)

^{19}F NMR (acetone d6, ppm) δ : no peak at -39 (no- $\text{CH}_2\text{-CF}_2\text{I}$); -69.2 to -71.6 ($-\text{CH}_2\text{C}^*\text{HCF}_3-$; 3F); -78.5 (t, $^3J_{\text{FF}} = 9.5$ Hz, $(\text{CF}_3)_2\text{CF}-$; 6F); -98 to -99 ($-\text{CH}_2\text{-CF}_2-$; 2F) ; -184 ($>\text{CF}-$; 1F).

2.4.3 Example of sequential cotelomerization of vinylidene fluoride (VDF) with $(\text{CF}_3)_2\text{CF-CH}_2\text{CH}(\text{CF}_3)\text{-I}$ (Runs #12-17 in Tables 2 and 3)

To the 160 mL degassed autoclave under vacuum were added via a funnel *tert*-butylperoxypivalate (TBPPi) (0.815 g, $4.7 \cdot 10^{-3}$ mol) and $(\text{CF}_3)_2\text{CF-CH}_2\text{CH}(\text{CF}_3)\text{-I}$ (73.4 g, 0.187 mol) obtained from the radical addition of $i\text{C}_3\text{F}_7\text{I}$ onto TFP.²⁰ To that mixture, VDF

(10.0 g, 0.156 mol) was added by double weighing to form the reaction mixture that was progressively heated to 75 °C whereupon an exotherm of about 10 °C and an increase of pressure from 7 bars up to 17 bars and then a drop of pressure down to 12 bars in 8 hours were observed. The autoclave was then placed in an ice bath for about 60 minutes and 6 grams of non-reacted VDF was progressively released (the conversion of VDF was 40 wt.%). The autoclave was opened and about 73 grams of a brown liquid was obtained. That mixture, assessed by GC, was observed to comprise of 16 % of non-reacted $(\text{CF}_3)_2\text{CFCH}_2\text{CH}(\text{CF}_3)\text{I}$ (retention time RT = 1.5 min, b.p. = 104 °C/atm), 55 % of TFP/VDF monoadduct (RT = 3.3-3.8 min and b.p. = 20 °C at 1 mm Hg) and 29 % diadduct (RT = 6.4 min). The double distillation yielded the monoadduct ($Y_d = 36$ wt.%, purity 97 %) that was characterized by ^{19}F and ^1H NMR spectroscopy and the molar ratio of TFP/VDF in the cotelomer was found to be 50/50 mole %.

^1H NMR (acetone d_6 , ppm) δ : 3.8–3.6 (q, $-\text{CF}_2\text{CH}_2\text{I}$, 2H); 3.2-3.1 and 2.85-2.75 (AB system, $-\text{CH}_2\text{CF}_2\text{I}$; 2 isomers, 2H); 2.9-2.75 [m, $(\text{CF}_3)_2\text{CFCH}_2\text{C}^*\text{H}(\text{CF}_3)-$, 1H); 3.0 and 2.7 (AB system, $(\text{CF}_3)_2\text{CFCH}_2\text{C}^*\text{H}(\text{CF}_3)-$, 2H).

^{19}F NMR (acetone d_6 , ppm) δ : -39 (q, $-\text{CH}_2-\text{CF}_2\text{I}$; 2F); -69.2 to -71.6 ($-\text{CH}_2\text{C}^*\text{HCF}_3-$; 3F); -78.5 (t, $(\text{CF}_3)\text{CF}-$, 6F); -184 ($>\text{CF}-$, 1F).

2.5 Random cotelomerization

2.5.1 Example of random solution cotelomerization of vinylidene fluoride (VDF) and 3,3,3-trifluoropropene (TFP) with (CF₃)₂CFI (Run #18 in Tables 4 and 5).

To the 160 mL autoclave purged and under vacuum, *tert*-butylperoxypivalate (TBPPi) (1.9 g, 11.10⁻³ mol), (CF₃)₂CFI (4.6 g, 1.56.10⁻² mol), and 1,1,1,3,3-pentafluorobutane (80 mL) were introduced via a funnel. By double weighing, TFP (30.0 g, 0.312 mol) and VDF (15.0 g, 0.234 mol) were introduced to complete the reaction mixture. The autoclave was then progressively heated to 75 °C and an exotherm of about 10 °C followed by an increase of pressure of from 8 to 24 bars, and then a drop of pressure to 20 bars over a period of about 10 hours were observed. The autoclave was then placed in an ice bath for about 60 minutes and vented to release 28 grams of non-reacted TFP and VDF (the conversion of (TFP+VDF) was 39 wt%) and, upon opening the autoclave, about 115 grams of a brown liquid was isolated. The solvent (C₄F₅H₅) and non-reacted *i*-C₃F₇I (b.p. = 35 and 40 °C at atmospheric pressure, respectively) were distilled and the concentrate was precipitated in chilled pentane to isolate the cotelomer that was dried under vacuum (0.1 mm Hg/40 °C) overnight (Y= 39 wt%). The cotelomer was characterized by ¹⁹F and ¹H NMR spectroscopy leading to a TFP/VDF molar ratio in the cotelomer to be 75.2/24.8 mole %.

¹H NMR (acetone d₆, ppm) δ: 5.0-4.5 (-CH₂C*H(CF₃); 1H); 3.4-2.8, 3.1 (m, H_A,H_B in AB system R_FCH₂CF₂-, 2H); 3.0 (C*H(CF₃)CH₂I; 2H); 2.7-2.2 (CH₂C*H(CF₃); 2H)

¹⁹F NMR (acetone d₆, ppm) δ: no signal at -39 (no -CH₂CF₂I); -65.2-71.6 (-CH₂CH(CF₃)-; 3F); -78.5 ((CF₃)₂CF-; 6F); -90 to -102 (-CH₂-CF₂-; 2F); -184 (>CF-; 1F).

Average molecular weight by NMR: 2,200 g.mol⁻¹

2.5.2 Example of random emulsion cotelomerization of vinylidene fluoride (VDF) and 3,3,3-trifluoropropene (TFP) with (CF₃)₂CFI (Run #26, Tables 4 and 5).

To the 160 mL degassed autoclave, (CF₃)₂CFI (0.43 g, 1.5·10⁻³ mol), deionized water (80 mL), and Na₂S₂O₈ (0.28 g, 1.2·10⁻³ mol) were introduced under vacuum via a funnel. To that mixture, TFP (29.0 g, 0.3 mol) and VDF (9.0 g, 0.14 mol) were inserted by double weighing and the loaded autoclave was progressively heated to 80 °C after a few minutes stirring at room temperature to allow the emulsion to form. It was then observed an increase of autoclave pressure from 7 up to 70 bars and a drop of pressure to 53 bars in 10 hours. The autoclave was left at RT for about 60 minutes and 20 grams of non-reacted TFP and VDF were progressively released (the conversion of (TFP+VDF) gases was 47 wt.%). Opening the autoclave, about 86 g of emulsion was poured into a plastic bottle and frozen in liquid nitrogen to break the emulsion and to decantate into two phases: the lower one containing the fluorinated product and the upper one being the water layer. Upon reaching room temperature the lower product layer was separated from the upper water layer, dissolved in acetone and precipitated in chilled pentane. The product was filtered and dried under vacuum (0.1 mm Hg/40 °C) overnight (Y = 13 wt. %), and characterized by ¹⁹F and ¹H NMR spectroscopy. The molar ratio of TFP/VDF in the product was found to be 90.5/9.5 mole %.

¹H NMR (acetone d₆, ppm) δ: 3.9-3.6, (m, X part of AB-X system, -CH₂C*H(CF₃)-; 1H); 3.0–2.6 and 2.8 (H_A,H_B of AB system R_F-CH₂CF₂-; 2H); 3.0 (m, -C*H(CF₃)CH₂I; 2H); 2.8-2.6 (AB system, -CH₂C*H(CF₃)-; 2H); 2.5-2.3 (reverse VDF chaining -CF₂CH₂-CH₂CF₂-; 4H).

^{19}F NMR (acetone d_6 , ppm) δ : no signal at -39 (no $-\text{CH}_2\text{CF}_2\text{I}$); -62.2, -72 ($-\text{CH}_2\text{C}^*\text{HCF}_3$; 3F); -78.5 ($(\text{CF}_3)_2\text{CF}$ -, 6F); -90 to -102 ($-\text{CH}_2-\text{CF}_2$ -, 2F), -184 ($>\text{CF}$ -, 1F).

Average molecular weight by NMR: $65,700 \text{ g}\cdot\text{mol}^{-1}$

2.5.3 Examples of scale up for the random solution cotelomerization of vinylidene fluoride (VDF) and 3,3,3-trifluoropropene (TFP) with $(\text{CF}_3)_2\text{CFI}$ (Run #29, Tables 4 and 5).

In the 2 L Hastelloy autoclave, *tert*-butylperoxypivalate (TBPPi) (9.7 g, $5.6\cdot 10^{-2}$ mol), $(\text{CF}_3)_2\text{CFI}$ (93.6 g, 0.316 mol), and 1,1,1,3,3-pentafluorobutane (500 mL) were placed to form a mixture. By double weighing, TFP (80.0 g, 0.83 mol) and VDF (80.0 g, 1.25 mol) were introduced in the mixture. The autoclave pressure reached 12 bars at 75 °C, and after about 30 minutes, some TBPPi (9.7 g, 0.06 mol) dissolved in $\text{C}_4\text{F}_5\text{H}_5$ (20 mL) were added continuously (3 mL/min) into the reactor by a dosage pump to initiate the telomerization. After about 22 hours, the autoclave pressure decreased to 9.0 bars. Venting the autoclave released 48 grams of non-reacted VDF and TFP (conversion of 70 wt %). After opening the autoclave, 712 grams of a dark-brown viscous liquid were recovered. $\text{C}_4\text{F}_5\text{H}_5$ was first distilled followed by the other products. The average product corresponds to the general formulae $i\text{-C}_3\text{F}_7(\text{VDF})_2(\text{TFP})_3\text{I}$ ($Y_{\text{dist}}=69$ wt %). The total product mixture (assessed by GC, wt.%) was composed of $\text{C}_4\text{F}_5\text{H}_5 < 1.2$ % (b.p. = 35 °C/atm); $(\text{CF}_3)_2\text{CFI} < 3$ % (b.p. = 40 °C/atm); $i\text{-C}_3\text{F}_7(\text{VDF})\text{I}$ and, $i\text{-C}_3\text{F}_7(\text{TFP})\text{I}$ monoadducts 5.7 % (RT=1.1-1.4 min, b.p. 98-104°C/atm); $i\text{-C}_3\text{F}_7(\text{TFP})(\text{VDF})\text{I}$ diadduct 14.8 % (RT=3.3-3.8 min, b.p. =28°C at 3 mm Hg); $i\text{-C}_3\text{F}_7(\text{TFP})_x(\text{VDF})_y\text{I}$; $x=2,y=1$ or $x=1,y=2$ triadduct 17.9 % (RT = 6.4-6.8 min); $x=3,y=2$ main product 36.2 % (RT=8.1-9.2 min); $x>3, y>2$ residue 22.3 %. The main

product was characterized by ^{19}F and ^1H NMR spectroscopy and the molar ratio of TFP/VDF in the main product was found to be about 62/38 mol %.

^1H NMR (acetone d_6 , ppm) δ : 5.0- 4.6 (m, $-\text{CH}_2\text{C}^*\text{H}(\text{CF}_3)$; 1H); 3.5–2.7 and 3.2 ($\text{H}_\text{A}, \text{H}_\text{B}$ in AB system $\text{R}_\text{F}-\text{CH}_2\text{CF}_2-$; 2H); 2.8-2.6 (AB system, $-\text{CH}_2\text{C}^*\text{H}(\text{CF}_3)-$; 2H); 2.5 -2.2 (reverse VDF $-\text{CF}_2\text{CH}_2-\text{CH}_2\text{CF}_2-$; 4H).

^{19}F NMR (acetone d_6 , ppm) δ : small signal at -39 ($-\text{CH}_2\text{CF}_2\text{I}$; 2F); -65 to -72.4 ($-\text{CH}_2\text{C}^*\text{H}(\text{CF}_3)-$; 3F); -78.5 ($(\text{CF}_3)_2\text{CF}$, 6F); -91 to -102 ($-\text{CH}_2-\text{CF}_2-$; 2F); very small peak at -107, -113, and -116 (reverse VDF $-\text{CH}_2\text{CF}_2-\text{CF}_2\text{CH}_2$, 4F); -184 ($>\text{CF}-$; 1F).

Average molecular weight by NMR: $700 \text{ g}\cdot\text{mol}^{-1}$.

3 RESULTS AND DISCUSSION

3.1 Sequential cotelomerization

In this section, 3,3,3-trifluoropropene (TFP) and vinylidene fluoride (VDF) were successively telomerized to prepare the cotelomers of VDF and TFP as indicated in the Scheme 1. The first step consist of the telomerization of the monomer A (either TFP or VDF) in the presence of 2-iodoperfluoropropane ($\text{iC}_3\text{F}_7\text{I}$) as the telogen. The second step consists of the telomerization of monomer B (VDF or TFP, respectively) in the presence of the monoadduct of the first telomerization to obtain the cotelomers.

Insert Scheme 1

3.1.1 Telomers

3.1.1.1 R_F -VDF-I telomers

Numerous works dealing with the radical telomerization of VDF and perfluoroalkyliodides have been published and reviewed.³ Different telogens were used, especially linear and branched perfluoroalkyl iodides ($C_nF_{2n+1}I$), and various initiations (thermal and redox)^{34,35} gave low DP_n telomers. Few works on photoinitiation and different radical initiators have also been performed.⁵³⁻⁵⁵ On the other hand, iodine transfer polymerization (ITP) of VDF with $C_6F_{13}I$, $C_6F_{13}CH_2CH_2I$ or $HCF_2CF_2CH_2I$, initiated by *tert*-butylperoxypivalate (TBPPi) has been reported,^{56,57} but to our best knowledge no telomerization of VDF with $(CF_3)_2CFI$ has been initiated by TBPPi.

Insert Table 1

The VDF telomers were synthesized based on descriptions available from the literature³³⁻³⁵ that was adapted to our purpose. It consisted of a radical telomerization of VDF with iC_3F_7I as the telogen initiated by TBPPi in acetonitrile at 74 °C, different from previous above studies where thermal^{33,34} and redox^{34,35} initiations were used. The results are presented in Table 1. The monoadduct was separated from other adducts by distillation under vacuum and characterized by GC and NMR to check its purity and isomers ratios. The reaction carried out in bulk (without solvent) produced the highest proportion of monoadduct (≥ 50 %) and the lowest amount of diadduct. It was also noted that whatever the reaction

conditions, a small proportion of unreacted ($\cong 20\%$) telogen remained in the total product mixture.

It was found that the higher the initial pressure during the reaction, the lower the amount of unreacted telogen at the end. The same effect was observed when decreasing the R_0 value. It was also noted that the pressure was higher in the case of the bulk telomerization although the liquid phase was smaller (hence the gas has more space to expand). This can indicate that VDF has a non-negligible solubility in acetonitrile. In conclusion, the best results were obtained when the reaction was carried out without any solvent (i.e. in bulk) with $R_0 < 1$, and the reaction yielded more than 50 % monoadduct in less than 10 hrs (Runs #4 and #5 in Table 1).

The signal centered at -39 ppm on the ^{19}F NMR spectra is characteristic of the normal addition of the chain transfer agent onto $-\text{CH}_2\text{CF}_2^\bullet$ radical yielding $(\text{CF}_3)_2\text{CF}-\text{CH}_2-\text{CF}_2-\text{I}$, while for the reverse adduct $(\text{CF}_3)_2\text{CF}-\text{CF}_2-\text{CH}_2-\text{I}$, the perfluoromethylene appears at -109 ppm.³ From these ^{19}F NMR signals, it was possible to assess the percentage of normal and reverse addition that was found to be 96.6 % normal. This was expected due to the electron-withdrawing character of the fluorine atom, that makes the methylene of VDF electron-poor, and consequently more prompt to the addition of the electron-rich radicals. Also the signals from both CF_3- and $>\text{CF}-$ groups of the telogen can be used as a label to assess the molecular weight by ^{19}F NMR spectroscopy.

From the ^1H NMR spectra, the normal methylene group appears at 3.8 ppm, while the reverse appears at 3.15 ppm. From these ^1H NMR signals, the percentage of the normal

addition was found to be 98.4 %, which correlates well with the one assessed from the ^{19}F NMR (96.6 %).

3.1.1.2 R_F -TFP-I telomers

The TFP telomers were synthesized according to Kostov et al.²⁰, i.e. by radical telomerization in bulk of TFP initiated by di-*tert*-butylperoxide (DTBP) at 150 °C with $i\text{C}_3\text{F}_7\text{I}$ as the telogen. The monoadduct in 50-60 % yield was isolated by distillation and characterized as previously indicated. We showed that the telomerization of TFP in the presence of perfluorohexyl iodide ($\text{C}_6\text{F}_{13}\text{I}$) as the telogen led to both normal and reverse adducts but also that in the case of perfluoro-*iso*-propyl iodide ($i\text{-C}_3\text{F}_7\text{I}$), used in the present paper, no reverse addition product was observed.²⁰ The ^{19}F NMR spectrum of the monoadduct does not show any signal at -67 ppm (attributed to the CF_3 of TFP in case of a reverse addition) but a peak at -72 ppm (attributed to the normal addition of TFP).

The preparation and characterization of these telomers based on VDF or TFP was required as they can be further used as models for the cotelomerization or copolymerization of VDF and TFP, especially for the attribution of the chemical shifts in the NMR spectra, reported below.

3.1.2 Sequential Cotelomers of VDF and TFP

In a second step, each produced telomer was used as a chain-transfer agent (telogen) in a radical telomerization of the other monomer to obtain cotelomers based on both VDF and TFP units (Scheme 1). Though the telomers used in all cases contain only one unit of the

first monomer (either VDF or TFP), the cotelomerization can lead to several products, i.e. the monoadduct ($n=1$), the diadduct ($n=2$) and polyadducts ($n\geq 3$). The total product mixture was vacuum distilled to separate the mono and diadducts from the mixture and the results are given in Table 3.

3.1.2.1 Radical telomerization of TFP with R_F -VDF-I

Most reactions were carried out in the presence of a mixture of two initiators that were used at the temperature for which their half-lives were about 1 hour (75 °C and 140 °C for TBPPi and di-*tert*-butylperoxide (DTBP), respectively). The reaction was allowed to proceed either in bulk (Runs #7, 12, and 13) or in presence of solvent ($C_4F_5H_5$ except for Run #17, *tert*-butanol). The experimental conditions are listed in Table 2 while the characterizations of the products are summarized in Table 3.

Insert Table 2

Insert Table 3

The TFP conversion was high (37-81 wt%) but the yield after distillation was smaller meaning that there is a sizable amount of triadducts or higher adducts, signifying that propagation took place. It was also noted that the fraction of unreacted telomer (R_F -VDF-I) could be high especially in the case of Runs #7 and #8. It was observed that though the pressure was substantially higher in the case of Run #8 due to the elevated quantity of TFP

used, the yield was lower and 73 % of unreacted telogen was recovered. Run #7 dealt with a bulk cotelomerization (i.e. without any solvent) in the presence of a high quantity of TFP, and even though the conversion was higher (expected), a rather high amount of unreacted telogen still remained (41 %). It seems that the reaction was favored at higher dilution (Run #10) where the reaction led mainly to the monoadduct in contrast to reactions with higher concentrations of TFP (Runs #7,8). Scaling that reaction up (Run #11) was attempted using the same conditions as for Run #10, and that reaction led to better conversion (81 vs 65 wt.%).

Insert Figure 1

The $(\text{CF}_3)_2\text{CFCH}_2\text{CF}_2\text{CH}_2\text{CH}(\text{CF}_3)\text{I}$ was characterized by NMR spectroscopy and the spectra are presented in Figure 1 and 2. The ^{19}F NMR spectrum (Figure 1) exhibits the absence of the characteristic signal assigned to $-\text{CH}_2-\text{CF}_2-\text{I}$ (at -39 ppm) in the chain transfer agent, shifting to -93 ppm, and the presence of the signal centered at -69 ppm, attributed to $-\text{CH}_2\text{CH}(\text{CF}_3)\text{I}$ confirming previous assignments.²⁰

From the ^1H NMR, it is not possible to be certain that all the telogen was consumed during the reaction since its signal is overlapping with the methylene protons of both VDF and TFP. The multiplet centered at 4.8 ppm indicates the $>\text{CH}-$ of the TFP but it is not possible either to conclude between normal and reverse addition of TFP to the telomer.

Insert Figure 2

Comparing the $R_FCH_2CF_2\cdot$ and $R_FCH_2CH(CF_3)\cdot$ radicals, the latter is less electrophilic than the former and may expect to react on both sites of VDF, leading to two isomers. However, ^{19}F and 1H NMR spectra (Figure 1 and 2) show that only 2.7 % of $R_FCH_2CH(CF_3)CF_2CH_2I$ was produced. Although the signal centered at ca. -95 ppm, assigned to CF_2CH_2I is negligible in this isomer, that of CH_2I , centered at 3.65 ppm enabled us to assess the normal:reverse ratio (97:3).

3.1.2.2 Radical telomerization of VDF with R_F -TFP-I

The VDF conversion was lower than that of TFP in the previous series. This tends to demonstrate that TFP is more reactive than VDF (and this is also going to be shown from the random cotelomerization and from the assessment of the reactivity ratios). The conversion is constant over all samples (31-50 wt.%) and yield relates to the conversion. As the yield after distillation remains close to the conversion, this shows that predominantly mono- and di-adduct were produced and for such, no propagation occurs noticeably. For several samples (Runs #15, 16, and 17), about half of the telogen did not react. This happened for reactions where the pressure was higher. It seems that again, high pressure does not allow all the telogen to react although the yield remains constant. A couple of runs were attempted in bulk (Runs #12, 13) which, on the contrary to the previous series, seem to generate a higher amount of monoadduct (up to 74 wt%) without decreasing the yield.

The ^{19}F NMR spectra (Figure 1) show the presence of the characteristic signal centered at -39 ppm assigned to $-CH_2-CF_2-I$ and a satisfactory integral ratio 6:3:2:1 corresponding to $(CF_3)_2:CF_3:CF_2:CF$ groups, respectively, indicating a monoadduct $(CF_3)_2CF-CH_2-CH(CF_3)-$

CH₂-CF₂-I. A negligible peak could be observed in the -95 ppm region (-CH₂CF₂CH₂CH(CF₃)-), indicating the quasi-absence of reverse addition of VDF to the TFP telomer, and that the monoadduct mentioned above was formed quantitatively. This could be confirmed by ¹H NMR, where a small quartet centered at 3.7 ppm indicated a negligible amount of reverse addition (2.7 %) compared to normal addition (2.8 and 3.2 ppm for AB-X system).

In conclusion, the sequential cotelomerization of VDF and TFP with R_F-VDF-I was not only more efficient than that of TFP and VDF, but also led to polyadducts, indicating propagation. Surprisingly, it was observed that the cotelomerization was better achieved at low pressure even though a sizeable amount of telogen still remained in the mixture.

As the yield was low, it was of interest to investigate the random radical cotelomerization of both VDF and TFP with R_FI (R_F=iC₃F₇). Also the random radical cotelomerization could be carried out in emulsion which is expected to increase the molecular weights.

3.2 Random cotelomerization

Contrarily to the sequential cotelomerization, the random cotelomerization is a one pot synthesis where both monomers and the chain transfer agent (or telogen) are mixed together. The main difference is that the cotelomer formed in such a way does not have a block structure but a statistical structure.

Insert Scheme 2

Initially, the only report in the literature came from Shin Etsu (indeed that company claimed the random copolymerization of VDF and TFP).⁴³ However, this Japanese patent did not disclose (i) any details of the characterization of the polymer obtained, and (ii) which comonomers were more reactive. More recently, Chemtura patented the cotelomerization of VDF and TFP.⁴⁶ The cotelomerization was performed both in solution and in emulsion. The experimental conditions are listed in Table 4 while the characteristics of the products are gathered in Table 5.

Insert Table 4

As expected, the emulsion cotelomerization (Runs #19, 26, and 27) led to slightly lower yields (due to insolubility of the fluoroolefin and chain transfer agent in water, and also by lack of optimization of the process) but to products of higher molecular weights (the reaction was supposed to take place mainly in the dispersed phase). Scale-up reaction from 160 mL to 2000 mL led to comparable products with a substantially higher yield (80 wt.% vs. <60 wt.%) even with a higher telogen content.

Insert Table 5

Whatever synthesized by solution or emulsion processes, the molecular weights of the poly(VDF-*co*-TFP) cotelomers assessed from the NMR (as in the cases above) are a direct function of the reverse amount of the telogen (Table 5). A higher concentration induces the formation of low molecular weight telomers. Furthermore, it was also noted that the

number of TFP units in the cotelomer was unexpectedly higher than those of VDF units although the percentage of VDF in the feed was generally higher. However, cotelomers richer in VDF (≥ 50 mol%) could be obtained starting from VDF feed compositions higher than 70 mol% (Runs #21, 23, and 24). Some samples were characterized by size exclusion chromatography (SEC) to assess their molecular weights and polydispersities (See figure 1 in supporting information).

Insert Figure 3

A wide range of products was achieved by random cotelomerization since the observed compounds had molecular weights ranging from 700 to ca. 66,000 g.mol⁻¹. The average molecular weight, M_n , was assessed from the ¹⁹F NMR spectrum (Figure 3) where the peaks relative to the telogen (i-C₃F₇) (centered at -77 and -185 ppm, assigned to (CF₃)₂ and CF, respectively) were used as labels. The number of VDF units was determined as follows:

$$\#VDF = \frac{\int_{-39} CF_2I + \int_{-92} blockVDF + \int_{-95} diadVDF / TFP + \int_{-113} reverseVDF + \int_{-116} reverseVDF}{\frac{\int_{-77} (CF_3)_2}{6}}$$

The number of TFP units was determined following a similar calculation:

$$\#TFP = \frac{\frac{\int_{-72} CF_3}{3}}{\frac{\int_{-77} (CF_3)_2}{6}}$$

Hence, the average molecular weight could be assessed as follows:

$$M_n = M_n(T) + \#VDF \times M_n(VDF) + \#TFP \times M_n(TFP)$$

Where $M_n(T)$, $M_n(VDF)$, and $M_n(TFP)$ represent the molecular weight of the telogen, VDF, and TFP (295.93, 64.04, and 96.05 g.mol⁻¹), respectively. To the best of our knowledge, this is the first time that such high molecular weights were obtained for poly(VDF-co-TFP) copolymers. It can be noted from Figure 3 that the integration for the β fluorine atom (1F) give only half of what could be anticipated from that of α fluorine atom (6F). This was attributed to a low signal/noise ratio and the position on the edge of the spectrum.

The ¹H NMR spectrum (Figure 4) enabled us to confirm the presence of both VDF and TFP by the characteristic signals assigned to TFP (>CH- is isolated between 3.5 and 4.0 ppm, and -CH₂- centered at 2.4 ppm) and VDF (-CH₂- centered at 2.6). A peak centered at 1.8 ppm was attributed to the direct initiation. However the integrals values of the methyne and methylene protons of TFP do not present the right ratio, that was attributed to the overlapping of the signals between VDF and TFP methylene groups (see Table 1 in supporting information).

Insert Figure 4

From the wide range of feed compositions, it has been possible to plot (Figure 5) the copolymer composition (e.g. the molar percentage of VDF in the copolymer) vs. the feed composition (e.g. the molar percentage of VDF in the autoclave). Figure 5 enables us to assess the reactivity ratios of both comonomers. Different models can be applied such as

those of Fineman-Ross⁵⁸, of Kelen-Tüdös⁵⁹, and of the extended Kelen-Tüdös⁶⁰. To apply the Fineman-Ross and the Kelen-Tüdös models, the conversion was required to be lower than 20 %, and as a result only four runs were considered. On another hand, the Extended Kelen-Tüdös model takes the conversion of the reaction into account, and all seven points were used. The different methods led towards similar values of the reactivity ratios, and the results, gathered in Table 6, give an average value determined as $r_{\text{VDF}} = 0.28 \pm 0.07$ and $r_{\text{TFP}} = 2.35 \pm 0.26$ at 75 °C.

Insert Figure 5

Insert Table 6

Surprisingly, the results show that TFP is more reactive than VDF, while an opposite tendency was expected due to the perfluoro methyl substituent in the α position as in the case of hexafluoropropene (HFP) and perfluoromethylvinyl ether (PMVE). Table 7 display various values of the reactivity ratios of VDF with different comonomers M.⁶¹⁻⁸² It can be noted that TFP may behave as vinyl fluoride (VF) assuming that the electronic effect and steric effect of a CF_3 group is quasi-similar to that of a fluorine atom, and the vinyl function being the same for VF and TFP. Indeed, $r_{\text{VDF}} = 0.17-0.43$ and $r_{\text{VF}} = 3.8-5.5$ (Table 7) are in good agreement with the reactivity ratios of VDF and TFP. The observed higher reactivity of TFP compared to VDF also confirm the higher TFP yields that were observed in the case of the sequential cotelomerization compared to these of VDF.

Values of $1/r_{\text{VDF}}$ give an indication of the rate of crosspropagation to that of homopropagation, showing in the case of elevated value, a comonomer more able to react onto a VDF terminated macroradical than onto itself. From Table 7, it can be seen that the most reactive comonomer is ethylene (E) ($1/r_{\text{VDF}} = 20$)⁶⁴ and pentafluoropropene (PFP) is the least reactive (0.11)⁶⁶. It is noted then that TFP has a similar reactivity with respect to VDF as tetrafluoroethylene (TFE) (3.5 vs. 4.3), α -trifluoromethacrylic acid (MAF) (3.0) or vinyl fluoride (VF) (2.5-5.0)^{65,68,69} indicating the important role of the substituent with an electron-withdrawing inductive effect (CF_3 , $2\times\text{F}$, $4\times\text{F}$, CF_3 , F , respectively). However, the steric effect has to be considered as well. The steric hindrance of the carbon bearing the bulky groups will not be the favored site for the addition of the radical. In addition, TFP is more reactive with VDF than its perfluorinated homologue (HFP). Also, ethylene (or vinyl acetate) are much more reactive than VDF ($r_{\text{VDF}} = -0.4$ and $r_{\text{VAc}} = 1.67$)⁷³, and it can be pointed out that TFP has a structure quite similar to vinyl acetate (VAc) which is an additional statement to confirm the higher reactivity of TFP than VDF. In our experimental conditions, the radical copolymerization of vinylidene fluoride with $\text{H}_2\text{C}=\text{CH}-\text{C}_6\text{F}_{13}$ failed indicating that a bulky substituent does not favor the copolymerization.

Insert Table 7

Q and e are intrinsic parameters of a monomer linked to the resonance and to the polarity, respectively. From the reactivity ratios values, it is possible to assess the values of Q and e for TFP, according to the following equations developed by Alfrey and Price:⁸³

$$r_{VDF} = \frac{Q_{VDF}}{Q_{TFP}} \exp[-e_{VDF}(e_{VDF} - e_{TFP})]$$

$$r_{TFP} = \frac{Q_{TFP}}{Q_{VDF}} \exp[-e_{TFP}(e_{TFP} - e_{VDF})]$$

and knowing the values of Q and e for VDF (Table 8).^{65,84,85} Only one publication refers to their values for TFP,⁸⁶ and it was of interest to evaluate these parameters to validate our work. Solving these two equations with two variables gave $e_{TFP} = 1.007-1.847$, and $Q_{TFP} = 0.037-0.279$. The values of e for TFP are higher than that of VDF (0.4)⁶⁵, but smaller than that of CTFE (1.84)⁷¹ and TFE (1.63)⁶⁸, which could be expected since TFP is less reactive than both latter monomers, and has also a less electron-withdrawing behavior. Furthermore, this value is in agreement with the previous values found in the literature (0.42 and 0.72).⁸⁶ In addition, Q values appear as in the same range or somewhat higher than these of most fluorinated monomers (VDF= 0.008-0.036, CTFE = 0.031, TFE = 0.032)^{65,68,71}, and the other values determined for TFP (0.130 and 0.008)⁸⁶.

Insert Table 8

4 CONCLUSIONS

The sequential cotelomerization of VDF and TFP with iC_3F_7I led to $(CF_3)_2CFCH_2CF_2CH_2CHICF_3$ and $(CF_3)_2CFCH_2CH(CF_3)CH_2CF_2I$ monoadducts in various yields. These reactions showed that TFP is more reactive than VDF, since propagation was observed when TFP was used in the cotelomerization (with R_F -VDF-I) while the

cotelomerization with VDF in the presence of $R_FCH_2CHICF_3$ mainly yielded to the monoadduct, and in low yield. Surprisingly, it was observed that when the pressure was high, the yield was lower, and a sizeable amount of unreacted telogen was recovered.

In contrast, the random cotelomerization of VDF and TFP carried out in solution or in emulsion led to a wider range of statistic cotelomers, the molecular weights of which ranged from 700 to ca. 66,000 $g.mol^{-1}$. These obtained high molecular weights are very interesting since the (co)telomerization is known to lead usually to low molecular weight polymers. Cotelomers richer in TFP were obtained when the initial VDF concentration was below 70 mol.%. It was also observed, as in the sequential cotelomerization, that TFP was more reactive than VDF. The reactivity ratios were assessed ($r_{VDF} = 0.28 \pm 0.07$ and $r_{TFP} = 2.35 \pm 0.26$ at 75 °C) showing that the perfluoromethyl group of TFP has a stronger electron-withdrawing effect than both fluorine atoms of VDF.

Comparing sequential and random cotelomerization shows that the yields were higher in the latter case. Random cotelomerization in emulsion allowed increasing the molecular weights of the cotelomers by several orders of magnitude, up to 66,000 $g.mol^{-1}$, and this was the first time that so high molecular weight-polymers based on TFP have been synthesized. Scale-ups in a two liter autoclave led to reproducible results, even with better yields.

Since the chains are not perfluorinated and present methylene groups that are prompt to enzymatic or hemolytic decompositions, a new series of precursors for non-bioaccumulable surfactants was synthesized and characterized. Further chemical modifications of those cotelomers to obtain functional materials for the above mentioned applications are in

progress to lead to the preparation of these new surfactants and will be the object of a forthcoming article.⁸⁷ In addition, the extension of this survey to the iodine transfer copolymerization of VDF and TFP is under progress.

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TABLE CAPTIONS

Table 1. Telomerization of vinylidene fluoride (VDF) with $i\text{-C}_3\text{F}_7\text{I}$: experimental conditions and results.

Table 2. Reaction conditions for the sequential cotelomerization of TFP (Runs #7-11) and VDF (Runs #12-17) with the corresponding R_F -VDF-I or R_F -TFP-I monoadducts as chain transfer agents (CTA).

Table 3. Conversion of the comonomer, and characterizations of adducts for the sequential cotelomerization of VDF (Runs #12-17) and TFP (Runs #7-11) with the corresponding monoadduct.

Table 4. Experimental conditions for random radical cotelomerization of VDF and TFP with $i\text{C}_3\text{F}_7\text{I}$.

Table 5. Adducts characterization for the random cotelomerization of VDF and TFP with $i\text{C}_3\text{F}_7\text{I}$.

Table 6. Reactivity ratios of the VDF and TFP comonomers assessed by the different models.

Table 7. Reactivity ratios of VDF, and different M comonomers.

Table 8. Q and e parameters for the TFP calculated from VDF values found in the literature.

SCHEME CAPTIONS

Scheme 1. Sequential (co)telomerization of vinylidene fluoride (VDF) and 3,3,3-trifluoropropene (TFP) in the presence of 2-iodoperfluoropropane, and composition of the products.

Scheme 2. Random radical cotelomerization of TFP and VDF with 2-iodoperfluoropropane.

FIGURE CAPTIONS

Figure 1. ^{19}F NMR spectra of cotelomers based on VDF and TFP obtained by sequential cotelomerization (recorded in deuterated acetone).

Figure 2. ^1H NMR spectra of cotelomers based on VDF and TFP obtained by sequential cotelomerization (recorded in deuterated acetone).

Figure 3. ^{19}F NMR spectra of poly(VDF-*co*-TFP) cotelomer obtained by random cotelomerization (recorded in deuterated acetone).

Figure 4. ^1H NMR spectra of poly(VDF-*co*-TFP) cotelomer obtained by random cotelomerization (recorded in deuterated acetone).

Figure 5. Monomer-copolymer composition curve of vinylidene fluoride (VDF) and 3,3,3-trifluoropropene (TFP) system, The points are experimental data (assessed from ^1H and ^{19}F NMR) while the lines represents the theoretical models: Fineman-Ross (dot line), Kelen-Tüdös (dash line), and extended Kelen-Tüdös (full line).

Graphical Abstract

The sequential and random cotelomerizations of vinylidene fluoride (VDF) and 3,3,3-trifluoropropene (TFP) with $(\text{CF}_3)_2\text{CFI}$ led to polyadducts with molecular weights ranging from 700 to 66,000 $\text{g}\cdot\text{mol}^{-1}$ in high yields. Both paths showed that TFP is more reactive than VDF and the random cotelomerization allowed the assessment of the reactivity ratios ($r_{\text{VDF}} = 0.28 \pm 0.07$ and $r_{\text{TFP}} = 2.35 \pm 0.26$ at 75°C) as well as the Q and e parameters for TFP ($Q_{\text{TFP}} = 0.037\text{-}0.279$, and $e_{\text{TFP}} = 1.007\text{-}1.847$).

