



Chain-End Functionality: the Key Factor toward Fluoropolymers Thermal Stability

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Chain-End Functionality: the Key Factor toward Fluoropolymers Thermal Stability.

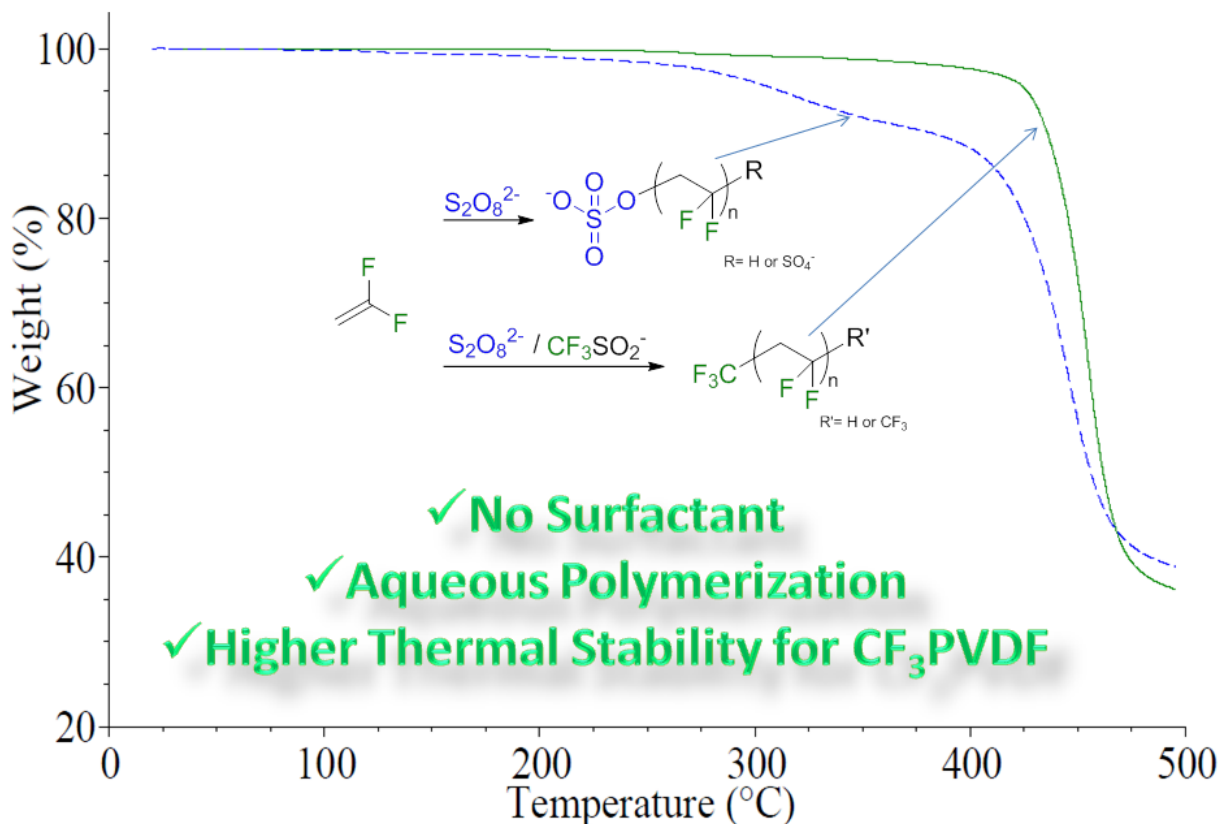
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TOC:



Abstract

The aqueous radical homopolymerization of vinylidene fluoride (VDF), as well as its *co*-polymerizations with hexafluoropropylene (HFP) or perfluoromethyl vinyl ether (PMVE), and its *ter*-polymerization with HFP and PMVE, initiated by trifluoromethyl radicals ($\bullet\text{CF}_3$), generated from ammonium persulfate (APS) and potassium trifluoromethyl sulfinate ($\text{CF}_3\text{SO}_2\text{K}$) redox system are presented. The optimization of the experimental conditions in terms of initial reactant molar ratios, temperature and reaction time was achieved. The best results were obtained at 60 °C, in water, without any surfactant, using 0.9 eq of APS as the oxidant with respect to $\text{CF}_3\text{SO}_2\text{K}$. PVDF, poly(VDF-*co*-HFP), poly(VDF-*co*-PMVE), or poly(VDF-*ter*-PMVE-*ter*-HFP) *co*-polymers were obtained in high yields (varying between 89 and 100%), and with molar masses up to 113,000 g/mol . The ^1H and ^{19}F NMR spectroscopy revealed that, under optimized conditions, the formed chain-ends were exclusively CF_3 or CF_2H . The influence of the nature of the chain-end on the thermal stability showed that PVDFs terminated by CF_3 were more stable than their analogues bearing sulfate end-groups by 120 °C. In addition, the prepared CF_3 -PVDFs had 53% of crystallinity (compared to 47% for PVDF initiated from APS alone), which offers excellent resistance to conventional organic solvents including dimethyl sulfoxide, acetone and dimethyl formamide.

Keywords: Co- and terpolymerization, NMR spectroscopy, poly(vinylidene fluoride), Surfactant free aqueous polymerization, trifluoromethyl radicals, trifluoromethylation, thermal stability.

Introduction

In everyday human activities, man-made machines are subjected to extreme conditions in respect to their applications. In order to ensure the targeted performances, a wide range of specialty materials have been developed such as ceramic composites,¹ and plastics.² High performance polymers are found to be attractive because of their lightweight compared to metals and ceramics. In addition, the properties of the materials can be tuned by controlling the structure and the compositions of the different monomers used.

Fluoropolymers are important class of these resins. They are used for high performance applications due to their unique thermal, mechanical, and chemical properties.³⁻⁵ For example, poly(vinylidene fluoride), PVDF, the second most produced fluorinated plastic after poly(tetrafluoroethylene), PTFE,⁶ has been used in many applications ranging from piezoelectric materials⁷ to water treatment,⁸ coatings,⁹⁻¹¹ and lithium ion batteries.¹¹⁻¹⁶

Commercially available PVDF is mainly prepared *via* either emulsion or suspension process in water, using a fluorinated or non-fluorinated surfactant, initiated by a wide variety of organic peroxides,^{17,18} or inorganic persulfate initiators.¹⁹⁻²¹ These synthetic methods are efficient, but the use of surfactants such as ammonium perfluorooctanoate (APFO), perfluorooctanoic acid (PFOA), and perfluorooctanesulfonic acid (PFOS),²² is a major drawback because of the bioaccumulation, toxicity, and persistence issues.²³

However, the nature of the chain-end functionality was found to be a crucial factor that affects the thermal stability of the polymers *via* the “Unzipping” thermal degradation.²⁴⁻²⁶ Tang *et al.*²⁷ showed that the thermal properties of poly(γ -butyrolactone) were strongly affected by the nature of its chain-end. For example, it increased from 222 °C, with an alcohol end-group, and to 334 °C when transformed to the corresponding silyl ether, thanks to the stronger Si-O bond. In the same manner, the thermal stability of PVDF can be reduced regarding the lability of the chain-end created after the ammonium persulfate (APS) initiation.²⁸

In order to overcome this issue, a thermostable fluoroalkyl end group, such as CF₃, was found to be of interest. In this context, several products able to release a •CF₃ radical have been used for the polymerization of fluorinated olefins (Figure 1)²⁹⁻³¹. For example, Asandei *et al.*³⁰ used bis[trifluoroacetoxy]iodobenzene as a •CF₃ radical generator in order to polymerize VDF under photochemical conditions. In addition, our group performed the radical telomerization of VDF using trifluoromethyl iodide as chain transfer agent to prepare CF₃(CH₂CF₂)_nI telomers.²⁹ The persistent perfluoroalkyl radical, perfluoro-3-ethyl-2,4-dimethyl-3-pentyl (PPFR), can release •CF₃ radicals when heated above 80 °C.³² Boschet *et al.*³³ used PPFR to initiate the radical polymerization of VDF. The octafluoro[2.2]paracyclophane generated a •CF₃ radicals under higher thermal conditions (ca. 180 °C)

and led to CF₃-ended PVDF.³⁴ In addition, this radical was also obtained from trifluoromethanesulfonate under photochemical irradiation and yielded CF₃(CH₂CF₂)_nSR telomers.³⁵

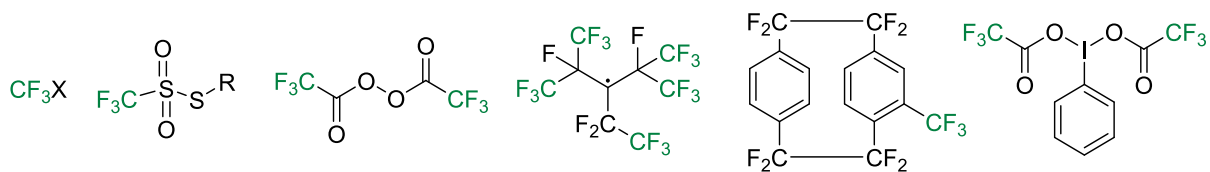


Figure 1: Generators of •CF₃ radical under various conditions able to initiate the telomerization or polymerization of fluorinated olefins (X= I or Br and R= phenyl or cyclohexyl)

As a matter of fact, sulfinate salts represent an important class of organic compounds. They are synthesized from the corresponding sulfonyl halides^{36–38} or by the addition of an organometallic reagent to sulfur dioxide.³⁹ Because of their stability toward air and moisture, they are mainly used as alternatives to sulfonyl chlorides in the preparation of sulfonamides.⁴⁰ Furthermore, sulinates can also be used to afford organic radicals under oxidative conditions.⁴¹ One significant example on the utility and the versatility of this synthetic approach is the radical trifluoromethylation of organic compounds using sodium trifluoromethanesulfinate (called the Langlois reagent).^{42–44} Using oxidants such as *tert*-butyl hydroperoxide or persulfates, •CF₃ radicals are generated under mild conditions, yielding the corresponding trifluoromethylated products in good yields.^{45–49}

However, a few studies describe the preparation of fluoroalkyl sulinates (C_nF_{2n+1}SO₂Na, with n > 5) from the corresponding fluoroalkyl sulfonyl halides and their use simultaneously as surfactants and fluororadical sources.^{50–56} To our knowledge, though involved in organic chemistry,^{43,44} the trifluoromethanesulfinate salts have never been used as initiators in radical polymerization. Hence, this article aims at describing a surfactant-free method for the preparation of PVDF in water using potassium trifluoromethanesulfinate as the initiator in the presence of ammonium persulfate as the oxidant. The reaction, performed at 60 °C, led to quantitative yields in less than 1.5 hours. The optimized system allowed the preparation of PVDF and VDF *co*- and *ter*- polymers with fluorocarbon chain-ends,

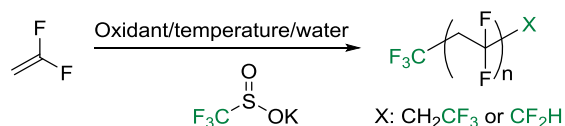
exclusively. In addition, the prepared PVDF displayed significant improved thermal stability and solvent resistance (due to high crystallinity) when compared to a PVDF prepared from APS as the initiator.

Results and discussion

In order to prepare a CF₃-terminated PVDF in a convenient way, potassium trifluoromethanesulfinate was selected as the •CF₃ radical source because of its commercial availability and its high solubility in water.

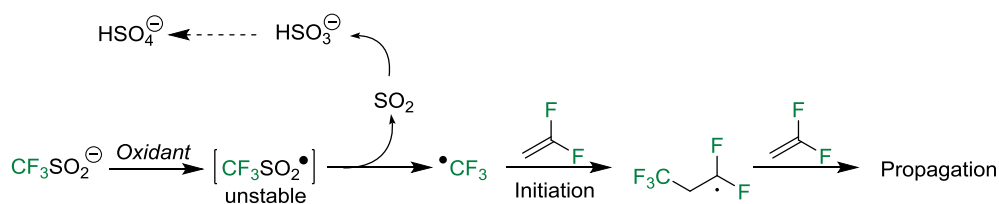
Choice of the Oxidant

The effects of the nature and the amounts of additives such as oxidants and surfactants were evaluated. Then, all reaction parameters were optimized in order to maximize the yield and the CF₃ content in the final polymers.



Scheme 1: Optimization of the oxidant nature in the aqueous CF₃- PVDF synthesis by radical polymerization of VDF initiated by •CF₃ radical

As mentioned above, sulfonates can afford the corresponding radical, only in the presence of an oxidant (Scheme 2).^{43,44} This feature was confirmed from the reaction conditions listed in Table 1, entry 1. For this reason, the effect of the nature of the oxidant on the yield of the reaction was studied (Scheme 1). Oxidant such as hydrogen peroxide (H₂O₂) (Table 1, entry 2), cumene hydroperoxide (CHP) (Table 1, entries 3 and 4), 2,2'-azobis(2-methylpropionamidine)dihydrochloride (V-50) (Table 1, entry 5), and di(4-*tert*-butylcyclohexyl) peroxydicarbonate (P-16s) (Table 1, entries 6-9), were not effective for the generation of radicals from the corresponding sulfinate. These reactions, instead of the polymerization of VDF, did not afford any products.



Scheme 2: Mechanism of the oxidation of trifluoromethyl sulfinate, leading to the generation of $\bullet\text{CF}_3$ radicals

In contrast, ammonium perfluorooctanoate (APFO) was added in order to ensure the formation of an emulsion in the medium, while ammonium persulfate was tested as the oxidant at 80 °C (Table 1, entry 10).⁵⁷ A full VDF conversion was achieved after 25 min and PVDF was isolated as a white powder soluble in DMSO and DMF, in quantitative yield.

NMR spectroscopy

All PVDFs achieved from the $\text{APS}:\text{CF}_3\text{SO}_2\text{K}$ systems (Tables 2-4) were characterized by ^1H and ^{19}F NMR spectroscopy. The spectra confirm the formation of PVDF from the following features: i) VDF head-to-tail normal addition was evidenced by a signal at -92 ppm related to $-\text{CF}_2\text{-CH}_2-$ moiety (^{19}F NMR), and a triplet centered at 2.9 ppm (^1H NMR: $-\text{CF}_2\text{-CH}_2-$)⁵⁸; ii) the reverse tail-to-tail inversion was identified by ^1H NMR as a triplet at 2.2-2.4 ppm ($-\text{CF}_2\text{CH}_2\text{-CH}_2\text{CF}_2-$, Figure 2), while, the head-to-head inversions were highlighted in ^{19}F NMR spectrum at -114 ppm and -116 ppm ($-\text{CH}_2\text{CF}_2\text{-CF}_2\text{CH}_2-$, Figure 3).^{29,30,33,34,58,59} The molar mass was 3,000 g/mol (eq. 8), with low head-to-head (2.5%) and tail-to-tail (3.5%) inversion rates (eq. 2) (Figure 2 and Figure 3).

The analysis of the chain-end composition revealed a competition between both initiators, i.e. the sulfate and $\bullet\text{CF}_3$ radicals. The $\text{CF}_3\text{-CH}_2-$ signal (quintet, $^3J_{\text{FH}} = ^4J_{\text{HH}} = 9.9$ Hz) was centered at -61 ppm.^{29,30,33-35,59} In addition, the methylene in $\text{CF}_3\text{-CH}_2\text{CF}_2-$ group was identified by ^1H NMR by a multiplet at 3.1 ppm^{30,59} while that of $-\text{O}_3\text{SO-CH}_2\text{CF}_2-$ was high field shifted to -103 ppm. It was observed that the addition of $\bullet\text{CF}_3$ occurred exclusively on the tail of VDF molecule, and this was confirmed by the absence of any end-group signal attributed to $\text{CF}_3\text{-CF}_2\text{CH}_2-$ sequence at -83 ppm.⁶⁰

Table 1: Choice of the oxidant and the solvent for the radical polymerization of VDF in presence of CF₃SO₂K

Entry	T(min)	T(°C)	Oxidant	[VDF]: [Oxidant]: [CF ₃ SO ₂ K] (mol%)	Solvent (mL)	P _{max} (ΔP)	Yield (%)	CF ₃ :CH ₂ OH ^a	H- H (%) _a	DPn _a
1	1,200	80	-	100.0: 0.0: 1.0	Water (20)	30	0	Nd	Nd	Nd
2	1,200	55	H ₂ O ₂	100.0:10.0:1.0	DMC (20)	13 (0)	0	Nd	Nd	Nd
3	1,200	50	CHP	100.0:1.5:1.0	DMC:Water (1:1, 20)	14 (0)	0	Nd	Nd	Nd
4	1,200	50	CHP	100.0:1.5:1.0	Water (20)	38 (0)	0	Nd	Nd	Nd
5	3,960	56**	V-50	100.0:1.5:1.0	Water (20)	31 (+2)	0	Nd	Nd	Nd
6	3,960	48**	P 16S	100.0:1.5:1.0	Water (20)	30 (16)	<2	Nd	Nd	Nd
7	1,200	64*	P 16S	100.0:1.5:1.0	Water (20)	31 (12)	0	Nd	Nd	Nd
8	1,200	64*	P 16S	100.0:1.5:1.0	Water:DMC (3:1, 20)	31 (4)	0	Nd	Nd	Nd
9 ^b	1,200	64*	P 16S	100.0:1.5:1.0	Water (20)	34 (0)	0	Nd	Nd	Nd
10 ^b	25	80	APS	100.0:1.5:1.0	Water (20)	33(23)	100	40:60	2.5	48

All reactions were performed in 50 mL hastelloy reactors, vinylidene fluoride (7 g) *: half life temperature = 1 h, **: half life temperature = 10 h. DMC: dimethyl carbonate, APFO: Ammonium pentadecafluorooctanoate 30% w/w in water (0.1 ml used), CHP= cumene hydroperoxide, V-50= 2,2'-azobis(2-methylpropionamidine)dihydrochloride, P 16s= Di(4-*tert*-butylcyclohexyl) peroxydicarbonate, APS= ammonium persulfate. DMC= dimethyl carbonate, Yield= isolated yield, ^a: determined by ¹⁹F NMR spectroscopy, H-H= head to head reverse addition, Nd= not determined. ^b: 1 wt% of APFO was added

This also justifies that no primary termination occurred at least on the PVDF macroradical terminated by a normal addition. In addition, $-\text{CF}_2\text{H}$ chain-end, resulting from hydrogen transfer either from the solvent, or from the polymer by backbiting,²⁸ is also identified by a triplet ($^2J_{\text{HF}} = 55.2$) of triplets ($^3J_{\text{HH}} =$

4.5 Hz), centered at 6.34 ppm (Figure 2), and a doublet of multiplets at -114.4 ppm (Figure 3). Next to expected signal in the 2.8-3.1 ppm range, assigned to VDF-VDF normal addition^{29,30,33,34,58,59}, and those at 2.2-2.4 ppm, attributed to reversed tail to tail addition, a small triplet, centered at 3.2 ppm (overlapping with the signal assigned to the Head to Tail VDF-VDF addition) corresponds to methylene in CF₃-CH₂-CF₂-CH₂-CF₂- end-group.^{30,59}

Table 2: Effect of the presence of the surfactant on the radical polymerization of VDF initiated by •CF₃ radicals

Entry	APFO (ml)	t (min)	P _{max} (ΔP)	Yield (%)	CF ₃ :CH ₂ OX ^a	H-H (%) ^a	DPn ^a
1	0.1	25	33 (23)	100	40:60	1.2	48
2	0	15	33 (27)	100	85:15	4.3	72

All reactions were performed in 50 mL hastelloy reactor, vinylidene fluoride (7g), X= OH or SO₄⁻ CF₃SO₂K (1 mol%), APS (1.5 mol%), T= 80 °C. APFO: Ammonium perfluorooctanoate 30% w/w in water.

^a: determined by ¹⁹F NMR spectroscopy, H-H= head to head reverse addition.

Further optimizations revealed that the presence of a surfactant was not mandatory (Table 2 **Erreur ! Signet non défini.**). The polymerization of VDF was performed in water using APS:CF₃SO₂K (1.5:1.0) at 80 °C without any surfactant. Full conversion of the monomer was achieved in 15 min only (Table 2, entry 1). The CF₃ chain-end content increased from 40% in the presence of APFO, (Table 2, entry 1) to 85% without APFO (Table 2, entry 2). In addition, the molar mass of the formed polymer also increased from 3,000 g/mol with surfactant (Table 2, entry 1) to 4,600 g/mol without any surfactant (Table 2, entry 2). In fact, the presence of a surfactant enhanced the miscibility of VDF in the system, by lowering the solvent surface tension, which favored the monomer to the polymerization initiation by sulfate radicals. However, in the absence of surfactant, the miscibility of VDF in the medium was limited: the CF₃SO₂K oxidation consumed the highest APS amount, and simultaneously generated more •CF₃ radical quantity, leading to the increase of the CF₃ content in the final PVDF.

Table 3: Effect of the stoichiometry of the reaction on the radical polymerization of VDF initiated by •CF₃ radicals

Entry	t(min)	APS (mol%)	P _{max} (ΔP)	Yield (%)	CF ₃ :CH ₂ OH ^a	H-H (%) ^a	DPn ^a	Mn ^b	Đ ^b
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								(g/mol)
								(GPC)
1	15	1.5	33 (27)	100	85:15	4.3	72	-
2	5	0.7	34 (17)	64	>99:1	4.5	85	-
3	5	0.9	33 (19)	62	>99:1	4.5	85	30,000

All reactions were performed in 50 mL hastelloy reactor with high stirring Rate, VDF (7 g) CF₃SO₂K

(1 mol%), APS (0.9 mol%), T= 80 °C. ^a: determined by ¹⁹F NMR spectroscopy, ^b: determined by

GPC (or SEC), H-H= head to head reverse addition

In order to have a full control of the chain-end functionality, the APS:CF₃SO₂K molar ratio was optimized in water at 80 °C (Table 3). An initial molar ratio of 0.9:1.0 in APS:sulfinate led to an exclusively CF₃ initiated VDF polymerization (Table 3, entry 3). Unlike the PVDF solubility behavior described in the literature,⁶¹ this PVDF was insoluble in DMSO, DMF, and acetone at room temperature due to its high crystallinity (53%, calculated by DSC). However, it was soluble in acetone: DMSO mixture (in 1:1 volume ratio).

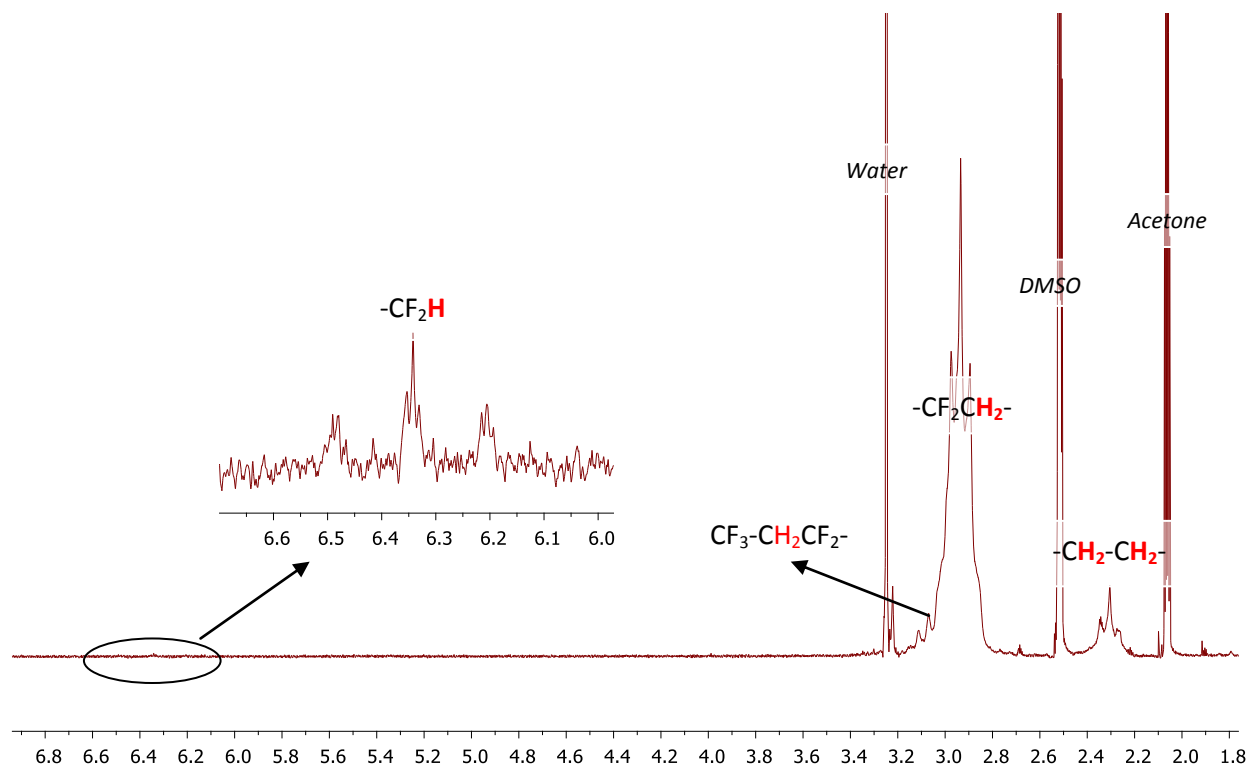


Figure 2: ¹H NMR spectrum of the CF₃-PVDF, recorded in DMSO-*d*₆:Acetone-*d*₆ (1:1) (Table 3, entry 2)

It was found that 60% of the end-chain consisted of CF_3 . By assuming that all produced $\bullet\text{CF}_3$ radicals initiate the radical polymerization of VDF, and as the primary recombination of $\bullet\text{CF}_3$ radicals with the propagating macroradicals was not evidenced, it can be deduced that the recombination termination reaction was predominant by 83%, while the hydrogen transfer represents 17%. In addition, from the GPC analysis of the CF_3 -PVDF (Table 3, entry 3), the calculated polydispersity was 10.5. Such a high value confirmed that the termination reaction of that conventional radical polymerization mainly occurred by recombination.

Table 4: effect of the temperature on the radical polymerization of VDF initiated by $\bullet\text{CF}_3$ radicals

Entry	t(min)	T (°C)	Pmax (ΔP)	Yield(%)	H-H (%) ^a	DPn ^a	Mn (g/mol) ^b	\bar{D} ^b
1	80	60	34 (28)	100	4.0	160	30,000	10.1
2	12	80	33 (19)	62	4.5	85	-	-
3	8	100	34 (32)	43	5.2	66	-	-

All reactions were performed in 50 mL hastelloy reactor, VDF

(7g) $\text{CF}_3\text{SO}_2\text{K}$ (1 mol%), APS (0.9 mol%);

^a: determined by ^{19}F NMR spectroscopy, ^b: determined by GPC;

H-H= head to head reverse addition

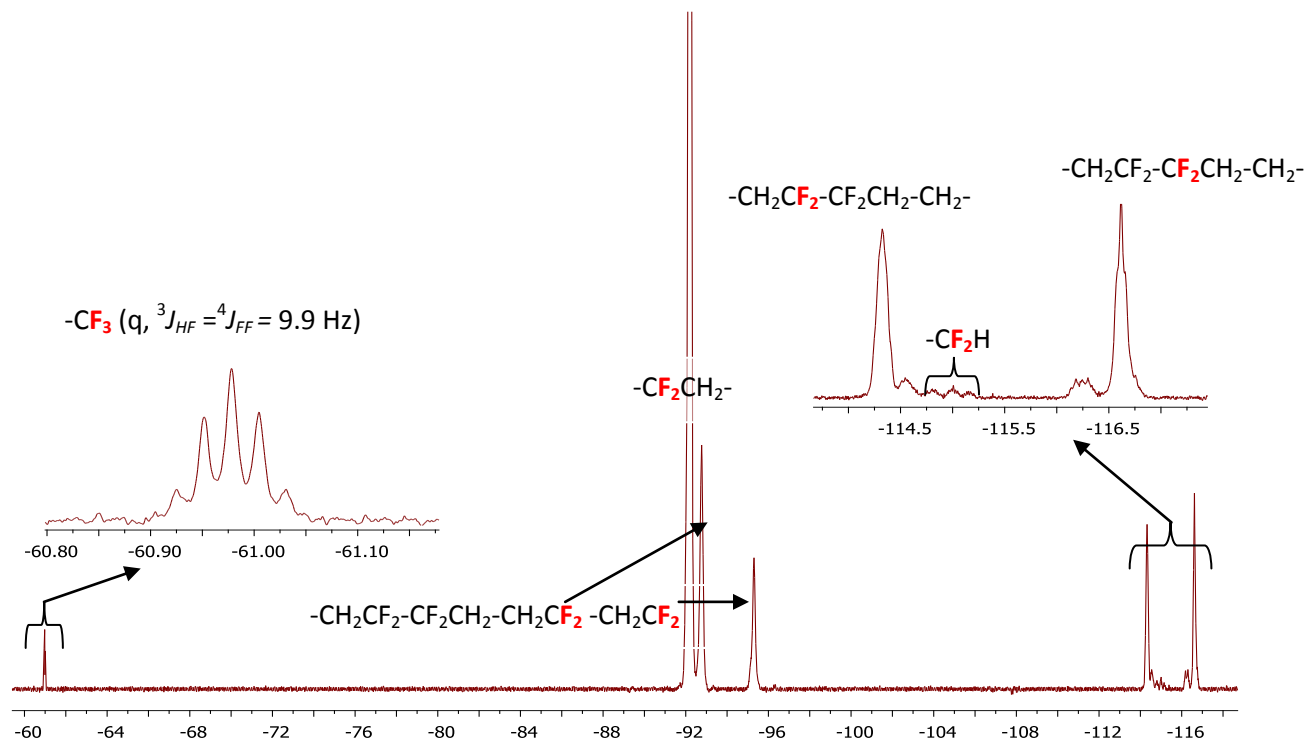


Figure 3: ^{19}F NMR spectrum of the CF_3 -PVDF, recorded in $\text{DMSO-}d_6$: $\text{Acetone-}d_6$ (1:1) (Table 3, entry 2)

MALDI-TOF spectrometry of CF_3 -PVDF

The prepared CF_3 -PVDF (Table 4, entry 1) was also characterized by Matrix-Assisted Laser Desorption Ionization time of flight (MALDI-TOF) (Figure 4), the spectrum in positive ion mode displays the series of $\text{CF}_3(\text{PVDF})_n\text{CF}_3$ oligomers as sodium adducts ($\text{M} + \text{Na}$, where M is $\text{CF}_3(\text{VDF})_n\text{CF}_3$), with molar masses ranging between 2000 and 9000, hence yielding n values ranging between 30 and 140. Some values correspond to monoisotopic mass m/z 5154, 5218, 5281 etc. (as listed in Table S1). In addition, $\text{CF}_3(\text{VDF})_n\text{H}$ oligomers were also detected as sodium adducts with similar n values as above, some of them corresponding to monoisotopic mass m/z of 5149.8, 5213.8 (Figure 4, inset), 5278, etc. Furthermore, $\text{CF}_3(\text{VDF})_n\text{CF}_3$ and $\text{CF}_3(\text{VDF})_n\text{H}$ oligomers were also observed as potassium adducts plus DMSO [$\text{M}_n + \text{K} + (\text{CH}_3\text{SOCH}_3)$, M_n being the molar masses of $\text{CF}_3(\text{VDF})_n\text{CF}_3$ and $\text{CF}_3(\text{VDF})_n\text{H}$ oligomers]. The DMSO moieties come from the preparation of samples for analysis. Detected $\text{CF}_3(\text{VDF})_n\text{CF}_2\text{C}$ and $\text{CF}_3(\text{VDF})_n\text{CF}_2\text{H}$ oligomers could arise from fragmentation of $\text{CF}_3(\text{VDF})_n\text{CF}_3$ and

$\text{CF}_3(\text{VDF})_n\text{H}$. The spectrum shows some intense peaks between m/z 2000 and 4600 corresponding to fragments of $\text{CF}_3(\text{VDF})_n\text{CF}_3$ series where the formula is $\text{CF}_3(\text{VDF})_n\text{CF}_2\text{C}$ (n values ranging between 37 and 130 and the mass m/z are 2435, 2499, 2563, 2627, 2691 etc. (inset in Figure 4)).

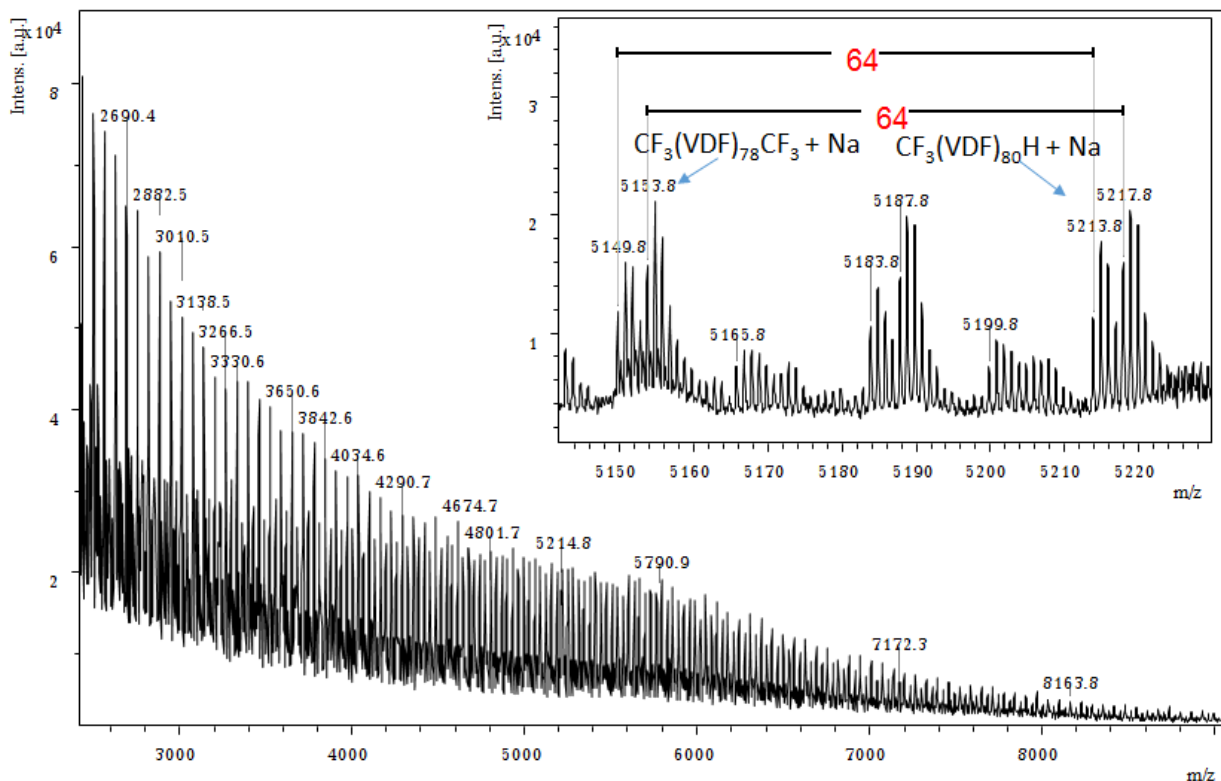


Figure 4: MALDI-TOF-MS mass spectrum in positive ion mode of sample CF_3 -PVDF with $\text{Na}^+ \text{CF}_3\text{COO}^-$ and DCTB as matrix (Table 3, entry 2).

Figure 5 exhibits the negative ion mode MALDI-TOF spectrum of $\text{F}_3\text{C}(\text{VDF})_n\text{CF}_3$ oligomers detected between m/z 657 and 5000 as deprotonated adducts ($\text{M}-\text{H}$) with $\text{Na}^+ \text{CF}_3\text{COO}^-$, M is $\text{F}_3\text{C}(\text{VDF})_n\text{CF}_3$, where n values range between 6 and 72 (the series of mass m/z corresponding at this series are 657, 721, 785, 849, 913, 977, 1041, 1105, 1169, 1233, 1297, 1361, etc (inset in Figure 5)). $\text{F}_3\text{C}(\text{VDF})_n\text{CF}_3$ oligomers were also observed as deprotonated adducts ($\text{M}-\text{H}$) with $\text{K}^+ \text{CF}_3\text{COO}^-$, the m/z monoisotopic mass corresponding to this series are 673, 737, 801, 865, 929, 993, 1057, 1121, 1185, 1249, 1313, 1377. Actually, $\text{Na}^+ \text{CF}_3\text{COO}^-$, used as cationizing agent contains some $\text{K}^+ \text{CF}_3\text{COO}^-$ impurities. The most

intense series were $F_3C(VDF)_nCF_2H$ oligomers detected as deprotonated adducts (M-H) with HF loss, M is $F_3C(VDF)_nCF_2H$ and the CF_2H end group could result from the loss of F atom in CF_3 end-group in $F_3C(VDF)_nCF_3$. This is rather surprising taking into account the high C-F stability. Finally, oligomers of formula $F_3C(VDF)_nCH_2F$ have also been observed as deprotonated adducts (M-H) in which the CH_2F end group could result from fragmentation of $F_3C(VDF)_nH$. Table S1 lists several peak assignments corresponding to the m/z fragments displayed in Figure 5.

The APS-PVDF sample was characterized by negative ion mode MALDI-TOF mass spectrum as shown in Figure S18. The $^-O_3SO(VDF)_nOSO_3^-NH_4^+$ oligomers were detected as deprotonated adducts (M-H) where M is $^-O_3SO(VDF)_nOSO_3^-NH_4^+$ between the mass molar ranging m/z of 1000 and 5000, the values of n being comprised between 7 and 70. The $^-O_3SO(PVDF)_nOSO_3^-$ oligomers also were detected as sodium or lithium adducts with formic acid as noted in the peak assignments of Table S2.

However from the NMR, the molar mass was estimated to be 10,500 g/mol (using eq. 7 and 8). This big difference may be attributed to different factors. Byrd and McEwen⁶² demonstrated that some significantly different MALDI-TOF data may be obtained for the same polymer, depending on the sample preparing conditions, the ionization agent, the matrix used, and the ion detection systems. In addition, the accuracy of such physical analytic methods may be affected by the dispersity of the sample which can lead to different molar mass estimations when compared to other methods such as GPC and NMR.⁶³

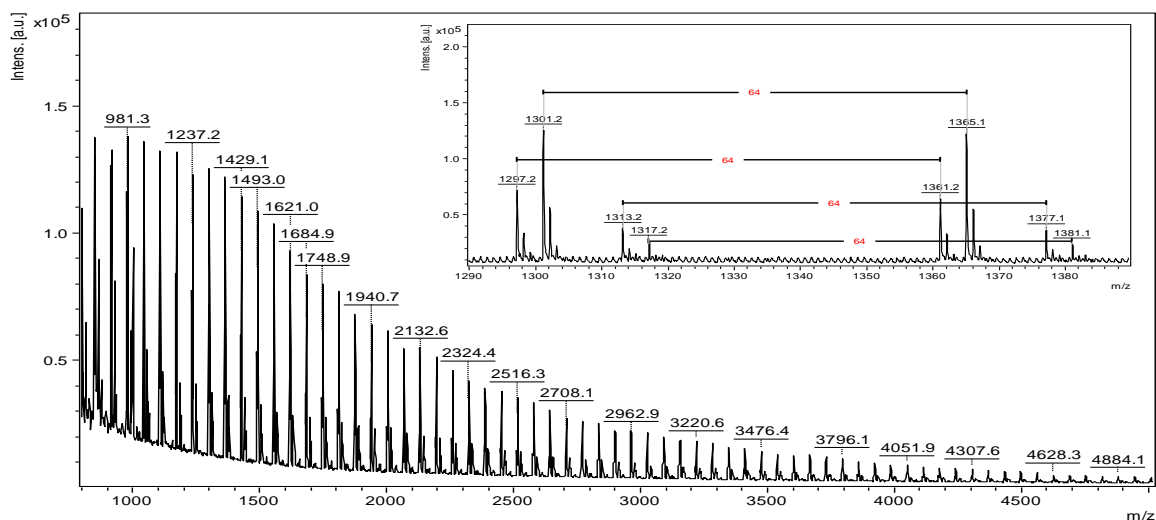


Figure 5: MALDI-TOF-MS mass spectrum in negative ion mode of sample CF₃-PVDF (Table 3, entry 2) with Na⁺ CF₃COO⁻ and DCTB as the cationization agent and the matrix, respectively. The inset is the expansion of the fragments between 1290 and 1400 m/z.

The molar masses of the obtained PVDFs were also assessed by gel permeation chromatography (GPC), after solubilizing the corresponding sample in a 0.1M solution of NaNO₃ in DMSO at 95 °C for 4 hours. The analysis revealed that the prepared CF₃-PVDF (Table 2, entry 1) had an Mw of 370,500 g/mol, Mn of 30,000 g/mol and a dispersity of 10.5.

Influence of the Temperature

Then, the effect of the temperature on the molar mass and the chain-end composition of the obtained PVDF was explored. First, when the temperature increased from 60 °C (Table 4, entry 1) to 100 °C (Table 4, entry 3), the yield of the reaction decreased from 100 to 43%. This can be explained by the enhanced hydrogen transfer reaction with the increase of the temperature. Hence, this transfer led to a DP_n decrease from 160 (at 60 °C, Table 4, entry 1) to 66 (at 100 °C, Table 4, entry 3).⁶⁴ As expected, the head-to-head inversions increased with the increase of the temperature⁶⁴ from 4.0% at 60 °C (Table 4, entry 1) to 5.2% at 100 °C (Table 4, entry 3).

Table 5: co- and ter-polymerizations of VDF with HFP and PMVE initiated by APS/CF₃SO₂K system

Entry	VDF (g)	HFP (g)	PMVE (g)	Feed VDF:HFP:PMVE (mol%)	P _{max} (ΔP)	Yield (%)	In copolymer VDF:HFP:PMVE ^a (mol%)	DP _n VDF:HFP:PMVE ^a	M _n ^b (g/mol) (GPC)	Đ ^b
1	5	4	-	75:25:0	31 (25)	100	86:14:0	174:29:0	45,200	3.8
2	5	-	5	72:0:28	29 (23)	94	74:0:26	251:0:88	40,000	2.3
3	5	2	2	76:13:11	30 (22)	89	74:13:13	318:54:54	113,000	2.6

All reactions were performed in 50 mL Hastelloy reactor with high stirring Rate, reaction time: 3 h, CF₃SO₂K (1 mol%), APS (0.9 mol%), ^a: mol% determined by ¹⁹F NMR spectroscopy (eq. 6), ^b: determined by GPC

Synthesis of VDF Co- and Terpolymers

This methodology is versatile and can be applied to the *co*- and *ter*-polymerization of VDF with other fluorinated monomers such as hexafluoropropylene (HFP) and perfluorinated methyl vinyl ether (PMVE). The copolymerization of VDF with HFP from a 75:25 molar feed ratio (Table 5, entry 1), afforded poly(VDF-*co*-HFP) copolymer in 100% yield. From eq. (4), the copolymer microstructure was assessed, composed of 86 mol% of VDF and 14 mol% of HFP, in good correlation with a previous study.⁶⁵ The ¹⁹F NMR spectrum (Figure S12) of the obtained poly(VDF-*co*-HFP) copolymer displays the characteristic signals of VDF units (as described above) and those assigned to HFP at -70, -75, -120 and -185 ppm, assigned to CF₃-, CF₂- and CF- respectively.⁶⁶ In addition, the CF₂ group of VDF in the VDF-HFP dyad was observed at -109 ppm. The CF₃- chain-ends from the initiation were also present at -62 ppm^{66,67}, confirming a regioselectivity of addition onto the tail site of VDF. As above, it enabled to calculate the molar mass of such a copolymer, using eq. (7) and (8), estimated to be around 16,500 g/mol.

Similarly, VDF was copolymerized with PMVE. The resulting poly(VDF-*co*-PMVE) copolymer of an estimated molar mass of 35,600 g/mol, was obtained with 74:26 of VDF:PMVE ratio (calculated from eq. 5) starting from VDF:PMVE = 70:30,⁶⁸ and in 94% yield. (Table 5, entry 2). Beside the characteristic signals of VDF units, the ¹⁹F NMR spectrum (Figure S9) of the copolymer showed those related to PMVE moiety at -53, -120 and -146 ppm related to the -O-CF₃, -CF₂-, and CF groups, respectively.

In addition, poly(VDF-*ter*-HFP-*ter*-PMVE) terpolymer was also synthesized from a molar feed ratio of VDF:HFP:PMVE = 76:13:11, and characterized by ^{19}F NMR spectroscopy, the spectrum of which (Figure 66) shows all corresponding signals assigned to VDF, HFP and PMVE units as described above, and composed of 74 mol% VDF, 13 mol% HFP, and 13 mol% of PMVE (Table 5, entry 3). Its estimated molar mass was 39,000 g/mol by ^{19}F NMR. However, in contrast with the CF_3 -terminated PVDF which was a powder, the *co* and *ter*-polymers were obtained as white gums due to the high contents of HFP and PMVE.^{67,69}

The TGA analysis highlights the good thermostability of such *co* and terpolymers, with 5 wt% loss at around 408 °C (Table 6, entries 2-4). In addition, the DSC thermograms showed that these copolymers were amorphous, with negative glass transition temperatures (Table 6, entries 2-4) and explained the waxy gum physical state (Figure S17).

In order to reveal the effect of the chain- end functionality on the thermal stability of the PVDF, two samples were prepared from the same process (solvent: water), at 60 °C, for 10 min. One sample was initiated with APS (1 mol%) only (Table 6, entry 1a), while the second one resulted from $\text{CF}_3\text{SO}_2\text{K}$: APS (1.0 mol%: 0.9 mol%) system (Table 6, entry 1). Both samples were analyzed by TGA at a heating rate of 10 °C/min. The earlier weight losses of the polymers (< 5%) were compared in order to highlight the most resistant PVDF toward the unzipping phenomenon.⁷⁰

The TGA thermograms (Figure 7) clearly show that the CF_3 -terminated PVDF (A, Table 6, entry 1) has a better thermal stability than that of PVDF initiated by APS (B, Table 6, entry 1a). The 5 wt% loss of polymer B occurred from 315 °C, while polymer A lost 5 wt% at 428 °C, hence displayed an increase of the thermal resistance by 113 °C. Interestingly, the synthesized CF_3 -PVDF showed a similar thermal behavior under air and nitrogen, the temperature corresponding to 5 wt% loss was around 430 °C under both oxidative and inert atmosphere (Figures S1 and S2).

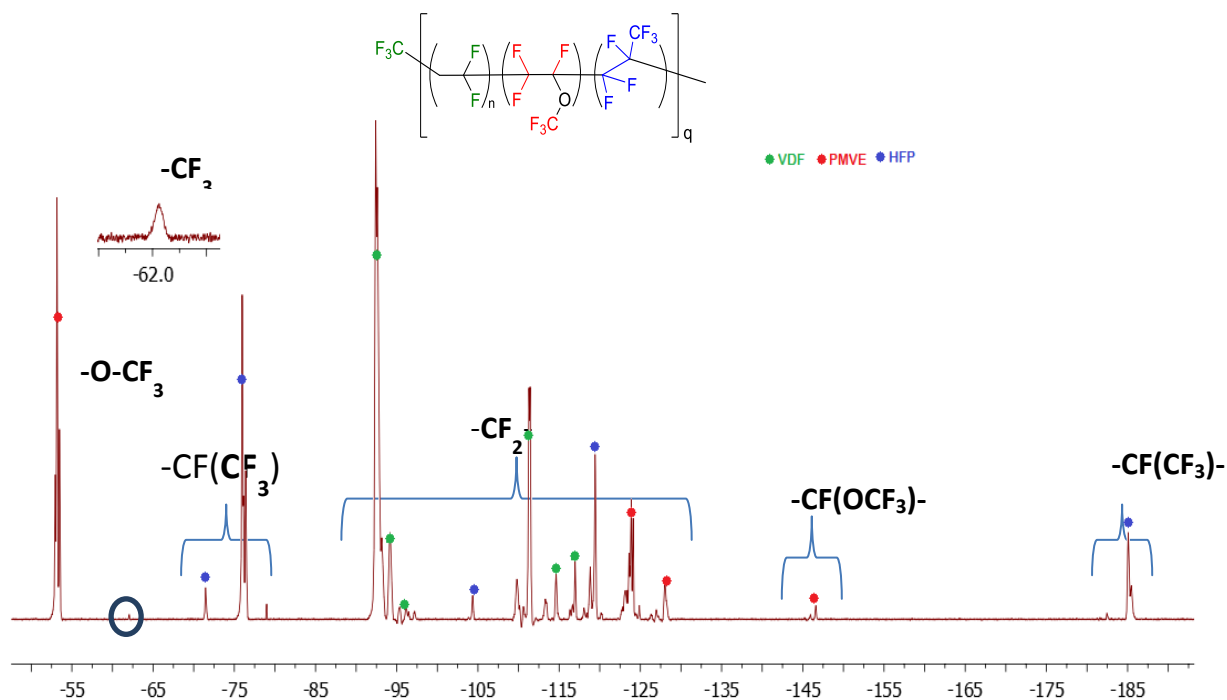


Figure 6: ^{19}F NMR spectrum of the poly(VDF-*ter*-HFP-*ter*-PMVE) terpolymer in acetone- d_6 (Table 5, entry 3)

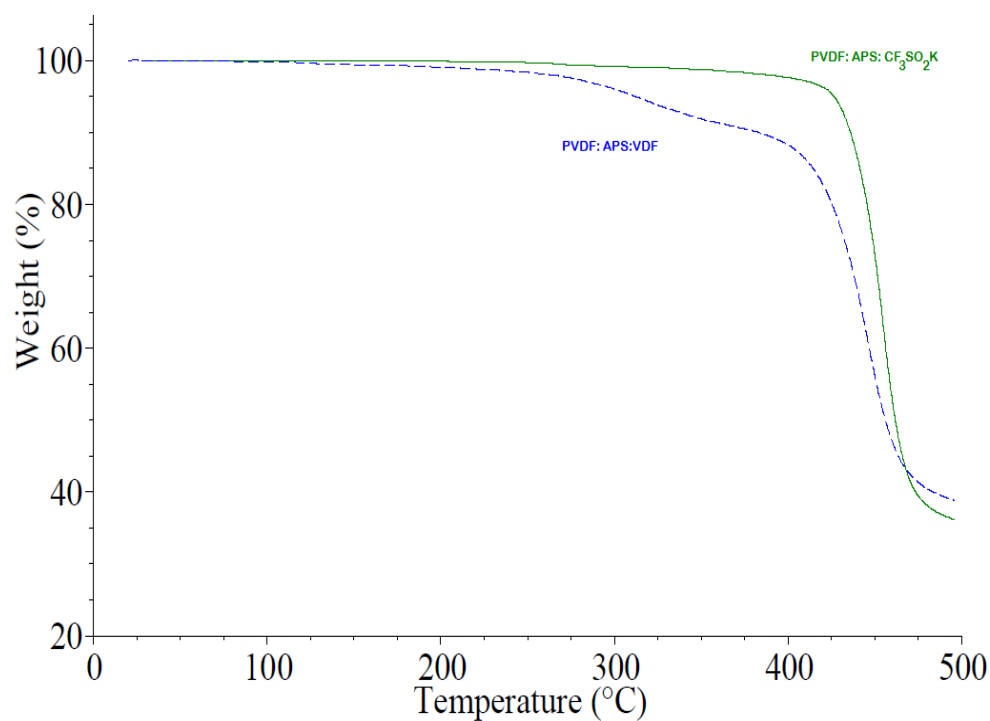


Figure 7: TGA thermograms of PVDF achieved in various initiations (APS only, dotted line, and $\text{CF}_3\text{SO}_2\text{K}$: APS (0.9: 1.0), full line) under nitrogen

Table 6: Thermal properties of prepared fluoropolymers relatively to the nature of the chain-end functionality

Entry	Polymer (Composition mol%)	Mn (g/mol) (by ^{19}F NMR)	Mn (g/mol) (by GPC)	\bar{D}	T_g $^{\circ}\text{C}$	T_c $^{\circ}\text{C}$	T_m $^{\circ}\text{C}$	$T_{\Delta m 5\%}$ $^{\circ}\text{C}$	Ref
1	CF_3 -PVDF-(H, CF_3)	10,500	30,000	10.5	-	134	170	428	This Work
1a	SO_3^- -O-CH ₂ - PVDF-(H, OH, O- SO_3^- , CH ₃)	9,000	35,000	9.8	-	128	164	315	This Work
-									
2	CF_3 -poly(VDF- <i>co</i> - HFP) (VDF: HFP= 86/14)	16,500	45,200	3.8	-26	44	95	407	This Work
2a	CF_3 -O-Poly(VDF- <i>co</i> -HFP)-(H, O- CF_3 , CH ₃) (VDF: HFP= 85:15)	75,000	NR	NR	-21	-	NR	375	71
2b	I-Poly(VDF- <i>co</i> - HFP)-I (VDF: HFP=74/26)	NR	13,000	NR	-30	-	160	350	72
3	CF_3 -poly(VDF- <i>co</i> - PMVE) (VDF: PMVE= 74:26)	35,500	40,000	4.1	-29	-	-	409	This Work
3a	I-Poly(VDF- <i>co</i> - PMVE)-I	NR	24,000	1.4	-52	-	-	320	68

	(VDF:PMVE= 65:35)								
3b	Poly(VDF- <i>co</i> - PMVE)	NR	37,700	7.2	-27			400	73
	Poly(VDF- <i>ter</i> - HFP- <i>ter</i> -PMVE)- (H, CF ₃)	40,000	113,000	6.0	-24	-	-	408	This Work
4	(VDF:HFP:PMVE= 74:13:13)								
NR: not reported									

The commercially available PVDF produced by Arkema (Kynar[®]) prepared by emulsion process, and initiated by KPS (Mn higher than 400,000 g/mol, estimated by GPC) showed a 1% weight loss at 375 °C under air, and at 410 °C under nitrogen (Figure S19). However, the prepared CF₃-terminated PVDF (A, Table 6, entry 1, Mn of 30,000 g/mol estimated by GPC), lost 1% of its weight at 370 °C under either nitrogen or air. These results confirmed the importance of the chain-end functionality on the overall thermal stability of PVDF, and its degradation mechanism under inert or oxidative atmosphere. The thermal stability of Kynar PVDF increased only of 40 °C when its molar mass was 13 times higher.

Furthermore, the chain-end effect on the thermal stability of such copolymers was also studied. Trifluoromethyl terminated poly(VDF-*co*-HFP) copolymer (Table 6, entry 2) displays a good thermal stability with 5 wt% loss at 404 °C under nitrogen. However, this thermal stability decreased by 35 °C when chain-end consisted of CF₃-O, even for a copolymer having a higher molar mass (Table 6, entry 2a).⁷¹ An additional decrease of 67 °C was reported for telechelic bis(iodo) terminated poly(VDF-*co*-HFP) (Table 6, entry 2b),⁷² knowing that the same behavior was observed with bis(iodo) poly(VDF-*co*-PMVE) (Table 6, entries 3 and 3a).⁶⁸ Finally, compared to a poly(VDF-*co*-PMVE) copolymer also

achieved in aqueous conditions from KPS,⁷³ that bearing a CF₃ end-group exhibits a better thermal stability.

Conclusion

Original CF₃-PVDF polymers were synthesized in high yields (89-100%) from trifluoromethyl sulfinate activated by ammonium persulfate (APS), in water, without any surfactant. This simple system enabled to generate a •CF₃ radical, as efficient initiator for the polymerization of VDF that was completed in 15 minutes. An optimization of the reaction suggests the best conditions: nCF₃SO₂K: nAPS= 1.0:0.9, at 60 °C, leading to CF₃-PVDF with an average degree of polymerization of 160, and with a head-to-head inversion rate of 4.5%. The microstructure of the obtained polymer was determined by ¹H and ¹⁹F NMR spectroscopy thanks to its dissolution in acetone-DMSO mixture, which perfectly solubilized the CF₃-PVDF. In addition, the presence of CF₃- end group acted as a label for the determination of the molar mass by ¹⁹F NMR spectroscopy. Interestingly, compared to an APS initiated PVDF, the CF₃-PVDF displays a much better thermal stability (of ca. 120 °C). The chain-end influence on the thermal resistance was also confirmed when the copolymers were compared with polymers from the literature bearing different chain- ends such as CF₃-O, iodine, or bromine atoms. In addition, the prepared PVDF showed a similar degradation behavior either under air or nitrogen, indicating a non-oxidative degradation mechanism, which is currently under study. This initiating system was also successfully applied to the co- and ter-polymerization of VDF with HFP and PMVE. The co- and ter-polymers were obtained in high yields and with satisfactory thermal properties. Because of the high HFP and PMVE contents, amorphous co- and terpolymers were obtained. A deeper investigation on the thermal degradation mechanism of CF₃-PVDF is required in order to reveal the important role of the chain-end functionality on the global thermal stability.

Experimental

Materials

VDF and HFP were kindly supplied by Arkema (Pierre-Bénite, France), while perfluoromethyl vinyl ether (PMVE) was purchased from Synquest. Ammonium persulfate, Potassium trifluoromethane sulfinate and dimethylphosphite were purchased from Merck while bis(4-*tert*-butylcyclohexyl) peroxydicarbonate (P-16s) from Akzo. Filtered and distilled water was used without any special purification treatment. Deuterated acetone (acetone- d_6), and deuterated dimethylsulfoxide (DMSO- d_6) (purity>99.8%), used for ^1H and ^{19}F NMR spectroscopy, were acquired from Eurisotop (Grenoble, France).

Characterization

Nuclear Magnetic Resonance (NMR) Spectroscopy

^1H and ^{19}F NMR spectra were recorded on a Bruker AC 400 Spectrometer (400 MHz for ^1H and 376 MHz for ^{19}F) using acetone- d_6 and DMSO- d_6 as solvents. The sample temperature was set to 298 K. Chemical shifts and coupling constants are given in Hertz (Hz) and parts per million (ppm), respectively. The experimental conditions for recording the ^1H [^{19}F] NMR spectra were as follows: flip angle 90° [30°], acquisition time 4.5 s [0.7 s], pulse delay 2 s [5 s], number of scans 100 [150], and a pulse width of 5 μs for ^{19}F NMR.

Thermogravimetric analysis (TGA)

The temperature of 5 wt% loss ($T_{5\%}$) was determined using Q50 equipment from TA Instruments. About 10 mg of sample was heated to 500 $^\circ\text{C}$, at a 10 $^\circ\text{C}/\text{min}$ rate under air or nitrogen (40 mL/min). Data were analyzed at TA Universal Analysis 2000 software.

Differential scanning calorimetry (DSC)

Thermal transitions were determined using a DSC200 F3 Maia system, from Netzsch, under nitrogen atmosphere at 40 mL/min. About 10 mg of polymer were weighed in a perforated cap pan. For the glass transition temperature (T_g), the following heating program was used: Cooling from room temperature

down to -100 °C at 10 °C/min rate; isotherm at -100 °C for 10 minutes, and then heating up to 250 °C at 10 °C/min. After isotherm at 250 °C for 10 minutes, the crystallization temperature (T_c) and the crystallization enthalpy (ΔH_c) were measured during cooling to 20 °C at 10 °C/min. The glass transition temperature (T_g), the melting temperature (T_m) and melting enthalpy (ΔH_m) were measured during the second heating cycle rate at 10 °C/min. All data were analyzed in a Proteus Analysis system, from Netzsch (Germany). Tgs were assessed from the mid-point in the heat capacity jump of the transition, while melting transitions were determined at the maximum of the enthalpy peaks, the area of which led to the determination of the melting enthalpy (ΔH_m). The degrees of crystallinity of the polymers ($\chi\%$) were determined using equation (1):

$$\chi\% = \frac{\Delta H_m}{\Delta H_{PVDF}} \cdot 100\% \quad (1)$$

where ΔH_m and ΔH_{PVDF} (104.5 J.g⁻¹) stand for the enthalpies of melting of the polymer (determined by DSC in J.g⁻¹) and a 100% crystalline PVDF, respectively.^{74,75}

The rates of VDF inversions (Head-to-Head) in PVDFs were calculated from ¹⁹F NMR using equation (2), and the Tail-to-Tail inversions from ¹H NMR using equation (3):

$$\% \text{ Head-to-Head inversion} = \left[\frac{\int_{-115}^{-117} I}{\int_{-90}^{-95} I + \int_{-113}^{-114} I + \int_{-115}^{-117} I} \right] \times 100 \quad (2)$$

$$\% \text{ Tail-to-Tail inversion} = \left[\left(\frac{\int_{2.0}^{2.4} I/2}{(\int_{2.0}^{2.4} I)/2 + \int_{2.7}^{3.3} I} \right) \right] \times 100 \quad (3)$$

where $\int_a^b I$ stands for the integral of the NMR signal ranging between a and b ppm.

The VDF molar content in the poly(VDF-co-HFP) co-polymer was obtained using equation (4) from ¹⁹F NMR:

$$VDF\% = \left[\frac{\frac{\int_{-92}^{-95} I + \int_{-107}^{-116} I}{2}}{\frac{\int_{-92}^{-95} I + \int_{-107}^{-116} I}{2} + \frac{\int_{-68}^{-75} I}{3}} \right] \times 100 \quad (4)$$

The VDF molar content in the poly(VDF-*co*-PMVE) copolymer was determined using equation (5) from ^{19}F NMR:

$$VDF\% = \left[\frac{\frac{\int_{-92}^{-95} I + \int_{-107}^{-116} I}{2}}{\frac{\int_{-92}^{-95} I + \int_{-107}^{-116} I}{2} + \frac{\int_{-53}^{-55} I}{3}} \right] \times 100 \quad (5)$$

The VDF molar content in the poly(VDF-*ter*-HFP-*ter*-PMVE) terpolymer was calculated using equation (6) from ^{19}F NMR:

$$VDF\% = \left[\frac{\frac{\int_{-92}^{-95} I + \int_{-107}^{-116} I}{2}}{\frac{\int_{-92}^{-95} I + \int_{-107}^{-116} I}{2} + \frac{\int_{-53}^{-55} I + \int_{-68}^{-75} I}{3}} \right] \times 100 \quad (6)$$

The average degree of polymerization, DP_n , of the obtained PVDFs was calculated using equation (7):

$$DP_n = \frac{\frac{\int_{-91}^{-97} CF_2 + \int_{-113}^{-114} CF_2 + \int_{-115}^{-117} CF_2}{2}}{\frac{\int_{-60}^{-63} CF_3}{3} + \frac{\int_{-114}^{-115} CF_2H}{2}} \quad (7)$$

The average molar mass of PVDF, from NMR, was obtained from equation (8):

$$M_{n,NMR} = DP_n \times M_{n,VDF} + M_{n,end-chain} \quad (8)$$

where $M_{n,VDF} = 64.05$ g/mol, M_{n,CF_3} chain-end = 69, and M_{n,CF_2H} chain-end = 51 g/mol.

Gel permeation chromatography:

The molar masses and the dispersities of the (co)polymers were determined by gel permeation chromatography, using a Wisp 717 + P600 instrument equipped with Waters P600 pump. A solution of 0.1M of NaNO_3 in dimethylsulfoxide was used as eluent with a flow rate of 1 ml/min, at 50 °C. The molar masses were determined by refractometry using a Waters 2414 RID detector and PMMA as standards. The samples were prepared from the corresponding polymers after dissolution in DMSO for 4 hours at 95 °C, then the obtained solutions were filtrated using a 0.45 μm ACRODISC GHP polypropylene filter.

Radical polymerization procedure

The radical polymerizations were performed in a 50 mL Hastelloy autoclave Parr System (HC 276) equipped with a manometer, a mechanical Hastelloy anchor, a rupture disk (2000 psi), inlet and outlet valves equipped with a special steel pipe, and a Parr electronic controller for both stirring speed and heating control.

Radical polymerization of VDF in the presence of $\text{CF}_3\text{SO}_2\text{K}$ and APS (Table 3, entry 1)

A purged solution comprising APS (0.24 g), $\text{CF}_3\text{SO}_2\text{K}$ (0.19 g), and water which was transferred into a vacuumed autoclave (2 mbars). Then, the reactor was cooled to ca. $-100\text{ }^\circ\text{C}$, and VDF gas (7g) was transferred ($n_{\text{APS}}:n_{\text{VDF}} = 0.009$ (0.9 mol %), $n_{\text{CF}_3\text{SO}_2\text{K}}:n_{\text{VDF}} = 0.01$ (1 mol %)). Subsequently, the autoclave was warmed up to room temperature and then gradually heated to $60\text{ }^\circ\text{C}$, while the reaction solution was mechanically stirred vigorously. After 1.5 hours, the pressure in the autoclave dropped from 34 to 6 bars. The autoclave was then cooled, immersed in a water-ice bath, then depressurized, and opened to air. The VDF conversion was 100 %. The reaction product was transferred to a beaker and the autoclave was washed with water to remove all the solids. The product was filtered using a Buchner apparatus and then washed with water. A small amount of acetone was added to the solid and the product was left to dry at $60\text{ }^\circ\text{C}$ under vacuum (10^{-3} bar) overnight. The final product was recovered as a white powder (yield 100 %, end-groups: 60 % CF_3 and 40 % CF_2H). The obtained polymer (6.8g) has a degradation temperature of $T_{\Delta m 5\%} = 430\text{ }^\circ\text{C}$ under air (Figure S1, Table 6, entry 1), a melting point of $170\text{ }^\circ\text{C}$, a crystallization temperature of $134\text{ }^\circ\text{C}$ and a degree of crystallinity of 44 % (Figure S3). The polymer had an average molar mass M_n of 10,250 g/mol (calculated by NMR).

^1H NMR (400 MHz, $\text{DMSO-}d_6$ -Acetone- d_6)(Figure 2) δ 6.34 (tt, $^2J_{\text{HF}} = 55.2$, $^3J_{\text{HH}} = 4.5$ Hz, $-\text{CF}_2\text{H}$), 3.01 – 2.77 (t, $^3J_{\text{HF}} = 16$ Hz, $-\text{CH}_2-\text{CF}_2-$, HT normal addition), 2.25-2.40 (t, $^3J_{\text{HF}} = 16.0$ Hz, $-\text{CF}_2-\text{CH}_2-\text{CH}_2-\text{CF}_2-$, T-T reverse addition), 1.78 (t, $^3J_{\text{HF}} = 20.0$ Hz, $-\text{CF}_2-\text{CH}_3$).

^{19}F NMR (377 MHz, $\text{DMSO-}d_6$ -Acetone- d_6) (Figure 3): -61.0 [(-CH $_2$ -CF $_3$) chain-end], δ -90.9 to -93.1 (-CF $_2$ -CH $_2$ - normal addition), -94.6 (-CF $_2$ -CH $_2$ - normal addition adjacent to H-H inversion), -106.8 to -107.1 (-CF $_2$ -CH $_3$), -113.8 (-CH $_2$ CF $_2$ -CF $_2$ CH $_2$ - reverse addition), -114.4 (-CF $_2$ H), -115.5 (-CH $_2$ CF $_2$ -CF $_2$ CH $_2$ -, H-H reverse addition).

Radical terpolymerization of VDF with HFP and PMVE in the presence of CF $_3$ SO $_2$ K and APS

The radical terpolymerization of VDF with PMVE and HFP was performed as above, from a nitrogen purged solution composed of 0.220 g of APS, 0.190 g of CF $_3$ SO $_2$ K and water (20 mL) transferred into the vacuumed autoclave. The reactor was then cooled. First, 2 g of HFP and 2 g of PMVE were transferred at $T < -21$ °C and then 5 g of VDF at $T < -100$ °C; $n_{\text{APS}_0}:(n_{\text{VDF}_0}+n_{\text{HFP}_0}+n_{\text{PMVE}_0}) = 0.0093$ (0.93 mol %), $n_{\text{CF}_3\text{SO}_2\text{K}_0}:(n_{\text{VDF}_0}+n_{\text{HFP}_0}+n_{\text{PMVE}_0}) = 0.01$ (1 mol %), and molar feed: %VDF:%HFP:%PMVE = 76:13:11). After warming up, the autoclave was gradually heated to 60 °C, under mechanical stirring. After 3 hours, the pressure in the autoclave decreased from 30 to 6 bar. The vessel was cooled, immersed in a water-ice bath, then depressurized by venting, and opened to air. The total product mixture was isolated as above and dried under vacuum. The final product was recovered as a white gum (7.9 g, yield 89%, molar content: %VDF: %HFP: %PMVE = 74:13:13) and characterized by ^{19}F NMR spectroscopy. Thermogravimetric analysis ($T_{\Delta m5\%} = 409$ °C, under N $_2$, Figure S12), and differential scanning calorimetry (DSC) ($T_g = -24$ °C, Figure S13).

^{19}F NMR (400 MHz, acetone- d_6) (Figure 66), δ (ppm): -52.0 (-OCF $_3$), -62.3 [-CH $_2$ -CF $_3$ chain-end], -68.3 to -75 [-CF(CF $_3$)-, HFP], -91.0 to -94.8 [-(CF $_2$ CH $_2$ -CF $_2$ CH $_2$ -) normal VDF-VDF H-T addition], -104.9 [-CF $_2$ CF(CF $_3$)-CF $_2$ CH $_2$ -CF $_2$ CF(CF $_3$)-CH $_2$ CF $_2$ -], -110.2 [-CF $_2$ -CF $_2$ CF(CF $_3$)-CH $_2$ CF $_2$ -CF $_2$ CF(CF $_3$)-CH $_2$ CF $_2$ -], -114.1 (-CH $_2$ CF $_2$ -CF $_2$ CH $_2$ -, H-H reverse addition) -116.2 (-CH $_2$ CF $_2$ -CF $_2$ CH $_2$ -CH $_2$ CF $_2$ -, H-H reverse addition), -117.1 to -119.4 [-CH $_2$ CF $_2$ -CF $_2$ CF(CF $_3$)-CH $_2$ CF $_2$ -, and -CF $_2$ CF(CF $_3$)-CH $_2$ CF $_2$ -CF $_2$ CF(CF $_3$)-CH $_2$ CF $_2$ -], -123.4 to -129.6 [-CH $_2$ -CF $_2$ CF(OCF $_3$)-CH $_2$ CF $_2$ -], -147.0 [-(CF $_2$ CF(OCF $_3$)-)], -185 [-(CF $_2$ CF(CF $_3$)-)].

Conflicts of interest

There are no conflicts of interest to declare.

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Supporting Information

FTIR spectra of CF₃-PVDF; ¹⁹F NMR spectra of CF₃-poly(VDF-*ter*-HFP-*ter*-PMVE) terpolymer; (DSC thermograms and TGA thermogram (under nitrogen and under air) of CF₃-PVDF, CF₃-poly(VDF-co-PMVE) and CF₃-poly(VDF-co-HFP) copolymers, and CF₃-poly(VDF-*ter*-HFP-*ter*-PMVE) terpolymer; MALDI-TOF-MS mass spectrum in negative ion mode of PVDF; peak assignments noted from the MALDI-TOF-MS mass spectrum of APS-PVDF in negative ion mode, TGA thermogram of commercially available PVDF under nitrogen; picture of the vessel opened after reaction (CF₃-PVDF) and different aspects of the VDF-containing copolymers and terpolymer.

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