Vinylidene fluoride polymerization by metal free selective activation of hydrogen peroxide: microstructure determination and mechanistic study

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Abstract

The hydrogen peroxide initiated radical polymerization of vinylidene fluoride (VDF) at 130 °C in dimethyl carbonate is presented. Various reaction parameters such as the nature of the solvent, the nature and the amount of the additive, and the reaction temperature were optimized. Hydrogen peroxide was activated by azobisisobutyronitrile (AIBN), which is not able to initiate the radical polymerization of VDF, but afforded hydroxyl radicals *via* selective homolytic cleavage of the O-O bond of H₂O₂. The reactivity of hydroxyl radicals with the different components of the medium was evaluated. Two pathways were highlighted: the first one is the radical polymerization of VDF initiated by OH[•] radical, while the second one is the hydrogen abstraction from the solvent that afforded carbon centered carbonate radicals. These latter were also able to initiate the radical polymerization of VDF. The microstructure of the resulting PVDFs was determined by NMR spectroscopy and MALDI-TOF spectrometry. Seven different chain-ends were identified and could be well revealed from synthesized models: 60% were functional, e.g., carbonates, alcohols, carboxylic acids and fluorinated olefins, whereas 40% were CF₂H and CF₂CH₃ fluoroalkyls as the products of hydrogen transfer termination reactions. Finally, based on the collected experimental data, a mechanistic pathway of the polymerization was proposed in order to explain the formation of such different functional and non-functional end-groups. In addition, the selectivity of the different radical additions onto VDF was studied and discussed.

Introduction

Fluoropolymers represent an important class of materials due to their exceptional properties.¹⁻³ Actually, poly(tetrafluoroethylene) (PTFE),⁴ poly(vinylidene fluoride) (PVDF),⁵ fluorinated ethylene propylene (FEP),⁶ and poly(ethylene-*alt*-tetrafluoroethylene) copolymer (ETFE),⁶ are involved in high performance applications such as composites,⁷ coatings,⁸ membranes,⁹ and for energy conversion and storage.¹⁰

Among them, PVDF is the second most used and produced.^{5,6} It can be prepared by radical polymerization of VDF from various processes ranging from solution, precipitation,¹¹ or aqueous (emulsion and suspension processes).¹²⁻¹⁴ For this propose, several radical initiators such as ammonium persulfate,¹⁵ organic peroxides (e.g. di-*tert*-butyl peroxide),¹⁶ peracid esters (e.g. *tert*-butyl peroxyphosphate),¹⁷ and peroxyarbonates (e.g. di(4-*tert*-butylcyclohexyl) peroxydicarbonate)¹⁸ are frequently used. Some other fluorinated initiators that can generate $\bullet\text{CF}_3$ ¹⁹ or $\text{CF}_3\text{-O}\bullet$ radicals²⁰ have also been efficient. PVDF can be also obtained *via* controlled radical polymerization techniques such as iodine transfer polymerization (ITP),²¹⁻²³ cobalt mediated radical polymerization,²⁴ and by RAFT technique.²⁵

Hydrogen peroxide is the simplest peroxide. It is prepared by oxygen reduction, using the anthraquinone process²⁶⁻²⁸ and widely used in organic synthesis as an oxidizing reagent.^{29,30} In addition, it is used for waste water treatment combined with catalysts such as iron³¹ and titanium,³² in order to degrade organic contaminants such as phenolic compounds.³³ These reactions generate a hydroxyl radical, which is considered as a non selective powerful oxidant.³⁴⁻³⁶

However, a few examples were reported considering hydrogen peroxide as initiator for radical polymerization due to a lack of selectivity during the decomposition.³⁷ These systems can be activated by specific additives such as ascorbic acid,³⁸ hydroxylamine,³⁹ perchloric acid,⁴⁰ and enzymes.⁴¹ Other procedures rely on the thermolysis of the hydrogen peroxide.⁴²⁻⁴⁴ Nearly all the described reactions suffer from the low selectivity toward the formation of one radical species. Generally, hydrogen, superoxide and hydroxyl radicals are formed.⁴⁵

A wide variety of unsaturated monomers such as isoprene,⁴³ butadiene,^{42,44} vinyl monomers,^{46,47} and styrenes^{48,49} can be polymerized using hydrogen peroxide as radical initiator. For example, Pradel *et.al.*⁴⁴ described the polymerization of 1,3-butadiene, initiated by H_2O_2 , and controlled by TEMPO. Another interesting example concerns the photochemical polymerization of VDF with hydrogen peroxide where telechelic oligo(VDF) were obtained,⁵⁰ with a molar mass ranging between 400 and 4000 g/mol, terminated by alcohols or carboxylic acid functions.

The redox system using hydrogen peroxide/ iron, also called Fenton reagent,⁴⁵ is an effective process to initiate radical polymerization of unsaturated monomers at temperatures below 50 °C in aqueous medium under emulsion conditions.^{51,52} This approach was found to be effective especially for the preparation of hydroxyl terminated polymers based on methyl metacrylates⁴⁷ or butadiene⁴⁰ as monomers.

This article describes a new method for the activation of hydrogen peroxide using AIBN as a promoter. This reaction proceeds with full selectivity toward the formation of the hydroxyl radicals, in dimethyl carbonate as the solvent at 130 °C. Hence, the radical polymerization of VDF involving this system was studied. All chain-end functionalities were identified *via* NMR spectroscopy, and the selectivity of the addition of different radical species onto VDF was evaluated using prepared model molecules containing carboxylic acids, carbonates and alcohols. The different mechanisms of H₂O₂ activation, propagation of VDF, and termination reactions have been proposed in order to explain the different obtained results.

Experimental

Materials

VDF was kindly supplied by Arkema France (Pierre-Bénite, France). Azobisisobutyronitrile, isopropanol, dimethylcarbonate, and hydrogen peroxide (35 wt.% in water), methyl chloroformate, triethylamine, sulfuric acid and chromium trioxide were purchased from Sigma-Aldrich and used as received. Deuterated acetone (acetone-*d*₆) (purity>99.8%) and dimethylsulfoxide (DMSO-*d*₆) (purity>99.8%), used for ¹H and ¹⁹F NMR spectroscopy, was purchased from Eurisotop (Grenoble, France). 2,2,3,3,3-pentafluoropropan-1-ol and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-1-ol were supplied by Atofina (Pierre-Bénite, France)

Characterization

MALDI-TOF Spectrometry

Matrix-Assisted Laser Desorption Ionization (MALDI-TOF) mass spectra were recorded using a Bruker Rapiflex time-of-flight mass spectrometer using a nitrogen laser for MALDI (λ 337 nm). The measurements in positive ion were performed with a voltage and reflector lens potential of 25 and 20 kV, respectively. Mixtures of peptides were used for external calibration. The matrix and cationizing agent were (trans-2-[3-(4-tertbutylphenyl)-2-methylprop-2-enylidene]malononitrile, DCTB, (10 mg/mL in CHCl₃) and LiCl (10 mg/mL in methanol), respectively. The polymer concentration was 20 mg/mL in acetone. The polymer and matrix were mixed in a 4:10 vol. ratio. LiCl was first deposited on the target.

After evaporation of the solvent, the mixture, composed of polymer and matrix, was placed on the MALDI target. The dry droplet sample preparation method was used.

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 , DMSO- d_6 or DMF- 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.

The average degree of polymerization, DP_n , was calculated using equation (1):

$$DP_n = \frac{\frac{\int_{-91}^{-97} CF_2 + \int_{-113}^{-114} CF_2 + \int_{-115}^{-117} CF_2}{2}}{\frac{\int_{-104}^{-105} CF_2CH_2OH}{2} + \frac{\int_{-114}^{-116} CF_2H}{2}} \quad (1)$$

$\int_i^j X$ represents the integral of the signal ranging from i to j (ppm) assigned to corresponding structure

The average molar mass of the resulting PVDF was obtained from equation (2):

$$M_{n,NMR} = DP_n \times M_{n,VDF} + M_{n,end-chain} \quad (2)$$

where $M_{n,VDF}$ and $M_{n,chain-end}$ stand for the molar masses of VDF (64 g mol^{-1}) and chain-end depending on organic function (OH: 17 g mol^{-1} , COOH: 45 g mol^{-1} , COF: 47 g mol^{-1} , CH_3 : 15 g mol^{-1} , H: 1 g mol^{-1} , $\text{CH}_2\text{CO}_3\text{CH}_3$: 89 g mol^{-1}), respectively.

The rates of inversion to VDF (Tail to Tail and Head to Head) were calculated using equations (3) and (4), respectively:

$$\text{From } ^1\text{H NMR: } \% T - T \text{ inversion} = \left[\left(\frac{\int_{2.0}^{2.4} I}{\int_{2.0}^{2.4} I + \int_{2.7}^{3.3} I} \right) / 2 \right] \times 100 \quad (3)$$

$$\text{From } ^{19}\text{F NMR: } \% H - H \text{ inversion} = \left[\frac{\int_{-115.8}^{-117} I}{\int_{-90}^{-95} I + \int_{-113.5}^{-114} I + \int_{-115.8}^{-117} I} \right] \times 100 \quad (4)$$

The rate of transfer to VDF was calculated from equation (5):

$$\% transfer = \left[\frac{\int_{6.0}^{6.5} I}{\frac{\int_{2.0}^{2.4} I + \int_{2.7}^{3.3} I}{2}} \right] \times 100 \quad (5)$$

Radical polymerization apparatus

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 (maximum pressure 2000 psi), inlet and outlet valves equipped with a special steel pipe, and a Parr electronic controller for controlling stirring speed and heating.

Radical polymerization of VDF initiated by Hydrogen peroxide

The radical polymerization of VDF was performed as follows (Table 5, entry 1): initially, 0.18 g of AIBN (1 mol%) was dissolved in 30 mL of dimethyl carbonate. 0.11 ml of hydrogen peroxide (35 wt% in water) was added to the solution, and the system was purged with 99.9% pure nitrogen for 20 min. The solution was transferred through a PTFE tube tightly connected to the inlet valve of the previously vacuumed autoclave (0.01 mbar). The reactor was then cooled in a liquid nitrogen bath ($T < -100\text{ }^{\circ}\text{C}$), and 7 g of VDF gas were transferred under weight control. Subsequently, the autoclave was warmed up to room temperature and then gradually heated to $130\text{ }^{\circ}\text{C}$, while the reaction solution was mechanically stirred. Finally, after 4 hours, the pressure dropped from 31 to 27 bars. It was then cooled, immersed in a water-ice bath, then depressurized, and opened to air. The solution was clear and no solids were present. The autoclave was washed with dimethyl carbonate and the solvent was removed under vacuum at $40\text{ }^{\circ}\text{C}$ resulting in a white powder. (3.7 g, Yield 53%, white powder).

^1H NMR (400 MHz, DMSO- d_6) (Figure 3) δ 6.34 (tt, $^2J_{\text{HF}} = 55.2$, $^3J_{\text{HH}} = 4.5$ Hz, $-\text{CF}_2\text{H}$), 5.65 (t, $^3J_{\text{HH}} = 6.6$ Hz, $\text{CH}_2=\text{CF}-$ from elimination), 4.46 (t, $^3J_{\text{HF}} = 13.2$ Hz, $-\text{CF}_2-\text{CH}_2\text{-carbonate}$), 4.27 (t, $^3J_{\text{HH}} = 6.3$ Hz, $-\text{CF}_2-\text{CH}_2-\text{CH}_2\text{-carbonate}$), 4.22 (t, $^3J_{\text{HF}} = 13.4$ Hz, $-\text{CF}_2-\text{CH}_2\text{-OH}$), 3.70 (s, $\text{CH}_3\text{-O-CO}_2-$), 3.59 (td, $^3J_{\text{HF}} = 13.8$, $^3J_{\text{HH}} = 6.3$ Hz, $-\text{CF}_2-\text{CH}_2\text{-CO}_2\text{H}$), 3.01 – 2.77 (t, $^3J_{\text{HF}} = 16$ Hz, $-\text{CH}_2\text{-CF}_2-$, HT normal addition), 2.25 (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, DMSO- d_6) (Figure 4) δ -90.93 to -93.10 ($-\text{CF}_2\text{-CH}_2-$ H-T, normal addition), -93.19 ($-\text{CF}_2\text{-CH}_2\text{-CH}_2\text{-carbonate}$), -93.46 ($\text{CH}_2=\text{CF}-$ from elimination), -94.69 ($-\text{CF}_2\text{-CH}_2-$ normal addition,

adjacent to a H-H reverse addition), -103.60 to -104.28 ($-\text{CF}_2\text{-CH}_2\text{-OH}$), -106.82 to -107.15 ($-\text{CF}_2\text{-CH}_3$), -113.80 ($-\text{CH}_2\text{-CF}_2\text{-CF}_2\text{-CH}_2-$, H-H reverse addition), -114.46 ($-\text{CF}_2\text{H}$), -115.57 ($-\text{CH}_2\text{-CF}_2\text{-CF}_2\text{-CH}_2-$, H-H reverse addition), -116.04 ($-\text{CH}_2\text{-CF}_2\text{-CF}_2\text{-CH}_2-$, H-H reverse addition).

Results and discussion

In order to explore the efficiency of hydrogen peroxide as a radical initiator of vinylidene fluoride (VDF) polymerization, different screened systems were evaluated in terms of isolated yields, chain-end functionality, and molar mass of the resulting PVDF (Scheme 1). Thus, various experimental parameters such as the solvent, temperature, and additives were varied.

Scheme 1: Benchmark reaction of radical polymerization of VDF initiated by hydrogen peroxide

First, the role of the solvent was evaluated in hydrogen peroxide initiated polymerization of VDF under thermolysis conditions without any additive. Solvents such as acetonitrile (Table 1, entries 1-3) dimethyl carbonate (Table 1, entries 4 and 7), isopropanol (Table 1, entry 6), and trimethylphosphate (Table 1, entry 5), water (Table 1, entry 8) and *tert*-butanol (Table 1, entry 9) failed to afford any product under different temperatures ranging between 85 and 130 °C.

Table 1: Solvents and temperature screening for hydrogen peroxide initiated polymerization of VDF

Entry	Solvent	Total volume (mL)	H ₂ O ₂ (mol%)	T (°C)
1	acetonitrile	3	10	105
2	acetonitrile	16	10	85
3	acetonitrile	30	23	105
4	dimethyl carbonate	30	20	105
5	trimethyl phosphate	30	20	100
6	isopropanol	30	10	130
7	dimethyl carbonate	30	10	130
8	Water	30	10	130
9	<i>tert</i> -butanol	30	10	130

All reactions were carried out in a 50 mL autoclave. The liquid phase was degassed with nitrogen. The reactor was vacuumed to remove any oxygen trace. Reaction time : 4 h

Then, the potential effect of using azobisisobutyronitrile (AIBN) as an additive was explored. All reactions were performed at 130 °C for 4 hours in DMC because of the high solubility of VDF in this solvent.²⁵ All results are summarized in Table 2.

Table 2: Polymerization of VDF using hydrogen peroxide as initiator in presence of AIBN at 130 °C

Entry	AIBN (y mol%)	H ₂ O ₂ (x mol%)	AIBN: H ₂ O ₂	P max (Bar)	ΔP (Bar)	Yield (%)	DPn ^a	H-H (%) ^a	H transfer (%) ^a
10	0	10.0	0:1	31	0	0	-	-	-
11	10.0	10.0	1:1	30	Nd	18	16	3.7	56
12	1.0	5.0	1:5	33	7	44	70	4.6	58
13	1.0	1.0	1:1	31	4	53	31	4.7	58
14	0.2	0.2	1:1	27	0	0	-	-	-
15	0.5	1.0	1:2	28	5	32	46	4.5	49
16	1.0	0	1:0	31	1	3	-	-	-
17	1.2	1.0	1.2:1	26	8	48	26	5.5	77

All reactions were carried out at 130 °C in 30 mL of DMC using 7 g of VDF, ^a: estimated by ¹⁹F NMR spectroscopy (eq. 1)

AIBN on its own was not able to initiate the polymerization of VDF (Table 2, entry 16) confirming previous results.⁵³ However, **its presence** was crucial to favor the polymerization. No reaction occurred without any AIBN addition (Table 2, entry 10). The effect of the initial AIBN:H₂O₂ molar ratio on the reaction was further studied. The addition of 10 mol% of AIBN afforded PVDF in 18% yield (Table 2, entry 11). The yield increased from 18 to 53% when the AIBN amount was lowered from 10 to 1 mol% (ratio of AIBN:H₂O₂ = 1:1) (Table 2, entries 11 and 13). **It is also noted an increase of both DPn, from 16 (Table 2, entry 11) to 31 (Table 2, entry 13), and the inversion rate from 3.7% (Table 2, entry 11) to 4.7% (Table 2, entry 13).** However, the hydrogen transfer from the solvent or the back-biting⁵⁷ (Table 2, entries 11 and 13, 56% and 58%, respectively) was not affected by the AIBN: H₂O₂ ratio.

No reaction was observed with further decreasing AIBN and H₂O₂ quantities to 0.16 mol% (VDF:H₂O₂:AIBN= 100.0:0.16:0.16), probably due to the absence of any interactions between AIBN and H₂O₂ because of the high dilution (Table 2, entry 14).

Furthermore, the yield decreased from 53% for AIBN:H₂O₂ = 1:1 (Table 2, entry 13) to 32% with AIBN:H₂O₂ = 1:2 (Table 2, entry 15). **It also slightly decreased from 53% to 48% when a slight excess of AIBN with respect to H₂O₂ was used (AIBN:H₂O₂= 1.2: 1 Table 2, entry 17).**

In summary, the reaction between AIBN and hydrogen peroxide is able to generate active species (OH[•]) that can further initiate the radical polymerization of VDF. The best initiating system for the reaction was VDF:AIBN: H₂O₂ =100:1:1, affording PVDF with 31 repeating units and 4.7% of H-H inversion, in 53% yield and the lowest hydrogen transfer (Table 2, entry 13).

Table 3: Effect of the temperature on VDF polymerization initiated by AIBN and H₂O₂ (VDF: H₂O₂:AIBN= 100:1:1) for 4 hours

Entry	T (°C)	P max (Bar)	ΔP (Bar)	Yield (%)	DPn ^a	H-H (%) ^a	H transfer (%) ^a
18	100	22	0	0	-	-	-
13	130	31	4	53	54	4.7	55
19	150	31	12	58	15	7.4	60

All reactions were carried out in 30 mL of DMC using 7 g of VDF, ^a: estimated by ¹⁹F NMR spectroscopy (eq. 1)

Then, the effect of the temperature on the radical polymerization of VDF initiated by AIBN:H₂O₂ was further studied. First, no reaction occurred at 100 °C (Table 3, entry 18), while the polymerization yield was 53% at 130 °C (Table 3, entry 13), and a slight increase of the yield to 58% was observed at 150 °C (Table 3, entry 19). As expected, a 5% increase of the hydrogen transfer reactions, from 55% at 130 °C (Table 3, entry 13) to 60% at 150 °C (Table 3, entry 19) was observed. In addition, H-H inversion rate increased with the increase of the temperature from 4.7% at 130 °C (Table 3, entry 13) to 7.4% at 150 °C (Table 3, entry 19), confirming Pladis *et al.*⁵⁴ study. Thus, an optimal temperature of 130 °C was selected for the polymerization in order to limit any temperature inducing side reactions such as hydrogen transfer from the solvent or the polymer chain ramifications.⁵⁵

Table 4: effect of solvents in the polymerization of VDF initiated by AIBN and H₂O₂ (VDF: H₂O₂:AIBN= 100:1:1) at 130 °C for 4 hours

Entry	Solvent	P max (Bar)	ΔP (Bar)	Yield (%)	DPn ^a	H-H (%) ^a	H transfer (%) ^a
13	DMC	31	4	53	31	4.7	58
20	ACN	28	2	26	18	7.3	35
21	DMC:CH ₃ CFCl ₂ (2:1)	26	4	22	35	5.6	53
22	DMC:C ₆ F ₁₄ (1:1)	29	0	0	-	-	-
23	CH ₃ CFCl ₂	28	0	0	-	-	-

All reactions were carried using 7 g of VDF, DMC= dimethyl carbonate, ACN= acetonitrile, ^a: estimated by ¹⁹F NMR spectroscopy (eq. 1)

Next, the potential effect of a fluorinated co-solvent was studied in the polymerization reaction. This type of solvent may enhance the solubility of VDF in the medium, affecting the reaction yield. All results are summarized in Table 4. In terms of yield, the polymerization in dimethyl carbonate (Table 4, entry 13) was more effective than that carried out in acetonitrile (Table 4, entry 20) and the reaction yields were 53% and 26%, respectively. Furthermore, the yield decreased from 53 to 22% when a mixture of 2:1 dimethyl carbonate:CH₃CFCl₂ (Table 4, entry 21) was used. However, no reaction occurred when perfluorohexane was used as the co-solvent (Table 4, entry 22) or in neat CH₃CFCl₂ (Table 4, entry 23).

This reactivity behavior can be attributed to the non-miscibility of aqueous hydrogen peroxide in such fluorinated solvents whereas no surfactant was used. The H-H inversion rates were ranging between 4.7% and 5.6% when DMC (Table 4, entry 13) or DMC:CH₃CFCl₂ (2:1) (Table 4, entry 21) mixture were used. However, in the case of ACN (Table 4, entry 20), 7.3% of inversion was observed. The hydrogen transfer was also highly affected by the nature of the solvent used: 58% and 53% of non-functional end chains were released from DMC (Table 4, entry 13) or DMC:CH₃CFCl₂ (2:1) mixture (Table 4, entry 21) while a noticeable decrease to 35% was observed in presence of ACN (Table 4, entry 20).

Table 5: effect of the additive on the radical polymerization of VDF initiated by azo compound and H₂O₂ (VDF:Azo compound: H₂O₂= 100.0:1.1:1.0) at 130 °C for 4 hours

Entry	Azo initiator	Peroxide	P max (Bar)	ΔP (Bar)	Rdt (%)	DPn ^a	H-H (%) ^a	H transfer (%) ^a
13	AIBN	H ₂ O ₂	26	8	53	31	4.7	58
24	V-70	H ₂ O ₂	26	5	45	23	6.6	53

All reactions were carried out in 30 mL of DMC using 7 g of VDF, V-70= 2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile), ^a: estimated by ¹⁹F NMR spectroscopy (eq. 1)

Finally, the effect of the nature of the azoic initiator was investigated on the reaction. Compared to 53% when AIBN was used (Table 5, entry 13), the yield slightly decreased to 43% when V-70 was involved in this reaction (Table 5, entry 24). This can be attributed to the half-life of the additive used: that of AIBN is 10 h at 65 °C, while that of V-70 is the same at 30 °C. The nature of the azo initiator do not seem to deeply affect the different parameters of the obtained oligomers. When V-70 (Table 5, entry 24) was used instead of AIBN (Table 5, entry 13), the DPn value decreased slightly from 31 to 23 as well as the hydrogen transfer from 58% to 53%. However, the inversion rate slightly increased from 4.7% to reach 6.6% with V-70. This can be explained by the role of the azo additive, this latter reacted with the hydrogen peroxide in order to generate hydroxyl radicals that further initiate the polymerization. Actually, no evidence of interaction was found between either the solvent or the monomer and the azo initiator (Scheme 2).

Mechanism of hydrogen peroxide activation

In order to identify the mechanism of the activation of hydrogen peroxide by AIBN, a model reaction was performed involving AIBN (1 eq.) and hydrogen peroxide (1 eq.) in DMC under nitrogen atmosphere at 100 °C, for 2 hours and without VDF. The resulting products were identified by ¹H NMR spectroscopy (Figure 1).

Figure 1: ^1H NMR spectrum of the crude reaction between AIBN and hydrogen peroxide (1:1) in DMC at 100 °C for 2 h (recorded in CDCl_3 , Scheme 2)

The presence of 2,2,3,3-tetramethylsuccinonitrile can be identified by the signal at 1.53 ppm, coming from the expected recombination product of two cyanoradicals generated from the dissociation of AIBN.⁵⁶ In addition, the signal centered at 1.62 ppm can be assigned to acetone cyanohydrin, generated by the radical dissociation of hydrogen peroxide, induced by the presence of the cyanoradicals (Scheme 2). However, isobutyronitrile (2.72 and 1.33 ppm) was not present in the final reaction mixture. This indicates that the cyano radicals were not able to abstract any hydrogen either from H_2O_2 , water or dimethyl carbonate. It can be concluded that the initiation mechanism begins with the formation of two cyanoradicals from AIBN. Then, these radicals reacted with hydrogen peroxide selectively to afford acetone cyanohydrin and hydroxyl radical. This latter radical is responsible to further initiate the radical reactions in the medium such as the radical polymerization of VDF (Scheme 2).

Scheme 2: Possible pathways of the activation of hydrogen peroxide by AIBN and resulting products

Chain-end characterization of obtained functional PVDF

After the hydroxyl radical was identified as the reactive radical species, and due to the high ability of the released PVDF• macroradicals to abstract a hydrogen from DMC, hence generating carbonate radicals which also initiated the polymerization, it was of interest to highlight the nature of the chain-ends and the molar masses of the resulting polymers. They were characterized by ^1H and ^{19}F NMR spectroscopy^{17,50,55,57–60} and MALDI-TOF spectrometry. Several model molecules were synthesized in order to ensure the presence of NMR signals assigned to carbonates, carboxylic acids and alcohols end-chains (Figure 2) and to evaluate the regioselectivity of hydroxyl and carbonate radical additions onto VDF.

Model molecules preparation and characterization

Considering the reactions which may occur on the VDF tail ($\text{CH}_2=\text{CF}_2$) by either hydroxyl or carbonate radical additions, $\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}$ and $\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{-O-CO}_2\text{CH}_3$ (Figure 2) was synthesized as models in order to identify the chemical shifts of $-\text{CF}_2\text{-CH}_2\text{-OH}$ and carbonate functionalities. The latter model was obtained after reacting $\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{OH}$ with methyl chloroformate, thus leading to $-\text{CF}_2\text{-CH}_2\text{-CH}_2\text{-O-CO-OCH}_3$ chain-end (Scheme 3).

Scheme 3: The preparation of fluorinated model molecules bearing carbonates and acid chain-ends ends (where DCM stands for dichloromethane)

In the same manner, $\text{CF}_3\text{CF}_2\text{CH}_2\text{-O-CO}_2\text{CH}_3$, and $\text{C}_6\text{F}_{13}\text{CH}_2\text{CO}_2\text{H}$, prepared *via* the Jones oxidation of the corresponding alcohol (Figure 2), were also used to identify the product of the addition of dimethyl carbonate and hydroxyl radicals onto the VDF head ($\text{CH}_2=\text{CF}_2$) (Scheme 3). The NMR spectra of all these models are supplied in the ESI (Figures S1, S3, S5, S7, S9-S10).

Figure 2: Fluorinated model molecules bearing carbonates, alcohols and carboxylic acids used for the identification of the end-chains of the resulting PVDF

Microstructure characterization of the obtained PVDF

Beside the signals at 2.8 to 3.1 ppm (^{19}F NMR: -90.9 to -93.1 ppm) Figure 4, the normal (or head to tail addition) VDF addition, and the triplet at 2.25 ppm ($^3J_{\text{HF}} = 16.0$ Hz), the reverse tail to tail addition of the VDF units (% of inversions = 5%), the ^1H NMR spectra showed the presence of a wide variety of chain-end functionalities. First, a triplet of triplets ($^2J_{\text{HF}} = 55.2$, $^3J_{\text{HH}} = 4.5$ Hz) centered at 6.34 ppm (^{19}F NMR: -114.46 ppm) Figure 4, refers to the CF_2H chain-end resulting from hydrogen transfer (40% of the total chain-ends).¹⁷ In addition, a signal at 5.65 ppm (^{19}F NMR: -93.46 ppm) was identified as $\text{CH}_2=\text{CF}-$ generated by the β -F elimination reaction.⁶⁰⁻⁶² In addition, three triplets assigned to the dimethyl carbonate radicals initiated polymerization of VDF^{60,63} were identified in the 4.46 to 4.27 ppm range (^{19}F NMR: -93.19 ppm).

Figure 3: ^1H NMR spectrum of PVDF obtained from $\text{H}_2\text{O}_2/\text{AIBN}$ (1/1) in DMC at 130 °C, recorded in $\text{DMSO}-d_6$ (Table 5, entry 13)

The addition of OH• onto VDF tail leads to the formation of the primary alcohol -CF₂-CH₂-OH evidenced by ¹H NMR as a triplet centered at 4.2 ppm (t, ³J_{HF} = 13.4 Hz) (¹⁹F NMR: -104.3 ppm).⁵⁰ However, the triplet of doublets centered at 3.59 ppm (³J_{HF} = 13.8, ⁴J_{HH} = 6.3 Hz) is assigned to the carboxylic acid chain-end CF₂-CH₂-CO₂H, generated from the addition of the hydroxyl radical on the VDF head to afford the unstable alcohol CH₂-CF₂-OH which spontaneously undergoes a dehydrofluorination into CH₂-COF (+43.8 ppm in ¹⁹F NMR),⁶⁴ further reacting with water to afford the corresponding carboxylic acid.^{23,65} Finally, at 1.78 ppm (¹⁹F NMR: -106.82 to -107.15 ppm), the CF₂-CH₃ chain-end was obtained by hydrogen transfer reaction to the reverse macro radical terminated by reversed -CF₂CH₂ group.^{21,58}

Figure 4: ¹⁹F NMR spectrum of obtained PVDF from the radical polymerization of VDF initiated by H₂O₂/AIBN (VDF:H₂O₂:AIBN: 100:1:1) in DMC at 130 °C, recorded in DMSO-*d*₆ (Table 5, entry 13)

After the qualitative identification of the chain-end functions of the prepared PVDFs (Table 5, entry 13), the relative quantity of each of them could be estimated based on NMR analysis. All results are summarized in Table 6.

Table 6: Chain-end composition of prepared PVDF (Table 5, entry 13) estimated by ¹H and ¹⁹F NMR spectroscopy

Chain-end	%	Functional chain-ends 60%
-COF	<1	
-CF ₂ -CH ₂ -COOH	9	
-CF ₂ -CH ₂ OH	9	
-CF ₂ -CH ₂ -Carbonate	37	

CH ₂ =CF-	4	Non functional chain-ends 40%
-CF ₂ -CH ₃	16	
-CF ₂ H	24	

From the calculated proportions, the functional end-groups represented 60%, whereas the hydrogen transfer termination reactions were determined as 40%. 33% of the functional chain-ends was alcohols and carboxylic acids while 67% was carbonate moieties.

Next, the ¹⁹F NMR spectroscopy enables to estimate that the obtained PVDF is composed of 23 successive VDF units, with an average molar mass of 1450 g/mol (determined from eq. 2).

Figure 5: MALDI-TOF spectrum of resulting PVDF (Table 5, entry 13)

The MALDI-TOF spectrum shows the formation of a series of oligomers with different molar masses ranging between $m/z = 545$ ($DP_n = 8$) and $m/z = 5284$ ($DP_n = 82$), with a mass difference that corresponds to VDF moiety ($m/z = 64$). However, the majority of the formed oligo(VDF) contains a DP_n varying between 9 and 34, and the average molar mass, around 1400 g/mol, which confirms that calculated from NMR spectroscopy.

Mechanism of the polymerization

Based on the identified chain-end and products obtained after the VDF radical polymerization with H₂O₂:AIBN system, an initiation mechanism can be suggested as follows: First, AIBN decomposes to generate two cyano radicals. Both these radicals react selectively with hydrogen peroxide in order to

generate hydroxyl radicals and acetone cyanohydrin. Then, such hydroxyl radicals can directly initiate the polymerization of VDF or can generate a dimethyl carbonate radical by hydrogen abstraction, this radical being able to further initiate the polymerization of VDF (Scheme 4).

Scheme 4: Mechanism of the activation of hydrogen peroxide by AIBN in dimethyl carbonate and possible polymerization pathways of VDF

Once the radicals are generated, two pathways are possible: i) the direct initiation of VDF polymerization by the addition of the hydroxyl radical onto VDF to afford alcohols and carboxylic acids chain-ends (30% of the total functional chain-end)(Table 6); ii) the second route is the hydrogen abstraction from DMC by hydroxyl radicals in order to generate carbon centered radicals that can also initiate the polymerization of VDF (67% of carbonate function from the total functional polymers (estimated by NMR) (Table 6)). From these proportions (Table 6), it can be deduced that the hydrogen abstraction reaction from the DMC is 2.3 times more favorable than the direct addition of hydroxyl radicals onto VDF. This behavior may be assigned to two factors: the high reactivity of the hydroxyl radicals and the high DMC amount (used as a solvent) in the reaction medium (nDMC: nVDF = 2:1) which favors the hydrogen abstraction from DMC over the addition on VDF.

Regioselectivity of radicals addition on VDF

The ^1H NMR study shows that the addition of hydroxyl radicals onto VDF was not regioselective, and can occur onto both sites in a 1:1 ratio (Scheme 5). This can be deduced from the equal amount of hydroxyl and the acid chain-end present in the final reaction mixture (Table 6). The same regioselectivity behavior is observed with the addition of hydroxymethyl radicals ($\bullet\text{CH}_2\text{OH}$) onto VDF.⁶⁶ This lack of

regioselectivity is due to the electron density of the HOMO orbitals and to the strength of the formed bonds.⁶⁷

However, the addition of DMC radicals onto VDF occurred majorly onto the VDF tail (92%) than onto the head (8%). This behavior can be linked to the steric hindrance of the fluorine atoms (Scheme 5).

Scheme 5: Propagation mechanism for the polymerization of VDF initiated by hydrogen peroxide in dimethyl carbonate

Termination reaction

As expected and known, recombination of PVDF• macroradical occurred. According to the ¹H NMR chain-end analysis, hydrogen transfer reaction to the PVDF• macroradical was highly favorable under the reaction conditions. For this reason, the non-functional chain-ends represent 40% (Table 6). This hydrogen transfer rate was high when compared with other approaches. For example, in RAFT polymerization of VDF, 25% of -CF₂H chain-end was detected.^{21,25} However, from iodine transfer polymerization process, almost no proton transfer was observed.^{21,22,25}

Many potential hydrogen sources are present in the medium such as DMC, water, and hydrogen peroxide. A control reaction between water and AIBN at 100 °C also afforded acetone cyanohydrin and probably hydrogen radical which can initiate the polymerization of VDF, thus leading to PVDF terminated by CH₃ or CF₂H end-groups (Scheme 6). In addition, no signals in ¹⁹F NMR spectra at -97 and -98 ppm referring to chain ramification were present.⁵⁸ In conclusion, the internal hydrogen transfer was not present under our reaction conditions.

Scheme 6: Reaction between water and AIBN at 100 °C for 1 hour

Conclusion

VDF was successfully polymerized *via* metal free generation of hydroxyl radicals from hydrogen peroxide in the presence of AIBN. The best results were obtained using $\text{H}_2\text{O}_2\text{:AIBN} = 1\text{:}1$, 1 mol% with respect to VDF at 130 °C in dimethyl carbonate for 4 hours. The microstructure of the prepared PVDFs was identified using ^1H , ^{19}F NMR spectroscopy and MALDI-TOF spectrometry. The chain-ends consisted in 37% $\text{CF}_2\text{CH}_2\text{-carbonate}$, 9% $\text{CF}_2\text{CH}_2\text{OH}$, 9% $\text{CF}_2\text{CO}_2\text{H}$, 4% $\text{CH}_2\text{=CFR}$, 14% CF_2H , and 16% of CF_2CH_3 . In addition, molar mass was estimated around 1400 g/mol. From a mechanistic point of view, the formed $\text{OH}^\bullet$ radicals added onto the VDF on both head and tail sites without regioselectivity and further initiated the radical polymerization, leading to α -hydroxyl and carboxylic acid terminated PVDF. However, the main reaction of the hydroxyl radical was the hydrogen abstraction from the solvent to generate the dimethyl carbonate radicals. Then, these radicals also initiated the radical polymerization of VDF to afford carbonate terminated PVDF. This reaction occurred with 92% of selectivity toward the addition of carbonate radicals onto the VDF tail. The use or chemical modification of such an α -group into hydroxyl end-group for original (meth)acrylate oligo(VDF) macromonomers are under progress.

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Conflicts of Interest

There are no conflicts of interest to declare.

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