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1 Type of the Paper (Article, Review, Communication, etc.)

2 Unexpected radical telomerisation of vinylidene fluoride with 3 2-mercaptoethanol

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7
8 **Abstract:** The radical telomerisation of vinylidene fluoride (VDF) with 2-mercaptoethanol as chain
9 transfer agent (CTA) was studied to synthesise fluorinated telomers which bear a hydroxy
10 end-group, as H(VDF)_nS(CH₂)₂OH, under thermal (di-*tert*-butyl peroxide as the initiator) or pho-
11 tochemical initiations. A careful structural study of typical H-VDF-S(CH₂)₂OH telomer was per-
12 formed by ¹H and ¹⁹F NMR spectroscopies. These analytical methods allowed us to evidence the
13 selective addition of the thiyl radical onto the hydrogenated side of VDF, and the telomer con-
14 taining one VDF unit was obtained selectively. Surprisingly, for higher [VDF]₀ initial concentra-
15 tions, monoadduct telomer was produced as well as PVDF homopolymer. This feature was related
16 to the fast consumption of the CTA. The kinetics of radical telomerisation led to a quite high
17 transfer constant of the CTA (40 at 140 °C) that evidences the formation of monoadduct as the only
18 telomer formed.

19 **Keywords:** vinylidene fluoride; radical; telomerisation; mercaptan; chain transfer constant

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22 1. Introduction

23 Fluorinated polymers represent a unique class of materials that exhibit outstanding
24 properties such as low surface energy, high thermostability, resistance to oxidation,
25 chemicals (to acids, oils and solvents) and to ageing, low refractive index and water
26 absorptivity, and excellent weatherability. [1-7]

27 Hence, they can be involved in many applications such as coatings, optical fibers, high
28 performance elastomers, antifouling agents, piezoelectric devices, fuel cell membranes,
29 separators and polymer electrolytes for Li-ion batteries, cables and wires[1-7].

30 These (co)polymers are usually produced by radical (co)polymerization. A valuable and
31 practical approach is to consider the radical telomerisation of fluorinated olefins with a
32 chain transfer agent (CTA or telogen), since that reaction is regarded as a suitable model
33 of polymerisation [8]. Such a reaction can be initiated thermally, photochemically and
34 gamma rays, or in the presence of radical initiators or catalysts. [3,8] The molar mass of
35 the resulting telomers greatly depends on the stoichiometry of the reactants, and most
36 of all, on the chain transfer constant (C_T) value: the lower the C_T value, the higher the
37 molar mass of the resulting telomers.[3] This constant can be assessed from the ratio of
38 the transfer rate to the propagation rate and various methods have been used to
39 calculate it.[3] C_T is thus a key factor in determining the most probable reaction pathway.
40 Although various articles report the C_T values of different chain transfer agents in the
41 radical telomerisation of vinylidene fluoride (VDF) (Table 1), to the best of our
42 knowledge, there is a lack of information for the assessment of the chain transfer
43 constant of mercaptan. Such a CTA is rather well-used in thiol ene reactions. [9]

44 Actually, the radical telomerisation of VDF has been comprehensively studied and
45 reviewed 17 years ago.[3] Several kinetics of radical telomerisation of VDF were achieved
46 from methanol [10], diethyl phosphonate [11], chloroform [12-13],
47 bromotrchloromethane [12-13], carbon tetrachloride [12-13], BrCF₂CFCIBr [14], CF₃I [15],
48 C₆F₁₃I [16], HCF₂CF₂CH₂I [16], xanthate [17], iodine monochloride [18] and more recently

isopropanol, ethyl acetate and octyl acetate.[19] In addition, 1-iodoperfluoroalkanes [3, 8] have also been successfully involved as efficient CTAs in iodine transfer polymerization either in supercritical CO₂ [20] or under photochemical initiation catalyzed by Mn₂(CO)₁₀. [21-22] However, a few radical telomerisations of VDF have been reported with mercaptans [23-24], disulfides [25-27] or alkyl (or aryl) trifluoromethanesulfonates [28] while functional mercaptans have not been used and no transfer constants have been assessed. This also contributes to a further objective of this present article, as well as the characterization of the resulting telomers and unexpected side-products.

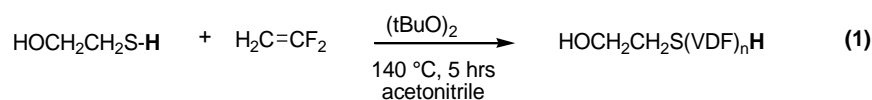
Chain transfer agent	Transfer Constant (T /°C)	References
HOCH ₃	8·10 ⁻³ (140)	10
(EtO) ₂ P(O)-H	0.34 (140)	11
Cl ₃ C-H	0.06 (141)	12,13
Cl ₃ C-Cl	0.25 (141)	12,13
BrCF ₂ CFCl-Br	1.30 (75)	14
C ₆ F ₁₃ -I	7.4 (75)	16
HCF ₂ CF ₂ CH ₂ I	0.3 (75)	16
Xanthate	49 (73)	17
Cl ₃ C-Br	34 (141)	12,13
ICI	>40 (130)	18
RSH	40 (140)	This work

Table 1: summary of radical telomerisations of VDF with various chain transfer agents and their transfer constants

2. Results

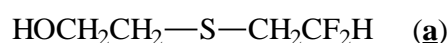
2.1. Radical Telomerisation of VDF with 2-mercaptoethanol: Synthesis and characterisation

2.1.1. First adducts: VDF being a gas, the first adducts of the telomerisation of VDF with 2-mercaptoethanol as CTA were synthesized in an autoclave using di-*tert*-butyl peroxide, (tBuO)₂, as the initiator (with an initial molar ratio to VDF: "C₀" = [(tBuO)₂]₀/[VDF]₀ = 0.01) and acetonitrile as the solvent, at 140 °C (at this temperature, the half-life of di-*t*-butyl peroxide is ca. 1 hr).



The initial mixture was composed of initial molar ratio $R_0 = [\text{CTA}]_0/[\text{VDF}]_0 = 1$. The use of a solvent was required to improve the homogeneity of the liquid phase and the VDF dissolution in that medium and acetonitrile was chosen also because of its poor transfer activity in the presence of VDF.[29] Thus, at 140 °C, the initial pressures in the autoclave did not exceed 35 bars for 100 g of VDF (in a one liter-autoclave), in the presence of acetonitrile and then dropped to 11 bars. After reaction, the overall VDF

79 conversion was ca. 42 %, according to the released fluorinated gas. On the other hand,
80 after degassing, the reaction mixture was presented as a slightly colored liquid phase,
81 which showed the characteristic natsy smell of the residual presence of thiol. After
82 evaporation of the solvent, a distillation of the total product mixture was achieved to
83 remove residual 2-mercaptoethanol and indicated that 50% of that chain transfer agent
84 was converted. The product was then analysed by gas chromatography (GC) that
85 evidences the formation of one telomeric species (purity about 96% in response factors)
86 further isolated by distillation. The monoadduct was characterised by ^1H and ^{19}F NMR
87 spectroscopies (detailed in the experimental section). The ^1H and ^{19}F NMR spectrum
88 (Figures 1a and 1b) for the distilled telomer highlights the exclusive formulae (a):



89 ^1H NMR (Figure 1b) and ^{19}F (Figure 1a) NMR spectra allowed us to determine the
90 structure of monoadduct without any ambiguity, and therefore, the regioselective
91 addition of $\text{HOC}_2\text{H}_4\text{S}^\bullet$ thiyl radical onto methylene site of VDF. On the one hand, the
92 addition of a single effective VDF unit was demonstrated by the presence of a triplet ($^2J_{\text{HF}}$
93 = 56.5 Hz) centered at 5.8 ppm characteristic of a difluoromethyl $-\text{CF}_2\text{-H}$ end-group in the
94 the ^1H NMR spectrum of the product. This confirms previous studies that report the
95 telomerisation of VDF with methanol [10], diethyl phosphonate [11] and chloroform [12].
96 On the other hand, the presence of the hydroxyl function, provided by the CTA, can also
97 be identifiable by a triplet ($^3J_{\text{HH}} = 6.0$ Hz) centered at 3.7 ppm and a broad singlet that
98 shifts with the concentration (or dilution) of the sample (hydroxyl- OH), respectively. [30]
99 The nature of the hydroxyl end group was further confirmed by adding one drop of
100 CCl_3NCO in the NMR tube that induced a chemical shift of 1.0 ppm of the triplet, as a
101 feature of the hydroxymethyl function and the vanishing of the broad singlet above. A
102 distinction is finally on the ^1H NMR spectrum of the isolated product that features two
103 structures of methylene groups in the 2.6-3.0 ppm region. One of both groups is in the
104 end α -difluoromethyl, as evidenced by the nature of the resonance bands, namely a
105 triplet ($^3J_{\text{HF}} = 15.7$ Hz) of triplets ($^3J_{\text{HH}} = 4.4$ Hz). The other one is adjacent to another
106 methylene group and resonates as a simple triplet ($^3J_{\text{HH}} = 6.0$ Hz). Therefore, the general
107 structure of the monoadduct of the telomerisation of VDF with 2-mercaptoethanol is in
108 formulae (a) above.
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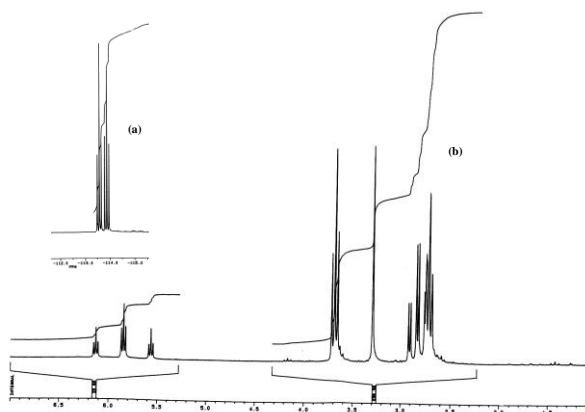


Figure 1: NMR spectra of HOCH₂CH₂SCH₂CF₂H monoadduct: (a) ¹⁹F NMR spectrum and (b) ¹H NMR spectrum, recorded in CDCl₃ at 20 °C.

The ¹H NMR spectrum (Figure 1b) also reveals the absence of structure attributed to a CF₂-CH₃ end group arising from the addition of CTA radicals onto the fluorinated carbon of VDF. Methyl end group would indeed be identified by a triplet (³J_{HF} = 19.0 Hz) centered around 1.8 ppm, as observed in the ¹H NMR spectrum of the compound model CH₃CF₂CH₂PVDF.[10] It can be concluded that HOC₂H₄S• radical added selectively onto the less substituted carbon atom (CH₂=) of VDF. In addition, that radical is electrophilic and thus reacts onto the nucleophilic methylene site. The regioselectivity of the addition is also confirmed by ¹⁹F NMR analysis of the monoadduct, which indicates a doublet (²J_{FH} = 56.5 Hz) of triplets (³J_{FH} = 15.2 Hz) centered at -113.9 ppm characteristic of the fluorine atoms in CF₂-H difluoromethyl end group.[10]

Infrared spectroscopy (Figure 3) [31] revealed the complete vanishing of the characteristic frequency of S-H bond (ν = 2556 cm⁻¹) initially present in the CTA and the presence of specific bands assigned to difluoromethylene -CF₂- groups at 1100-1200 cm⁻¹.

The total product mixture obtained after the telomerisation of VDF with equimolar quantities of 2-mercaptoethanol contained the monoadduct (based on analysis GC) that represents more than 95% of synthesised telomers.

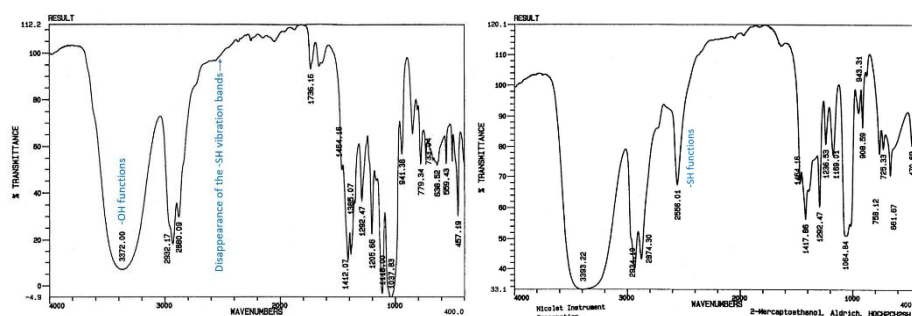


Figure 3: FTIR spectra of the total product mixture from the radical telomerization of VDF with 2-mercaptoethanol (left) and of the 2-mercaptoethanol (right)

2.1.2. Higher molar mass-telomers: The telomers with higher degrees of telomerisation were synthesised in a 1 L-autoclave using the same initiator ($C_0 = [(tBuO)_2]_0/[VDF]_0 = 0.01$), a 10 folder excess of VDF ($R_0 = [CTA]_0/[VDF]_0 = 0.1$) and acetonitrile as the solvent, at 140 °C. After 5 hr-reaction, the total total of the reaction was purified and characterised by a marked staining (brown). According to Boutevin *et al.* [30], VDF-2-mercaptoethanol cotelomers with higher order are distinguished by very high boiling points and poor solubility in conventional organic solvents. To overcome the solubility issue, the obtained telomers were acetylated making them soluble in polar solvents (as acetone, DMF, DMSO, NMP).

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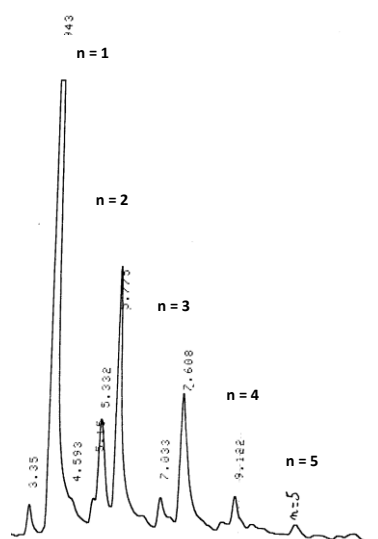
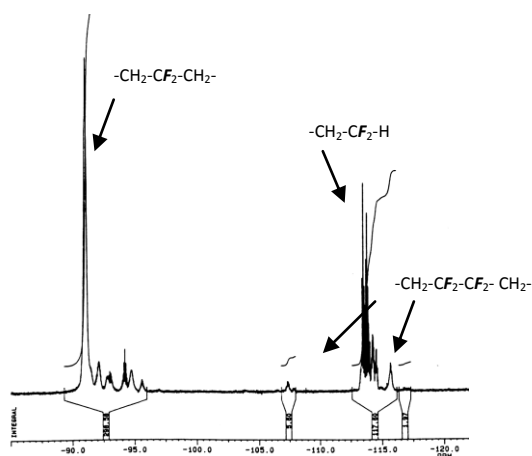


Figure 2: GC chromatogram of acetylated telomers mixture obtained from the telomerisation of VDF with 2-mercaptoethanol (initiated by di-*tert*-butyl peroxide, $R_0 = [\text{CTA}]_0/[\text{VDF}]_0 = 0.1$, in acetonitrile as the solvent, at 140 °C, 5 hrs).

After evaporation of the solvent, the total product mixture was analysed by GC, the chromatogram of which (Figure 2) evidences the formation of a classical telomeric distribution with the first five produced adducts. The number-average degree of polymerisation, DP_n , of these telomers was assessed (1.4), corresponding to an average molar mass, M_n , of about 150, assuming that each adduct has the following formulae: $\text{H}(\text{VDF})_n\text{S}(\text{CH}_2)_2\text{OH}$.

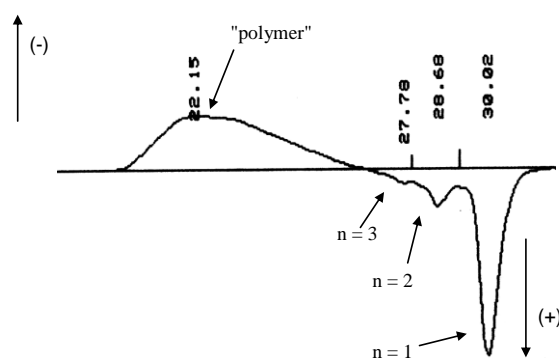
The ^{19}F NMR spectrum (Figure 4) of the acetylated crude telomers displays main VDF units as highlighted by a doublet ($^2J_{\text{FH}} = 56.5$ Hz), centered at -114.2 ppm, assigned to the fluorine atoms of difluoromethyl HCF_2 -end-group and an intense peak centered at -91.8 ppm corresponding to $(-\text{CH}_2-\text{CF}_2-\text{CH}_2-\text{CF}_2-)$ [10-12, 15, 20-22] normal chaining in VDF-VDF dyads while the reverse isomer exhibits a methyl end-group resulting from a reversed addition of a VDF unit as evidenced by the presence of a peaks centered at -94.7, -107.4, and -115.7 ppm. [10-12, 15, 20-22] The amount of these head-to-head defects of chaining assessed by the corresponding integrals, were evaluated to 12 % that represents a high value (since usually PVDF contains 5-8% defects [4]).



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214 Figure 4: ^{19}F NMR spectrum of crude acetylated $\text{H}(\text{VDF})_n\text{S}(\text{CH}_2)_2\text{OCOCH}_3$ telomers
215 (from a radical telomerisation of a 10 folder excess-VDF with 2-mercaptoethanol) re-
216 corded in CDCl_3 at 20°C .
217

218 The number-average degree of telomerisation, DP_n , has also been assessed by ^{19}F
219 NMR spectroscopy. The ratio of integral of the areas of difluoromethylene groups of both
220 normal and reversed VDF-VDF sequences to that of difluoromethyl HCF_2 -end-group
221 (Figure 3) gives $DP_n = 2.4$. Surprisingly, this value does not match with the result
222 obtained from the GC analysis.

223 The explanation for this discrepancy was provided by analysis of the telomers by size
224 exclusion chromatography (SEC or GPC). The corresponding chromatogram (Figure 4)
225 exhibits that the crude reaction product contain real telomers (including the first three
226 adducts) and other species with a much higher average degree of polymerization (ca.
227 5100 equivalent PMMA as the standards displayed with a negative polarity [32], Figure
228 5).
229



244 Figure 5: SEC chromatogram (in DMF, with a refractive index detector) of the
245 acetylated telomers mixture obtained by telomerisation of VDF with 2-mercaptoethanol
246 (using di-t-butyl peroxide as the initiator, $R_0 = [\text{CTA}]_0/[\text{VDF}]_0 = 0.1$, acetonitrile as the
247 solvent, at 140°C , reaction times: 5 hrs).
248

249 As expected, VDF oligomers of high molar masses are not detected by GC but can
250 be observed in the ^{19}F NMR spectra. The formation of these polymeric species could arise
251 from the direct homopolymerisation of VDF in the presence of remaining initiator after
252 the total consumption of the CTA.

253 In fact, it cannot be excluded the possibility that these high molar mass-species are
254 "heavy" telomers, (i.e. with a high fluorine content) which would explain the reversal
255 polarity observed in the SEC chromatograms. Indeed, it was worth attempting to verify if
256 polymeric species were still formed when the reaction was interrupted before the com-

plete vanishing of the CTA. Thus, a telomerisation of VDF with the same CTA was carried out according to an exactly same protocol (including the same initial molar ratio $R_0 = 0.1$), but within 30 minutes only.

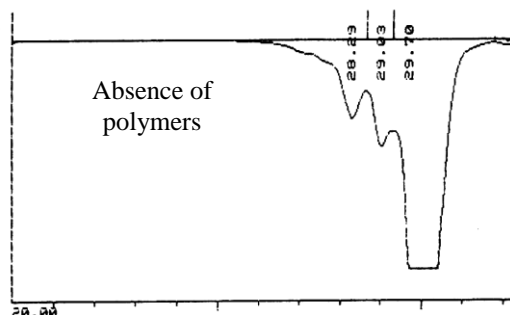


Figure 6: SEC chromatogram (in DMF with a refractive index detector) of the acetylated telomers mixture obtained by telomerisation of VDF with 2-mercaptoethanol (initiated by di-*t*-butyl peroxide, initial $[CTA]_0/[VDF]_0$ molar ratio of 0.1) and acetonitrile as the solvent, at 140 °C, reaction times: 30 min).

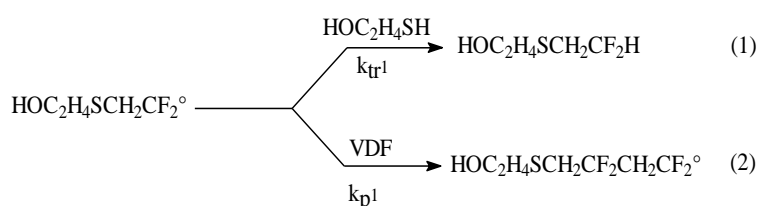
After reaction and removing the solvent, the SEC chromatogram of the total product mixture (Figure 6) displayed the presence of telomers with low DP_n only (and thus highlighting the absence of any polymers traces).

2. Kinetics of radical telomerisation of VDF with 2-mercaptoethanol

The transfer efficiency of 2-mercaptoethanol in the presence of VDF is characterised by the transfer constant, C_{T^n} , that may be defined for each growing telomeric radical as the ratio of the transfer rate constant of the CTA, k_{tr}^n , to the rate constant of propagation of VDF, k_p^n , as follows:

$$C_{T^n} = k_{tr}^n / k_p^n$$

The evaluation of the kinetic constants of transfer of the first orders of such a telomerisation was performed out using the method of David and Gosselain [33], which considers each telomer of i order as a CTA. Thus, the radical of order 1, $HO(CH_2)_2S(CH_2CF_2)^\bullet$, can react in two competing ways: (1) by transfer to CTA or (2) by propagation of VDF. These rate constants characterise reaction (1) of formation of telomers of first order from first order radicals and reaction (2) of formation of $(n+1)$ order telomer radicals from these same radicals, respectively, as follows:

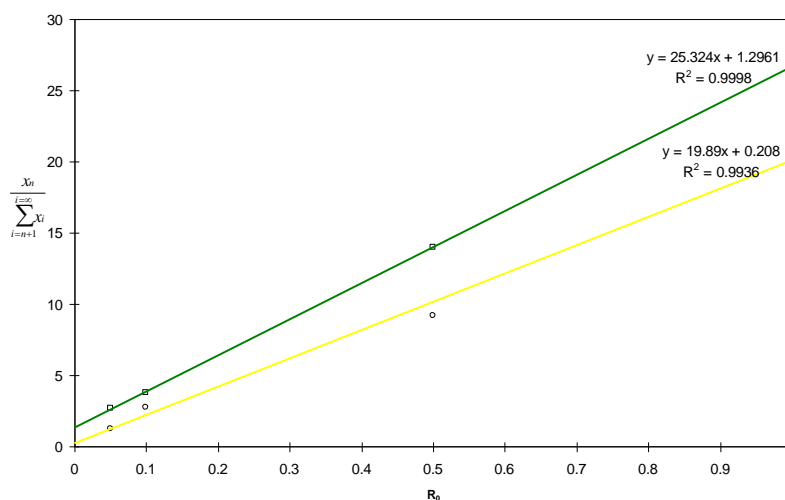


304 The produced telomers from step (1) are unable to participate to further radical
 305 reaction, especially as CTAs. Indeed, we have checked that HOCH₂CH₂SCH₂CF₂H pro-
 306 duced by this telomerisation could not act as a new CTA when it was involved in the
 307 presence of organic initiator ((tBuO)₂ or *tert*-butyl peroxyvalate) and VDF, in contrast
 308 to telomers/polymers of TFE [34] and VDF [16,20,21,35] with 1-iodo perfluoroalkanes,
 309 that were further used as original CTAs.

310 The transfer constant values of n order were obtained by assessing the slope of the
 311 straight lines representing the molar fractions of each telomer (obtained from the area of
 312 the corresponding peak in the gas chromatogram) *versus* R₀' for a given n value (Figure
 313 7). [31]

314 We considered R₀ as the ratio of the initial CTA concentration to the initial overall
 315 VDF concentration (i.e. the total VDF initial moles by volume of the liquid phase). [36]

$$316 C_n = \frac{T_n}{R_0' \cdot \sum_{i=n+1}^{\infty} T_i} \quad (3)$$



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Figure 7: molar fractions of each n telomer *versus* initial [CTA]₀/[VDF]₀ molar ratio (R₀) for a given n value obtained from the telomerisation of VDF with 2-mercaptoethanol (initiated by di-*tert*-butyl peroxide at 140 °C, reaction times: 30 min).

David and Gosselain's law [33] enabled us to assess the transfer constant to 2-mercaptoethanol of 40 at 140 °C. This high value is compared to those of other chain transfer agents (Table 1) and is related to the dissociation energies of the S-H (307 kJ.mol⁻¹), C-H (402 kJ.mol⁻¹), P-H (322 kJ.mol⁻¹), C₄F₉-I (225 kJ.mol⁻¹), or I-Cl (211 kJ.mol⁻¹) bonds. [37] Hence, that efficient transfer step can explain that remaining radicals, arising from unreacted initiator, are able to initiate the homopolymerisation of VDF, hence leading to PVDF. That observation was already noted in the radical telomerisation of

335 styrene with mercapto-2-ammonium chloride that also generated polystyrene next to
336 monoadduct telomer. [38]

337 4. Materials and Methods

338 4.1 Materials

339 Vinylidene fluoride (VDF) was kindly supplied by Elf Atochem (now Arkema)
340 (Pierre-Bénite, France), *di-tert*-butyl peroxide was generously offered by Akzo France
341 (Chalons sur Marne), and 2-mercaptoethanol (99 %) was purchased from Aldrich (Saint
342 Quentin Fallavier, France). These reactants were used as received. Acetonitrile (Aldrich)
343 was distilled from CaH₂ and kept over activated 4Å molecular sieves.

344 4.2 Reactions

345 To obtain a suitable amount of VDF telomers, the telomerisation was carried out in
346 a 1L Parr Hastelloy autoclave equipped with a manometer, a rupture disk, inner and
347 outlet valves. An electronic device regulated and controlled both the stirring and heating
348 of the autoclave. Prior to reaction, the autoclave was pressurised with 30 bar of nitrogen
349 for 1 h to check for leaks. It was then conditioned for the reaction with several
350 nitrogen/vacuum cycles (10⁻² mbar) to remove any trace of oxygen. *Di-tert*-butyl peroxide,
351 2-mercaptoethanol, and acetonitrile were transferred into the autoclave under vacuum
352 *via* a funnel tightly connected to the vessel. Then, after cooling in a liquid
353 nitrogen/acetone mixture, VDF was introduced by double weighing (i.e., the difference of
354 weight before and after filling the autoclave with the gases). The vessel was heated
355 gradually up to 140 °C, and the evolution of pressure and temperature were recorded.
356 The pressure increased up to ca. 25 bars and after 4 hr at the same temperature, it dropped
357 to 11 bars. Reaction was stopped after desired times and the autoclave was cooled to
358 room temperature and then placed in an ice bath. After purging the non-reacted
359 monomer, the conversion of gaseous monomer was determined by double weighing.
360 After evaporation of acetonitrile, the total product mixture was fractionally distilled. The
361 first fraction contained unreacted 2-mercaptoethanol for a [CTA]/[VDF] initial molar
362 ratio lower than 1 while the other pure fractions were composed of various VDF
363 telomeric adducts (mainly mono- and diadduct) and the residue was PVDF.

364 4.3 Apparatus and analysis of products

365 After reaction and evaporation of the solvent, the total product mixture was
366 analyzed by gas chromatography (GC) using a Delsi apparatus (model 330) equipped
367 with a SE 30 column, 2 m, 1/8 in. (i.d.). The nitrogen pressure at the entrance to the
368 column was maintained at 1 bar and the detector and injector temperatures were 240
369 and 235 °C, respectively. The temperature program started from 50 °C and reached
370 220 °C at a heating rate of 10 °C/min. The GC apparatus was connected to a Hewlett
371 Packard integrator (model 3390). The sensitivity of the apparatus and the resolution of
372 the chromatogram limit the detection of telomers to the fifth adduct (Figure 2). The
373 structure of the telomers was characterised by NMR spectroscopy at room temperature.
374 The ¹H, ¹⁹F, and ¹³C NMR spectra were recorded on a Bruker AC-250 or Bruker AC-200
375 instruments using deuterated chloroform or acetone-d₆, and tetramethyl silane or CFCl₃,
376

377 as the solvent and internal references, respectively. Coupling constants and chemical
378 shifts are given in hertz (Hz) and in part per million (ppm). The experimental conditions
379 for recording ^1H (or ^{19}F) NMR spectra were the following: flip angle 90° (30°);
380 acquisition time 4.5 s (0.7 s); pulse delay 2 s (5 s); 36 (200) scans and pulse width of 5 ms
381 for ^{19}F NMR. The letters s, d, t, q and m represent singlet, doublet, triplet, quartet and
382 multiplet, respectively. The IR spectra were performed with a Nicolet spectrophotometer
383 coupled to a compatible PC for data acquisition. The position of the bands is given in
384 cm^{-1} , with an accuracy of $\pm 2 \text{ cm}^{-1}$. Average molar mass (\bar{M}_n) and molar mass distribution
385 (\bar{M}_w/\bar{M}_n , Đ) values were determined from chromatograms recorded by size exclusion
386 chromatography (SEC or GPC) in DMF at 30°C (flow rate = $0.8 \text{ mL}\cdot\text{min}^{-1}$) on apparatus
387 equipped with an isocratic pump Spectra-Physics SP 8640 with an integrator and a
388 computer unit for processing the chromatogram. The polymer samples were dissolved
389 in DMF ($2 \text{ mg}\cdot\text{mL}^{-1}$). All elution curves were calibrated with PMMA standards.

390 4.4 Typical procedure for the radical telomerisation of VDF with 2-mercaptoethanol: from an
391 initial molar ratio $R_0 = [\text{CTA}]_0/[\text{VDF}]_0 = 1$

392 The VDF (100.0 g, 1.56 mol) reacted in a 1 liter-autoclave as described above with
393 2-mercaptoethanol (122.0 g, 1.56 mol) and acetonitrile (300.0 g, 7.31 mol) as the solvent.
394 The telomerisation was initiated by di-*tert*-butyl peroxide (2.5 g, 0.0171 mol). The reactor
395 was heated gradually up to 140°C , and the evolution of pressure and temperature were
396 recorded. After 5 hr-reaction (or 5 half-lives of the organic initiator), the telomerisation
397 was stopped by quenching in an ice bath. After purging the non-reacted monomer, the
398 conversion of gaseous monomer was determined by double weighing (the conversion
399 rate overall VDF was estimated at 42%). A fraction of the crude reaction product was
400 removed for analysis (GC, SEC). After evaporation of acetonitrile, the total product
401 mixture was fractionally distilled. The first fraction contained the residual thiol (b.p. =
402 157°C or $65\text{--}66^\circ\text{C}/22 \text{ mm Hg}$) while the other pure fractions were composed of the var-
403 ious VDF telomeric adducts. The first adduct of telomerisation ($m = 55.0 \text{ g}$) was isolated
404 by vacuum distillation (b.p. = $101\text{--}103^\circ\text{C}/20 \text{ mmHg}$) with a purity of ca. 96% (from GC).

405 Monoadduct: 5,5-difluoro-3-thia-pentanol.

406 b.p. = $101\text{--}103^\circ\text{C}/20 \text{ mmHg}$, colorless liquid.

407 ^1H NMR (CDCl_3) δ : 2.68 (t, $^3J_{\text{HH}} = 6.0 \text{ Hz}$, $-\text{S}-\text{CH}_2-\text{CH}_2\text{OH}$, 2 H); 2.75 (td, $^3J_{\text{H-F}} = 15.7$
408 Hz; $^3J_{\text{H-H}} = 4.4 \text{ Hz}$, $-\text{S}-\text{CH}_2-\text{CF}_2-\text{H}$, 2 H); 3.39 (broad s, shifted with dilution $-\text{CH}_2\text{OH}$, 1H);
409 3.70 (t, $^3J_{\text{HH}} = 6.0 \text{ Hz}$, shifted to 4.68 ppm with CCl_3NCO , $-\text{CH}_2\text{OH}$, 2 H); 5.85 (tt, $^2J_{\text{H-F}} = 56.5$
410 Hz; $^3J_{\text{H-H}} = 4.4 \text{ Hz}$, $-\text{CF}_2\text{H}$, 1 H) ppm.

411 ^{19}F NMR (CDCl_3) δ : -113.9 (dt, $^2J_{\text{F-H}} = 56.5 \text{ Hz}$; $^3J_{\text{F-H}} = 15.7 \text{ Hz}$, $-\text{CF}_2\text{H}$, 2 F).

412 4.5 Photochemical telomerisation

413 The photochemical telomerisation was carried out by UV lamp irradiation (Philips
414 HPK 125 W) of a sealed Pyrex tube (capacity: $\sim 25 \text{ cc.}$) containing a mixture of VDF (16.2 g,
415 0.253 mole) and 2-mercaptoethanol (2.1 g, 0.027 mole), dissolved in acetonitrile (10.4 g,
416 0.25 mole) benzophenone (0.5 g, $2,70\cdot 10^{-3}$ mole) was used as a photoinitiator. After 12
417 hr-irradiation at room temperature, the reaction mixture was quenched into liquid
418 nitrogen. Once the tube was opened, the mixture was degassed to remove the residual

VDF (ca. 12 g). After evaporation of acetonitrile, the total product mixture was fractionally distilled. The first fraction contained the residual thiol while in the other pure fraction was only the monoadduct, identified as the reaction product (checked by GC analysis and NMR spectroscopy).

5. Conclusions

The radical telomerisation of VDF with 2-mercaptoethanol led to ω -hydroxyl VDF-telomers. The stoichiometry of the reactants plays a crucial role on both the molar masses and the purity of the products. An excess of mercaptan led to quite low molar mass-telomers only (especially HOCH₂CH₂SCH₂CF₂H monoadduct that results from the regioselective addition of thiyl radicals onto the less hindered site of VDF). When an excess of VDF was used, the monoadduct and slightly higher telomers (lower than hexadduct) were produced as well as PVDF homopolymer. Such an unexpected observation arises from the high transfer constant to thiol ($C_T = 40$ at 140 °C) that is quickly consumed, followed by the direct initiation of unreacted VDF from the remaining radical initiator. That efficient step is linked to the low dissociation energy of S-H bond in the mercaptan. For the first time, such a behavior has been observed in radical telomerization of fluorinated alkenes. The kinetic study further enabled to complete the series of C_T values of various CTA in telomerisation of VDF.

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