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Synthesis of fluoro-substituted acrylic monomers bearing a functionalized lateral chain

Part 1. Preparation of sulfur-containing monomers

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Abstract

The synthesis of sulfur-containing fluoroacrylic monomers $C_mF_{2m+1}(CH_2)_2S(CH_2)_nOC(O)CH{=}CH_2$ (where $m = 6$, 8 and $n = 2$–4, 11) is presented from a two-step procedure. The first deals with the radical addition of fluorinated mercaptans $C_mF_{2m+1}(CH_2)_2SH$ onto ω-unsaturated alcohols leading to new ω-perfluorinated alcohols containing various polymethylene spacers $C_mF_{2m+1}(CH_2)_2S(CH_2)_nOH$ according to the nature of the unsaturated alcohols. By-products were noted, resulting from the β-addition of the thiyl radical onto the more hindered side of the alcohol. The proportion of linear and branched isomers is discussed according to the stability of the radical intermediates. These minor products were obtained selectively from other routes to confirm their presence in the reaction media. The second step deals with the acrylation reaction that occurred either in the presence of acryloyl chloride or from a Fisher esterification. Both reactions are described and discussed taking into account the nature of the starting alcohols. The formation of thiiranium ions as intermediates in the esterification of β-sulfur-containing alcohols in acidic medium is established and the formation of regioisomers described according to this thiiranium moieties interposition. © 2001 Elsevier Science B.V. All rights reserved.

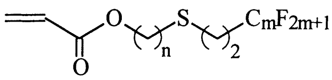
Keywords: Fluorinated tails; Thiyl radicals; Thiiranium ion; Acrylic monomers; Radical addition; Fluorinated alcohols

1. Introduction

The synthesis of fluorinated monomers is of increasing interest because of a wide range of applications of fluorocarbon polymers [1–3]. Due to their low surface energy [4], low friction coefficient [5] and aggressive chemicals resistance [6], these materials find applications in many areas such as adhesion and lubricants [7,8], biocompatibility [9], solvent resistance [10], material coatings [11] (for textiles [12–15], optical fibers [16], stone [17,18], leather [19,20], metal [21,22], wood [23] and paper [24]). Fluorinated polymers have mainly been prepared according to two ways: free radical polymerization of fluoroolefins and polycondensation (polyesters [25], polyurethanes [26], polystyrenes [27], polyacrylamides [28] or polysiloxanes [29]) or fluorination of polymers [30,31]. Fluorinated acrylics are of great interest mainly for their good surface properties, and they have been widely investigated (wettability and surface properties [32–35], structural properties [36–40] and polymerization [41–47]).

Usually, fluoroacrylates synthesized industrially are achieved in a three-step procedure: by ethylenation of perfluoroalkyl iodides, followed by a hydrolysis leading to 2-perfluoroalkyl-ethanol and then by acrylation of hydroxyl end-group. Many fluoroacrylic monomers have been achieved, however, quite a few contain a thioether bridge [48].

The aim of the present work is the preparation of fluorinated acrylates containing a thioether function as a spacer link between the fluorinated chain and the acrylic group, as follows:



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It is well known that the homopolymers and copolymers are useful in textile treatment to allow the oil and water repellency [49,50]. The route presented in this work is an interesting way to achieve the synthesis of several monomers ($n = 3$–11 and $m = 6$–8), thanks to a large range of ω-unsaturated alcohols used with different 2-perfluoroalkyl-ethanethiols.

2. Experimental details

2.1. General comments

Acrylic acid, hydroquinone monomethyl ether (HQME), 2-perfluorohexyl-ethanethiol, 2-perfluorooctyl-ethanethiol, and 1-iodo-2-perfluorooctyl-ethane were kindly supplied by Elf-Atochem. The last reactant was treated with a dilute solution of $Na_2S_2O_3$ prior to use while the other did not undergo any purification. Allyl alcohol, but-3-en-1-ol, undec-10-en-1-ol, 2-chloro-ethan-1-ol, 3-chloro-propan-1-ol, 1-mercapto-propan-1-ol, thiolactic acid, lithium aluminum hydride, sodium, *p*-toluenesulfonic acid (APTS), acryloyl chloride and triethylamine were supplied from Aldrich and used as received, excepting for triethylamine which was distilled over CaH_2 under nitrogen. 2,2′-Azobisisobutyronitrile (AIBN), anhydrous sodium sulfate, sodium hydroxide, calcium hydride, calcium chloride, sodium hydrogen carbonate, sodium carbonate, potassium carbonate and ammonium chloride were purchased from Fluka. A 1N solution of hydrochloric acid was supplied from SDS. Dichloromethane, chloroform, toluene, cyclohexane, acetonitrile, ethanol and tetrahydrofuran were purchased from Carlo-Erba. Anhydrous solvents were distilled under nitrogen over $CaCl_2$ for dichloromethane and over sodium for tetrahydrofuran.

After esterification the monomers were stabilized with 250 ppm of HQME.

^{1}H, ^{13}C and ^{19}F NMR spectra were obtained on a Bruker AC-250 spectrometer using tetramethylsilane (TMS) (for ^{1}H and ^{13}C) and $CFCl_3$ (for ^{19}F) as internal references and $CDCl_3$ as solvent. The letters s, d, t, q and m designate singlet, doublet, triplet, quartet and multiplet, respectively. The ^{19}F NMR analysis of every compound could be described as two types of spectra, one type for each length of perfluorinated group.

Tail C_6F_{13}, δ (ppm): -81.2 (t, $J = 9.5$ Hz, $C\underline{F}_3$, 3F); -113.7 (m, $C\underline{F}_2CH_2$, 2F); -122.4 (m, $C\underline{F}_2C\underline{F}_2CF_2CH_2$, 4F); -123.5 (m, $C_2F_5C\underline{F}_2$, 2F); -126.6 (m, $CF_3C\underline{F}_2$, 2F).

Tail C_8F_{17}, δ (ppm): -81.1 (t, $J = 9.5$ Hz, $C\underline{F}_3$, 3F); -113.6 (m, $C\underline{F}_2CH_2$, 2F); -122.2 (m, $C\underline{F}_2C\underline{F}_2C\underline{F}_2CF_2CH_2$, 6F); -123.1 (m, $C_3F_7C\underline{F}_2$, 2F); -123.4 (m, $C_2F_5C\underline{F}_2$, 2F); -126.5 (m, $CF_3C\underline{F}_2$, 2F).

After reaction, some compounds were analyzed by gas chromatography (GC) using a Hewlett-Packard apparatus (model 5890 SII) equipped with an "WCOT Fused Silica" type column (25 m × 0.25 mm, stationary phase: CPSil5CB (0.12 μm)). Helium was used as the carrier gas, the detector and the injector temperature were 300 and 280°C, respectively. The temperature program started from 60°C and reached 300°C at a heating rate of 4°C min^{-1}. The GC apparatus was connected to a Hewlett-Packard mass spectrometer (MS) (model 5971 A, 70 eV electron-impact ion source).

2.2. Synthesis

2.2.1. Radical addition of 2-perfluoroalkyl-ethanethiol onto ω-unsaturated alcohol or allyl phenyl ether

A mixture of 1.3 equiv. of ω-unsaturated adduct, 0.03 equiv. of AIBN and cyclohexane or acetonitrile was purged with nitrogen and heated at 80°C under nitrogen. Then, a solution of 1 equiv. of 2-perfluoroalkyl-ethanethiol in cyclohexane or acetonitrile was added dropwise and the mixture was refluxed for 4 h.

For compounds **a**, the reaction mixture was dried over Na_2SO_4 and the solvent evaporated under vacuum. The mixture of isomers **$\underline{1}$a** and **$\underline{2}$a** was distilled under reduced pressure.

For compounds **b**, **d**, **e**, **f** and **g**, after cooling down to room temperature, the reaction mixture was dissolved in chloroform and dried over anhydrous Na_2SO_4. After evaporation of the solvents under vacuum, products were recrystallized from either cyclohexane or ethanol/water (70/30, v/v).

Mixture of **$\underline{1}$a** *and* **$\underline{2}$a** (90/10). Yield: 64%; yellow liquid; bp 145°C/0.5 mbar.

Compound **$\underline{1}$a**. ^{1}H NMR δ (ppm): 3.73 (t, $J = 6.1$ Hz, OCH_2); 2.74 (tt, ($^{4}J_{HF}$), $J_{HH} = 8.9$ Hz, $SC\underline{H}_2CH_2CF_2$); 2.67 (t, $J = 7.0$ Hz, CH_2S); 2.37 (tt, $J_{HH} = 8.9$ Hz, $^{3}J_{HF} = 17.8$ Hz, $CH_2C\underline{H}_2CF_2$); 1.90 (broad s, shifted with dilution, OH); 1.84 (tt, $J = 6.1$ Hz, $J = 7.0$ Hz, CH_2). ^{13}C NMR δ (ppm): 105–125 (m, $5CF_2$ and CF_3); 60.8 (s, OCH_2); 32.0 (t, $^{2}J_{CF} = 22.0$ Hz, $\underline{C}H_2CF_2$); 31.8 (s, CH_2S); 28.6 (s, CH_2); 22.5 (t, $^{3}J_{CF} = 4.4$ Hz, $S\underline{C}H_2CH_2CF_2$). GC-MS *m*/*z* (%): 59 (40); 69 (12); 105 (5); 119 (5); 131 (4); 169 (2); 379 (2); 407 (100); 438 (11).

Compound **$\underline{2}$a**. ^{1}H NMR δ (ppm): 3.70 (m, CH^{A}); 3.50 (m, CH^{B}); 2.90 (m, $CH^{X}S$); 2.74 (m, $SC\underline{H}_2CH_2CF_2$); 2.37 (m, $C\underline{H}_2CF_2$); 1.90 (broad s, shifted with dilution, OH); 1.29 (d, $J_{MX} = 6.9$ Hz, $CH_3{}^{M}$). ^{13}C NMR δ (ppm): 105–125 (m, $7CF_2$ and CF_3); 65.9 (s, OCH_2); 43.7 (s, CHS); 32.4 (t, $^{2}J_{CF} = 23.0$ Hz, $\underline{C}H_2CF_2$); 20.9 (m, $S\underline{C}H_2CH_2CF_2$); 17.7 (s, CH_3). GC-MS *m*/*z* (%): 45 (30); 59 (100); 69 (25); 119 (10); 131 (8); 169 (4); 393 (12); 407 (9); 438 (32).

Compound **$\underline{1}$b**. Yield: 56%; white solid; ^{1}H NMR δ (ppm): 3.64 (t, $J = 6.6$ Hz, OCH_2); 2.73 (tt, ($^{4}J_{HF}$), $^{3}J_{HH} = 8.3$ Hz, $SC\underline{H}_2CH_2CF_2$); 2.55 (t, $^{3}J_{HH} = 7.3$ Hz, CH_2S); 2.37 (tt, $^{3}J_{HH} = 8.4$ Hz, $^{3}J_{HF} = 17.4$ Hz, $CH_2C\underline{H}_2CF_2$); 1.56 (m, $2CH_2$); 1.29 (m, $7CH_2$ and OH). ^{13}C NMR δ (ppm): 105–125 (m, $5CF_2$ and CF_3); 63.1 (s, OCH_2); 32.8 (s, CH_2S); 32.3 (s, CH_2); 32.2 (t, $^{2}J_{CF} = 22.0$ Hz, $\underline{C}H_2CF_2$);

28.8–29.6 (m, 7CH_2); 25.7 (s, CH_2); 22.6 (t, $^3J_{CF} = 4.5$ Hz, $S\underline{C}H_2CH_2CF_2$).

Mixture of **1d** *and* **2d** (90/10). Yield: 87%; white solid; mp 66°C.

Compound **1d**. ^1H NMR δ (ppm): 3.78 (t, $J = 6.0$ Hz, OCH_2); 2.75 (tt, ($^4J_{HF}$), $^3J_{HH} = 8.5$ Hz, $SC\underline{H}_2CH_2CF_2$); 2.70 (t, $^3J_{HH} = 7.2$ Hz, CH_2S); 2.39 (tt, $^3J_{HH} = 8.5$ Hz, $^3J_{HF} = 17.1$ Hz, $CH_2C\underline{H}_2CF_2$); 1.87 (tt, $J = 6.0$ Hz, $J = 7.2$ Hz, CH_2); 1.59 (broad s, shifted with dilution, OH). ^{13}C NMR δ (ppm): 105–125 (m, 7CF_2 and CF_3); 61.3 (s, OCH_2); 32.1 (t, $^2J_{CF} = 22.1$ Hz, $\underline{C}H_2CF_2$); 31.8 (s, CH_2S); 28.8 (s, CH_2); 22.7 (t, $^3J_{CF} = 4.2$ Hz, $S\underline{C}H_2CH_2CF_2$). GC-MS *m/z* (%): 58 (100); 69 (26); 91 (11); 119 (10); 131 (10); 169 (6); 441 (2); 475 (3); 493 (5); 538 (8).

Compound **2d**. ^1H NMR δ (ppm): 3.68 (m, CH^A); 3.55 (m, CH^B); 2.92 (m, CH^XS); 2.79 (tt, ($^4J_{HF}$), $^3J_{HH} = 8.6$ Hz, $SC\underline{H}_2CH_2CF_2$); 2.39 (tt, $^3J_{HH} = 8.6$ Hz, $^3J_{HF} = 17.3$ Hz, $C\underline{H}_2CF_2$); 2.05 (broad s, shifted with dilution, OH); 1.31 (d, $J_{MX} = 7.1$ Hz, $CH_3{}^M$). ^{13}C NMR δ (ppm): 105–125 (m, 7CF_2 and CF_3); 65.9 (s, OCH_2); 43.6 (s, CHS); 32.4 (t, $^2J_{CF} = 22.0$ Hz, $\underline{C}H_2CF_2$); 20.9 (t, $^3J_{CF} = 4.5$ Hz, $S\underline{C}H_2CH_2CF_2$); 17.6 (s, CH_3). GC-MS *m/z* (%): 59 (100); 61 (50); 69 (35); 119 (12); 131 (11); 169 (6); 507 (100); 538 (10).

Mixture of **1e** *and* **2e** (95/05). Yield: 85%; white solid.

Compound **1e**. ^1H NMR δ (ppm): 3.68 (t, $^3J_{HH} = 5.8$ Hz, OCH_2); 2.74 (tt, ($^4J_{HF}$), $^3J_{HH} = 8.5$ Hz, $SC\underline{H}_2CH_2CF_2$); 2.60 (t, $^3J_{HH} = 6.8$ Hz, CH_2S); 2.37 (tt, $^3J_{HH} = 8.5$ Hz, $^3J_{HF} = 17.1$ Hz, $CH_2C\underline{H}_2CF_2$); 1.69 (m, 2CH_2); 1.50 (broad s, shifted with dilution, OH). ^{13}C NMR δ (ppm): 105–125 (m, 7CF_2 and CF_3); 62.3 (s, OCH_2); 32.2 (t, $^2J_{CF} = 22.2$ Hz, CH_2); 32.1 (s, CH_2); 31.5 (s, CH_2); 25.7 (s, CH_2); 21.6 (t, $^3J_{CF} = 4.4$ Hz, CH_2).

Compound **2e**. ^1H NMR δ (ppm): 3.68 (t, $^3J_{HH} = 5.8$ Hz, OCH_2); 3.0 (m, CHS); 2.79 (m, $SC\underline{H}_2CH_2CF_2$); 2.39 (m, $C\underline{H}_2CF_2$); 1.69 (m, CH_2); 1.50 (broad s, shifted with dilution, OH); 1.35 (d, $J = 6.7$ Hz, CH_3). GC-MS *m/z* (%): 59 (100); 61 (50); 69 (35); 119 (12); 131 (11); 169 (6); 507 (100); 538 (10).

Compound **1f**. Yield: 82%; white solid; mp 80°C; ^1H NMR δ (ppm): 3.64 (t, $^3J_{HH} = 6.5$ Hz, OCH_2); 2.73 (tt, ($^4J_{HF}$), $^3J_{HH} = 7.3$ Hz, $SC\underline{H}_2CH_2CF_2$); 2.55 (t, $^3J_{HH} = 7.3$ Hz, CH_2S); 2.37 (tt, $J_{HH} = 7.3$ Hz, $^3J_{HF} = 14.6$ Hz, $CH_2C\underline{H}_2CF_2$); 1.57 (m, 2CH_2); 1.29 (m, 7CH_2 and OH). ^{13}C NMR δ (ppm): 105–125 (m, 7CF_2 and CF_3); 63.0 (s, OCH_2); 32.8 (s, CH_2S); 32.3 (s, CH_2); 32.2 (t, $^2J_{CF} = 22$ Hz, $\underline{C}H_2CF_2$); 28.7–29.5 (m, 7CH_2); 25.7 (s, CH_2); 22.6 (t, $^3J_{CF} = 4.1$ Hz, $S\underline{C}H_2CH_2CF_2$). GC-MS *m/z* (%): 45 (47); 65 (100); 69 (85); 119 (30); 131 (25); 169 (21); 478 (6); 511 (8); 525 (9).

Mixture of **1g** *and* **2g** (85/15). Yield: 91%; white solid.

Compound **1g**. ^1H NMR δ (ppm): 6.89–7.32 (m, 5CH); 4.08 (t, $^3J_{HH} = 5.9$ Hz, OCH_2); 2.76 (m, $SC\underline{H}_2CH_2CF_2$ and CH_2S); 2.43 (m, $^3J_{HH} = 8.7$ Hz, $^3J_{HF} = 17.5$ Hz, $CH_2C\underline{H}_2CF_2$); 2.11 (m, CH_2).

Compound **2g**. ^1H NMR δ (ppm): 6.89–7.32 (m, 5CH); 4.07 (m, CH^A); 3.95 (m, CH^B); 2.90 (m, CH^XS); 2.76 (m, $SC\underline{H}_2CH_2CF_2$); 2.43 (tt, $^3J_{HH} = 8.7$ Hz, $^3J_{HF} = 17.5$ Hz, $C\underline{H}_2CF_2$); 1.40 (d, $J_{MX} = 7.1$ Hz, $CH_3{}^M$).

2.2.2. Radical addition of 2-perfluoroalkyl-ethanethiol onto vinyl acetate

A mixture of 1 equiv. of vinyl acetate, 1 equiv. of 2-perfluorooctyl-ethanethiol, 0.03 equiv. of 2,2′-azobisisobutyronitrile (AIBN) and cyclohexane was purged with nitrogen and refluxed for 4 h.

After cooling down to room temperature, the reaction mixture was dried over anhydrous Na_2SO_4 and solvent evaporated under vacuum.

Compound **1h**. Yield: 89%; colorless liquid; ^1H NMR δ (ppm): 4.25 (t, $^3J_{HH} = 6.4$ Hz, OCH_2); 2.79 (m, $SC\underline{H}_2CH_2CF_2$ and CH_2S); 2.39 (tt, $^3J_{HH} = 8.7$ Hz, $^3J_{HF} = 17.4$ Hz, $CH_2C\underline{H}_2CF_2$); 2.06 (s, CH_3). ^{13}C NMR δ (ppm): 170.6 (s, C=O), 105–125 (m, 7CF_2 and CF_3); 63.5 (s, OCH_2); 32.5 (t, $^2J_{CF} = 22.1$ Hz, $\underline{C}H_2CF_2$); 30.7 (s, $\underline{C}H_2S$); 23.0 (t, $^3J_{CF} = 4.3$ Hz, $S\underline{C}H_2CH_2CF_2$).

2.2.3. Esterification of 2-perfluoroalkyl-ethyl ω-hydroxy-alkyl sulfide

Method 1 (for **a**, **b**, **d**, **e**, **f**). Acrylic acid (1.25 equiv., 30% solution in toluene) was added to 1 equiv. of alcohol, 0.1 equiv. of *p*-toluenesulfonic acid (PTSA), 250 ppm of hydroquinone monomethyl ether (HQME) and toluene. This mixture was refluxed for 12 h under a water separator (Dean–Stark apparatus). When the theoretical amount of water was collected, the reaction was stopped and the solvent was removed by distillation under vacuum. The total product mixture was dissolved in chloroform and treated with NaOH 10% and washed with water until pH 7–8. After drying over anhydrous Na_2SO_4, solvent was distilled off in vacuum.

Mixture of **3a** *and* **5a** (90/10). Yield: 80%; orange liquid.

Compound **3a**. ^1H NMR δ (ppm): 6.41 (dd, $J_{AB} = 1.5$ Hz, $J_{AX} = 17.3$ Hz, CH^A); 6.11 (dd, $J_{AX} = 17.3$ Hz, $J_{BX} = 10.4$ Hz, CH^X); 5.83 (dd, $J_{BX} = 10.4$ Hz, $J_{AB} = 1.5$ Hz, CH^B); 4.27 (t, $^3J_{HH} = 6.2$ Hz, OCH_2); 2.73 (tt, ($^4J_{HF}$), $J_{HH} = 9.0$, $SC\underline{H}_2CH_2CF_2$); 2.65 (t, $^3J_{HH} = 7.3$ Hz, CH_2S); 2.37 (tt, $^3J_{HH} = 9.0$ Hz, $^3J_{HF} = 18.2$ Hz, $CH_2C\underline{H}_2CF_2$); 1.98 (tt, $^3J_{HH} = 6.2$ Hz, $^3J_{HH} = 7.3$ Hz, CH_2). ^{13}C NMR δ (ppm): 166.0 (s, $CH_2{=}CH{-}\underline{C}O$); 130.6 (s, $\underline{C}H_2{=}CH{-}CO$); 128.1 (s, $CH_2{=}\underline{C}H{-}CO$); 105–125 (m, 5$CF_2$ and CF_3); 62.8 (s, OCH_2); 32.0 (t, $^2J_{CF} = 22.1$ Hz, $\underline{C}H_2CF_2$); 28.7 (s, CH_2S); 28.6 (s, CH_2); 22.6 (t, $^3J_{CF} = 4.5$ Hz, $S\underline{C}H_2CH_2CF_2$). GC-MS *m/z* (%): 55 (100); 69 (16); 73 (100); 87 (30); 113 (22); 119 (5); 131 (6); 159 (5); 169 (2); 393 (6); 409 (4); 420 (40).

Compound **5a**. ^1H NMR δ (ppm): 6.41 (dd, $J_{AB} = 1.5$ Hz, $J_{AX} = 17.3$ Hz, CH^A); 6.11 (dd, $J_{AX} = 17.3$ Hz, $J_{BX} = 10.4$ Hz, CH^X); 5.83 (dd, $J_{BX} = 10.4$ Hz, $J_{AB} = 1.5$ Hz, CH^B); 5.15 (m, $OCH^{X'}$); 2.80 (m, $SC\underline{H}_2CH_2CF_2$); 2.80 (m, $CH^{A'}$); 2.50 (m, $CH^{B'}$); 2.37 (m, $C\underline{H}_2CF_2$); 1.36

(d, $J_{M'X'} = 7$ Hz, $CH_3^{M'}$). ^{13}C NMR δ (ppm): 166.0 (s, $CH_2{=}CH{-}\underline{C}O$); 130.6 (s, $\underline{C}H_2{=}CH{-}CO$); 128.1 (s, $CH_2{=}\underline{C}H{-}CO$); 105–125 (m, $5CF_2$ and CF_3); 70.1 (s, OCH); 37.5 (s, CH_2S); 32.0 (t, $^2J_{CF} = 22.1$ Hz, $\underline{C}H_2CF_2$); 22.6 (t, $^3J_{CF} = 4.5$ Hz, $S\underline{C}H_2CH_2CF_2$); 18.9 (s, CH_3). GC-MS *m/z* (%): 55 (100); 69 (8); 73 (31); 87 (8); 113 (4); 159 (2); 169 (3); 393 (8); 420 (43).

Compound **3b**. Yield: 83%; orange liquid; ^1H NMR δ (ppm): 6.39 (dd, $J_{AB} = 1.5$ Hz, $J_{AX} = 17.3$ Hz, CH^A); 6.11 (dd, $J_{AX} = 17.3$ Hz, $J_{BX} = 10.3$ Hz, CH^X); 5.80 (dd, $J_{BX} = 10.3$ Hz, $J_{AB} = 1.5$ Hz, CH^B); 4.14 (t, $^3J_{HH} = 6.7$ Hz, OCH_2); 2.73 (tt, ($^4J_{HF}$), $^3J_{HH} = 9.0$ Hz, $SC\underline{H}_2CH_2CF_2$); 2.55 (t, $^3J_{HH} = 7.3$ Hz, CH_2S); 2.37 (tt, $^3J_{HH} = 9.0$ Hz, $^3J_{HF} = 18.1$ Hz, $CH_2C\underline{H}_2CF_2$); 1.56 (m, $3CH_2$); 1.28 (m, $6CH_2$). ^{13}C NMR δ (ppm): 166.2 (s, $CH_2{=}CH{-}\underline{C}O$); 130.1 (s, $\underline{C}H_2{=}CH{-}CO$); 128.6 (s, $CH_2{=}\underline{C}H{-}CO$); 105–125 (m, $5CF_2$ and CF_3); 64.6 (s, OCH_2); 32.5 (s, CH_2S); 32.2 (t, $^2J_{CF} = 22.0$ Hz, $\underline{C}H_2CF_2$); 28.4–29.5 (m, $8CH_2$); 25.8 (s, CH_2); 22.5 (t, $^3J_{CF} = 4.0$ Hz, $S\underline{C}H_2CH_2CF_2$).

Mixture of **3d** *and* **5d** (90/10 + traces of **4d**). Yield: 83%; orange liquid.

Compound **3d**. ^1H NMR δ (ppm): 6.40 (dd, $J_{AB} = 1.2$ Hz, $J_{AX} = 17.3$ Hz, CH^A); 6.11 (dd, $J_{AX} = 17.3$ Hz, $J_{BX} = 10.4$ Hz, CH^X); 5.83 (dd, $J_{BX} = 10.4$ Hz, $J_{AB} = 1.2$ Hz, CH^B); 4.26 (t, $J = 6.1$ Hz, OCH_2); 2.73 (tt, ($^4J_{HF}$), $J_{HH} = 8.7$ Hz, $SC\underline{H}_2CH_2CF_2$); 2.65 (t, $^3J_{HH} = 7.2$ Hz, CH_2S); 2.40 (tt, $J_{HH} = 8.7$ Hz, $^3J_{HF} = 17.4$ Hz, $CH_2C\underline{H}_2CF_2$); 1.98 (tt, $J = 6.1$ Hz, $J = 7.2$ Hz, CH_2). ^{13}C NMR δ (ppm): 165.9 (s, $CH_2{=}CH{-}\underline{C}O$); 130.4 (s, $\underline{C}H_2{=}CH{-}CO$); 128.2 (s, $CH_2{=}\underline{C}H{-}CO$); 105–125 (m, $7CF_2$ and CF_3); 62.7 (s, OCH_2); 32.0 (t, $^2J_{CF} = 22.1$ Hz, $\underline{C}H_2CF_2$); 28.6 (s, CH_2S); 28.5 (s, CH_2); 22.5 (t, $^3J_{CF} = 4.2$ Hz, $S\underline{C}H_2CH_2CF_2$). GC-MS *m/z* (%): 41 (34); 45 (22); 47 (13); 55 (100); 69 (20); 73 (80); 89 (20); 113 (14); 119 (6); 131 (5); 169 (2); 219 (1); 478 (2); 493 (3); 507 (2); 520 (25); 537 (1).

Compound **5d**. ^1H NMR δ (ppm): 6.40 (dd, $J_{AB} = 1.5$ Hz, $J_{AX} = 17.4$ Hz, CH^A); 6.10 (dd, $J_{AX} = 17.4$ Hz, $J_{BX} = 10.4$ Hz, CH^X); 5.83 (dd, $J_{BX} = 10.4$ Hz, $J_{AB} = 1.5$ Hz, CH^B); 5.1 (m, $OCH^{X'}$); 2.80 (tt, ($^4J_{HF}$), $J_{HH} = 8.7$ Hz, $SC\underline{H}_2CH_2CF_2$); 2.74 (m, $CH^{A'}$); 2.47 (m, $CH^{B'}$); 2.38 (tt, $J_{HH} = 8.7$ Hz, $^3J_{HF} = 17.3$ Hz, $C\underline{H}_2CF_2$); 1.36 (d, $J_{M'X'} = 6.3$ Hz, $CH_3^{M'}$). ^{13}C NMR δ (ppm): 165.5 (s, $CH_2{=}CH{-}\underline{C}O$); 130.7 (s, $\underline{C}H_2{=}CH{-}CO$); 128.5 (s, $CH_2{=}\underline{C}H{-}CO$); 105–125 (m, $7CF_2$ and CF_3); 70.1 (s, OCH); 37.5 (s, CH_2S); 32.1 (t, $^2J_{CF} = 22.1$ Hz, $\underline{C}H_2CF_2$); 23.4 (t, $^3J_{CF} = 4.3$ Hz, $S\underline{C}H_2CH_2CF_2$); 18.9 (s, CH_3). GC-MS *m/z* (%): 41 (12); 45 (12); 55 (100); 69 (12); 73 (40); 113 (4); 119 (4); 131 (3); 169 (2); 219 (1); 478 (2); 493 (2); 520 (20).

Compound **4d**. ^1H NMR δ (ppm): 6.43 (dd, $J_{AB} = 1.5$ Hz, $J_{AX} = 17.6$ Hz, CH^A); 6.13 (dd, $J_{AX} = 17.6$ Hz, $J_{BX} = 10.4$ Hz, CH^X); 5.87 (dd, $J_{BX} = 10.4$ Hz, $J_{AB} = 1.5$ Hz, CH^B); 4.29 (dd, $J_{A'B'} = 11.1$ Hz, $J_{A'X'} = 6.1$ Hz, $CH^{A'}$); 4.14 (dd, $J_{A'B'} = 11.1$ Hz, $J_{B'X'} = 7.0$ Hz, $CH^{B'}$); 3.08 (ddt, $J_{A'X'} = 6.1$ Hz, $J_{B'X'} = 7.0$ Hz, $J_{M'X'} = 6.9$ Hz, $CH^{X'}S$); 2.85 (m, $SC\underline{H}_2CH_2CF_2$); 2.38 (tt, $J_{HH} = 8.8$ Hz, $^3J_{HF} = 17.6$ Hz, $C\underline{H}_2CF_2$); 1.32 (d, $J_{M'X'} = 6.9$ Hz, $CH_3^{M'}$). ^{13}C NMR δ (ppm): 165.7 (s, $CH_2{=}CH{-}\underline{C}O$); 130.8 (s, $\underline{C}H_2{=}CH{-}CO$); 128.0 (s, $CH_2{=}\underline{C}H{-}CO$); 105–125 (m, $7CF_2$ and CF_3); 68.3 (s, OCH_2); 38.9 (s, CHS); 32.4 (t, $^2J_{CF} = 21.9$ Hz, $\underline{C}H_2CF_2$); 21.5 (t, $^3J_{CF} = 4.2$ Hz, $S\underline{C}H_2CH_2CF_2$); 17.8 (s, CH_3). GC-MS *m/z* (%): 41 (30); 45 (15); 55 (100); 69 (12); 74 (80); 101 (8); 113 (5); 119 (4); 131 (4); 169 (2); 219 (1); 501 (6); 520 (10).

Mixture of **3e** *and* **4e** (95/05). Yield: 54%; yellow liquid.

Compound **3e**. ^1H NMR δ (ppm): 6.40 (dd, $J_{AB} = 1.2$ Hz, $J_{AX} = 17.2$ Hz, CH^A); 6.11 (dd, $J_{AX} = 17.2$ Hz, $J_{BX} = 10.4$ Hz, CH^X); 5.82 (dd, $J_{BX} = 10.4$ Hz, $J_{AB} = 1.2$ Hz, CH^B); 4.18 (t, $J = 6.1$ Hz, OCH_2); 2.73 (tt, ($^4J_{HF}$), $J_{HH} = 8.9$ Hz, $SC\underline{H}_2CH_2CF_2$); 2.60 (t, $J = 6.8$ Hz, CH_2S); 2.37 (tt, $^3J_{HH} = 8.9$ Hz, $^3J_{HF} = 17.2$ Hz, $CH_2C\underline{H}_2CF_2$); 1.76 (m, $2CH_2$). ^{13}C NMR δ (ppm): 166.0 (s, $CH_2{=}CH{-}\underline{C}O$); 130.2 (s, $\underline{C}H_2{=}CH{-}CO$); 128.4 (s, $CH_2{=}\underline{C}H{-}CO$); 105–125 (m, $7CF_2$ and CF_3); 63.7 (s, OCH_2); 32.0 (t, $^2J_{CF} = 22.1$ Hz, $\underline{C}H_2CF_2$); 31.6 (s, CH_2S); 27.6 (s, CH_2); 25.7 (s, CH_2); 22.4 (t, $^3J_{CF} = 3.8$ Hz, $S\underline{C}H_2CH_2CF_2$).

Compound **4e**. ^1H NMR δ (ppm): 6.40 (dd, $J_{AB} = 1.2$ Hz, $J_{AX} = 17.2$ Hz, CH^A); 6.11 (dd, $J_{AX} = 17.2$ Hz, $J_{BX} = 10.4$ Hz, CH^X); 5.82 (dd, $J_{BX} = 10.4$ Hz, $J_{AB} = 1.2$ Hz, CH^B); 4.18 (m, OCH_2); 2.90 (m, CHS); 2.73 (m, $SC\underline{H}_2CH_2CF_2$); 2.37 (m, $C\underline{H}_2CF_2$); 1.76 (m, CH_2); 1.37 (d, $J = 4.4$ Hz, CH_3).

Compound **3f**. Yield: 82%; white solid; mp 37°C; ^1H NMR δ (ppm): 6.40 (dd, $J_{AB} = 1.6$ Hz, $J_{AX} = 17.4$ Hz, CH^A); 6.12 (dd, $J_{AX} = 17.4$ Hz, $J_{BX} = 10.3$ Hz, CH^X); 5.81 (dd, $J_{BX} = 10.3$ Hz, $J_{AB} = 1.6$ Hz, CH^B); 4.15 (t, $^3J_{HH} = 6.7$ Hz, OCH_2); 2.73 (tt, ($^4J_{HF}$), $J_{HH} = 8.6$ Hz, $SC\underline{H}_2CH_2CF_2$); 2.55 (t, $^3J_{HH} = 7.3$ Hz, CH_2S); 2.37 (tt, $J_{HH} = 8.6$ Hz, $^3J_{HF} = 17.3$ Hz, $CH_2C\underline{H}_2CF_2$); 1.60 (m, $3CH_2$); 1.28 (m, $6CH_2$). ^{13}C NMR δ (ppm): 166.3 (s, $CH_2{=}CH{-}\underline{C}O$); 130.3 (s, $\underline{C}H_2{=}CH{-}CO$); 128.7 (s, $CH_2{=}\underline{C}H{-}CO$); 105–125 (m, $7CF_2$ and CF_3); 64.7 (s, OCH_2); 32.3 (s, CH_2S); 32.2 (t, $^2J_{CF} = 22.0$ Hz, $\underline{C}H_2CF_2$); 28.2–29.4 (m, $8CH_2$); 25.8 (s, CH_2); 22.6 (t, $^3J_{CF} = 4.4$ Hz, $S\underline{C}H_2CH_2CF_2$). GC-MS *m/z* (%): 55 (100); 69 (31); 81 (16); 119 (2); 131 (2); 152 (5); 169 (2); 185 (59); 225 (2); 239 (3); 257 (26); 409 (1); 455 (1); 493 (5); 507 (1); 535 (1).

Method 2 (for **a**, **b**, **d**, **f**). In a three necked flask fitted with a stirrer and a thermometer were placed under nitrogen 1.25 equiv. of acryloyl chloride, 250 ppm of HQME and anhydrous dichloromethane (freshly distilled over $CaCl_2$, 10 ml g^{-1} of acryloyl chloride) or toluene. The flask was surrounded by a ice bath cold enough to lower the temperature of the mixture close to 0°C. A solution of 1 equiv. of 2-perfluoroalkyl-ethyl ω-hydroxy-alkyl sulfide and 1.5 equiv. of triethylamine (freshly distilled over CaH_2) in anhydrous dichloromethane (freshly distilled over $CaCl_2$) or toluene was added cautiously, under stirring. After refluxing for 12 h, the resulting mixture was filtered and the organic phase treated with $NaHCO_3$ 10%, NaOH 10% and washed one time with water to obtain pH > 10. Then the solution was dried over anhydrous Na_2SO_4 and solvent and triethylamine were evaporated under vacuum.

Mixture of **3a** *and* **4a** (90/10). Yield: 80%, yellow liquid; bp 40°C/10^{-1} mbar.

Compound **3a**. NMR and GC-MS characterizations as above.

Compound **4a**. ^{1}H NMR δ (ppm): 6.41 (dd, $J_{AB} = 1.5$ Hz, $J_{AX} = 17.6$ Hz, CH^A); 6.11 (dd, $J_{AX} = 17.6$ Hz, $J_{BX} = 10.4$ Hz, CH^X); 5.83 (dd, $J_{BX} = 10.4$ Hz, $J_{AB} = 1.5$ Hz, CH^B); 4.20 (m, $CH^{A'}$); 4.10 (m, $CH^{B'}$); 3.02 (m, $CH^{X'}S$); 2.70 (m, $S\underline{CH_2}CH_2CF_2$); 2.40 (m, $\underline{CH_2}CF_2$); 1.20 (d, $J_{M'X'} = 6.5$ Hz, $CH_3^{M'}$).

Compound **3b**. Yield: 85%; orange liquid; NMR characterization as above.

2.2.4. Preparation of 2-perfluoroalkyl-ethyl-ω-hydroxy-alkyl sulfide

Method 3 (for **1a**, **1c**, **1d**). To a mixture of 1 equiv. of 2-perfluoroalkyl-ethanethiol and 1.1 equiv. of K_2CO_3 in ethanol/water (90/10, v/v), was added a solution of 1.1 equiv. of ω-hydroxy-alkyl halide in absolute ethanol at 75°C under nitrogen. Refluxing was continued for 6 h. After cooling to room temperature, the reaction mixture was poured into a large amount of dilute Na_2CO_3 aqueous solution and the precipitate was dissolved in chloroform. The chloroform layer was washed neutral with water, dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum.

Compound **1a**. Yield: 98%; yellow liquid; NMR and GC-MS characterizations as above.

Compound **1c**. Yield: 82%; yellow solid; mp 73°C; ^{1}H NMR δ (ppm): 3.79 (t, $^3J_{HH} = 5.8$ Hz, OCH_2); 2.79 (m, CH_2S & $S\underline{CH_2}CH_2CF_2$); 2.39 (tt, $^3J_{HH} = 8.8$ Hz, $^3J_{HF} = 17.6$ Hz, $CH_2\underline{CH_2}CF_2$); 1.99 (broad s, shifted with dilution, OH). ^{13}C NMR δ (ppm): 105–125 (m, $7CF_2$ and CF_3); 60.7 (s, OCH_2); 35.4 (s, CH_2S); 32.2 (t, $^2J_{CF} = 22.0$ Hz, $\underline{C}H_2CF_2$); 22.6 (t, $^3J_{CF} = 4.5$ Hz, $S\underline{C}H_2CH_2CF_2$). GC-MS *m/z* (%): 45 (100); 69 (30); 77 (20); 91 (9); 119 (7); 131 (6); 169 (2); 441 (1); 493 (8); 524 (3).

Compound **1d**. Yield: 91%; yellow solid; NMR and GC-MS characterizations as above.

Method 4 (for **6d**). A mixture of 1 equiv. of 1-iodo-2-perfluorooctyl-ethane, 1.2 equiv. of NaOH, 1.1 equiv. of 1-mercapto-propan-2-ol and ethanol/water (90/10, v/v) was refluxed under nitrogen for 6 h. The cooled mixture was diluted with a large amount of diluted Na_2CO_3 aqueous solution and the non-aqueous phase was taken up in chloroform, washed to pH 7–8 and dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum yielding a yellow solid.

Compound **6d**. Yield: 83%; yellow solid; ^{1}H NMR δ (ppm): 3.90 (ddt, $J_{BX} = 8.4$ Hz, $J_{AX} = 3.8$ Hz, $J_{MX} = 6.1$ Hz, OCH^X); 2.78 (tt, ($^4J_{HF}$), $J_{HH} = 8.8$ Hz, $S\underline{CH_2}CH_2CF_2$); 2.74 (dd, $J_{AB} = 13.6$ Hz, $J_{AX} = 3.8$ Hz, CH^A); 2.52 (dd, $J_{AB} = 13.6$ Hz, $J_{BX} = 8.4$ Hz, CH^B); 2.40 (tt, $^3J_{HH} = 8.8$ Hz, $^3J_{HF} = 17.5$ Hz, $\underline{CH_2}CF_2$); 1.26 (d, $J_{MX} = 6.1$ Hz, CH_3^M). ^{13}C NMR δ (ppm): 105–125 (m, $7CF_2$ and CF_3); 66.0 (s, OCH); 41.6 (s, CH_2S); 32.2 (t, $^2J_{CF} = 22.1$ Hz, $\underline{C}H_2CF_2$); 23.0 (t, $^3J_{CF} = 4.4$ Hz, $S\underline{C}H_2CH_2CF_2$); 22.0 (s, CH_3). GC-MS *m/z* (%): 45 (100); 47 (46); 59 (28); 61 (52); 69 (20); 119 (8); 131 (7); 169 (3); 475 (1); 494 (12); 523 (2).

Method 5 (for **2d**). The acid **7d** was prepared by reacting 1-iodo-2-perfluorooctyl-ethane to thiolactic acid, according to method 4 (except for the use of 2.4 equiv. of NaOH and the final reaction mixture was poured into a large amount of HCl 1N). A mixture of 1.25 equiv. of $LiAlH_4$ and anhydrous tetrahydrofuran (freshly distilled over Na) was purged with nitrogen. At room temperature, a solution of 1 equiv. of **7d** in tetrahydrofuran (freshly distilled over Na) was cautiously added for 1 h. Then, the reaction was carried out under reflux for additional 12 h. The resulting mixture was cooled to 0°C and a saturated solution of NH_4Cl was slowly added dropwise with vigorous stirring. This mixture was filtered and the precipitate was abundantly washed with chloroform. The organic layer was separated and dried over anhydrous Na_2SO_4. Solvents were distilled off under vacuum.

Compound **7d**. Yield: 75%; brown solid; ^{1}H NMR δ (ppm): 3.45 (q, $J = 7.1$ Hz, CH); 2.91 (m, $S\underline{CH_2}CH_2CF_2$); 2.43 (tt, $^3J_{HH} = 8.7$ Hz, $^3J_{HF} = 17.5$ Hz, $\underline{CH_2}CF_2$); 1.48 (d, $^3J_{HH} = 7.1$ Hz, CH_3). ^{13}C NMR δ (ppm): 179.5 (s, COOH); 105–125 (m, $7CF_2$ and CF_3); 41.1 (s, CHS); 31.8 (t, $^2J_{CF} = 22.2$ Hz, $\underline{C}H_2CF_2$); 22.4 (t, $^3J_{CF} = 4.2$ Hz, $S\underline{C}H_2CH_2CF_2$); 16.3 (s, CH_3).

Compound **2d**. Yield: 82%; brown solid; NMR and GC-MS characterizations as above.

2.2.5. Preparation of prop-2-en-1-oïc acid 2-perfluoroalkyl-ethyl thioalkyl ester

Compounds **3a** and **3d** were prepared according to method 1 (Fischer esterification) while compounds **4d** and **5d** according to method 2 (acryloyl chloride route).

Compound **3a**. Yield: 80%; yellow liquid; NMR and GC-MS characterizations as above.

Compound **3d**. Yield: 78%; yellow liquid; NMR and GC-MS characterizations as above.

Compound **4d**. Yield: 78%; brown liquid; NMR and GC-MS characterizations as above.

Compound **5d**. Yield: 83%; orange liquid; NMR and GC-MS characterizations as above.

3. Results and discussion

The synthesis of 2-(perfluoroalkyl)-ethyl alkyl thioethers is usually performed in a two step-procedure. The first one concerns the preparation of 2-(perfluoroalkyl)-ethyl ω-hydroxy-alkyl thioether A followed by its esterification leading to the corresponding acrylic monomer.

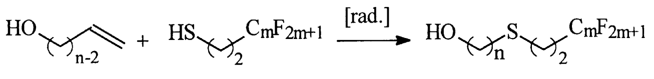
A

Obtaining the alcohol by nucleophilic substitution of the halogen atom X by the alkali salt of an ω-hydroxy-alkylthiolate is a well-known reaction [51,52].

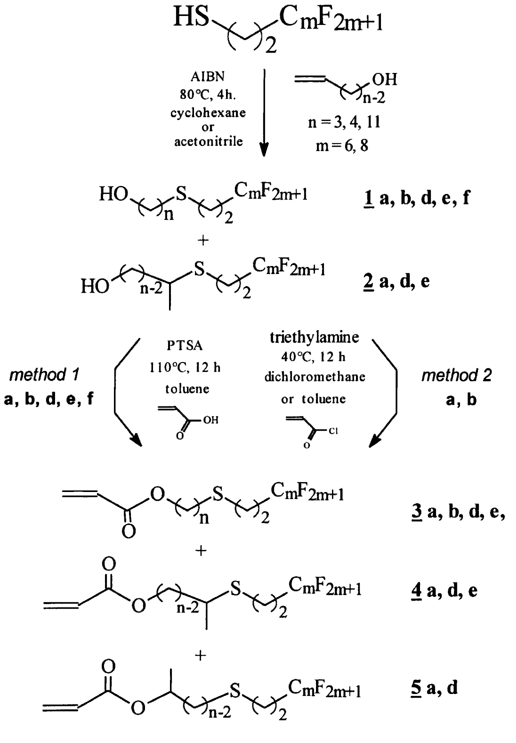
However, this process does not enable one to easily achieve a wide range of monomers. The size of the *n* methylene spacer between the hydroxy group and the thioether bridge of the resulting monomer depends on the structure of the involved ω-mercapto alcohol; but the diversity of these commercially available reactants is poor and their synthesis is not easy [53].

A previous article reports the radical addition of an ω-mercaptoalcohol to the double bond of an allylic monomer bearing a perfluorinated end-group [48] but this synthesis has the same limitation as that above.

Our present study relies on the radical addition of two different 2-perfluoroalkyl-ethanethiols ($m = 6$ or 8) onto various ω-unsaturated alcohols containing 3, 4 or 11 carbon atoms, as follows:

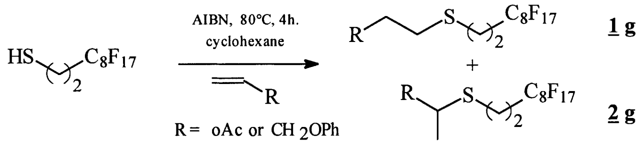


Thus, a wide range of original ω-hydroxy monomers bearing a thioether bridge and a perfluorinated end-group have been synthesized, as precursors of novel fluorinated acrylates (Scheme 1). These various intermediates and products have been well-identified as the eventual by-products and are described below (Scheme 2).



m =6		m =8			
n = 3	n = 11	n = 2	n = 3	n = 4	n = 11
a	b	c	d	e	f

Scheme 1.



	R	1	2
g	CH2OPh	85 %	15 %
h	oAc	100 %	-

Scheme 2.

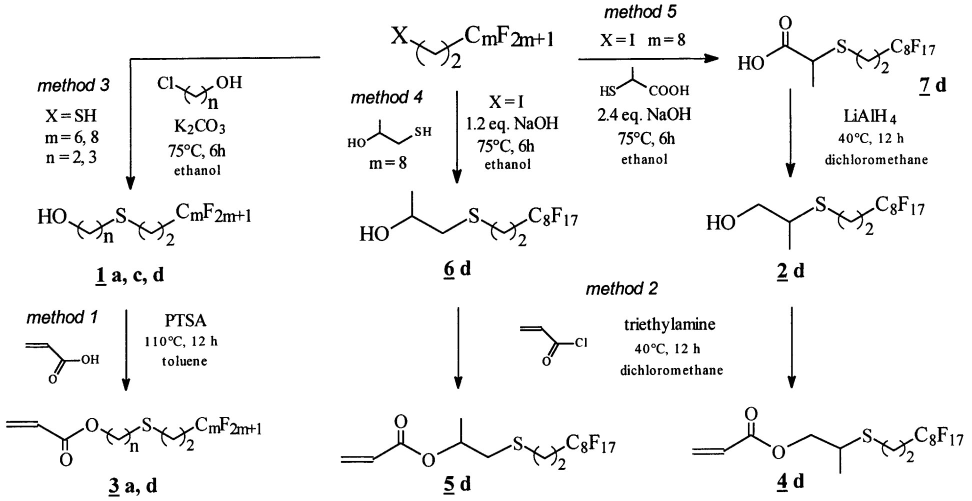
3.1. Radical addition of 2-perfluoroalkyl-ethanethiol to an ω-unsaturated alcohol

Usually, in the course of the radical initiation (that occurs either thermally or photochemically) the thiyl radical generated from the homolytic cleavage of the S–H bond of 2-perfluoroalkyl-ethanethiol can add onto the double bond of the ω-unsaturated alcohol [54]. For the present reaction, AIBN was chosen as the thermal initiator, at 80°C, in solution in cyclohexane or acetonitrile [55,56]. Such initiation enabled us to obtain a wide variety of 2-perfluoroalkyl-ethyl-ω-hydroxy-alkyl thioethers in good yields (65–90%, after purification) (Scheme 3). However, in certain cases, the presence of isomers was noted as a consequence of both possible attack sites of the thiyl radical toward the double bond of the ω-unsaturated alcohol (Scheme 4).

The presence of branched isomer **2** was detected by ^{1}H NMR spectroscopy: the doublet centered at 1.3 ppm is characteristic of the methyl group and can be neatly distinguished in the case of reactions involving allyl alcohol and but-3-en-1-ol. The assignment of that signal to the branched isomer was confirmed by the NMR characterization of pure **2d** isomer synthesized from another process (Scheme 3). Indeed, alcohols **1a**, **1d** and **2d** were prepared by ionic reactions which form desired isomers selectively. In the case of alcohol **2d**, 2-mercapto-propan-1-ol is not a commercially available reactant; hence, nucleophilic substitution of the iodine atom of 1-iodo-2-perfluorooctyl-ethane by sodium mercaptolactate was achieved. Acid **7d** thus prepared was then reduced into alcohol **2d** in the presence of lithium aluminum hydride.

Interestingly, we noted that the longer the ω-unsaturated alcohols, the lower the amount of isomer **2**. This isomer was not produced when 10-undecen-1-ol was used, whatever the 2-perfluoroalkyl-ethanethiol ($m = 6$ or 8). Such an observation can be interpreted by the study of the relative stability of the different intermediate radicals. As shown in Scheme 4, the double bond exhibits two possible attack sites (a and b) for the thiyl radical, leading to both intermediate radicals.

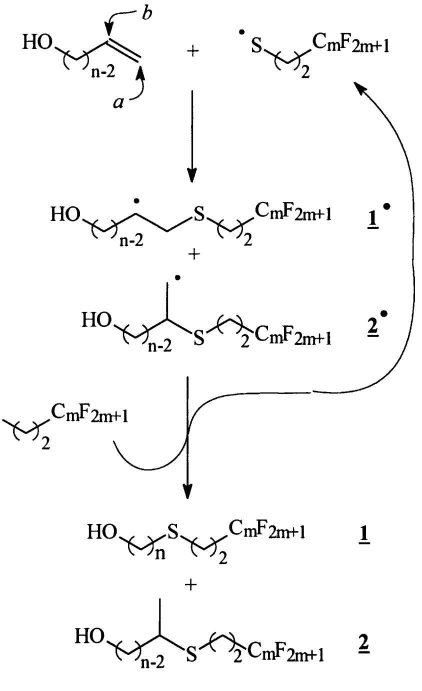
Intrinsically, secondary radical **1**$^{\bullet}$ is more stable than primary **2**$^{\bullet}$, as a secondary carbocation (R_2CH^+) is more



Scheme 3.

stable than a primary one (RCH_2^+) [57,58]. This explains the major amount of isomer 1 (anti Markovnikov product) in the resulting mixture of radical addition of a mercaptan onto an ω-unsaturated alcohol.

However, the hydroxyl group may have a certain influence on the stability of these radicals. The more the radical undergoes the electron-withdrawing effect of an adjacent group, the more destabilized the radical. Taft [59] showed that the inductive effect of an electron-withdrawing group decreases 2.7 times for each intercalated methylenic unit; thus in the case of an alcohol containing a small number of carbon atoms ($n = 3$ or 4), the destabilization of $1^{\bullet}$ radical by the close presence of the hydroxyl function is greater than in the case of $2^{\bullet}$ radical containing a further methylenic group. This destabilization of $1^{\bullet}$ radical allows $2^{\bullet}$ radical to be formed and to lead to a non-negligible amount of branched isomer $2^{\bullet}$. As for longer and longer ω-unsaturated alcohols, the methylene number is thus increased and the difference between $1^{\bullet}$ and $2^{\bullet}$ radicals decreases. This explains why the amount of $2^{\bullet}$ isomer decreases when the length of the unsaturated alcohol increases.

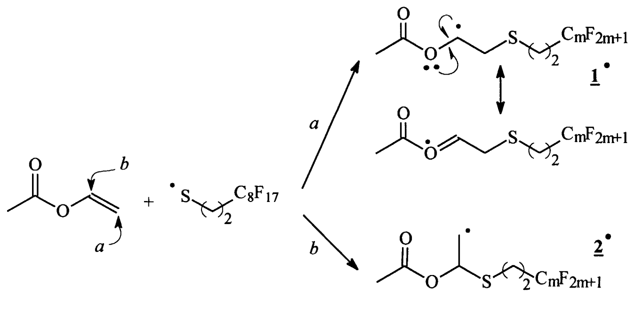


n	1	2
3	90 %	10 %
4	95 %	5%
11	100%	-

Scheme 4.

We have verified this hypothesis by carrying out the radical addition of 2-perfluorooctyl-ethanethiol to the double bond of allyl phenyl ether under the same conditions as those above (Scheme 2); only ^{1}H NMR spectra data appear in this present article. The intermediate radical of $1^{\bullet}$ type is thus in the β-position to a phenoxy function whose electron-withdrawing effect is higher than that of a hydroxyl function; the destabilization is stronger and isomer 2 is obtained in higher amount (15%). Besides, Brace [60] has previously investigated the radical addition of 2-perfluoroalkyl-ethanethiols to alkene and has reported that the reaction between 2-perfluorohexyl-ethanethiol and hexene led to 2-perfluorohexyl-ethyl hexyl sulfide with a small amount of 2-perfluorohexyl-ethyl-1-methyl-pentyl sulfide (2.29%). This shows that the use of an olefin without an electron-withdrawing group close to the double bond leads mainly to the 1 type isomer.

Nevertheless, by carrying out the radical addition of 2-perfluorooctyl-ethanethiol onto the double bond of vinyl acetate (Scheme 2), we have shown that the amount of isomer 2 was negligible although the electron-withdrawing effect group was directly linked to the double bond, as previously described by Brace [60]. This can be explained



Scheme 5.

by the stabilization of the intermediate radical of **1**$^{\bullet}$ as depicted in Scheme 5.

Further, whatever the ω-unsaturated alcohol used, a thio-2-(perfluoroalkyl)-ethyl group in a β-position in the radical influences **1**$^{\bullet}$ and **2**$^{\bullet}$ intermediates in the same way. The size of the perfluorinated chain does not influence the proportion of both isomers.

3.2. *Esterification of 2-(perfluoroalkyl)-ethyl ω-hydroxy-alkyl sulfide*

The second step of the synthesis of acrylic monomers relies on the esterification of alcohols (pure or as an isomer mixture). This was performed by two methods (Scheme 1): either the Fisher esterification of acrylic acid (method 1) or acylation in the presence of acryloyl chloride (method 2).

The esterification reaction according to the latter method allowed us to obtain desired monomer **3b** ($n = 11$) selectively or a **3a**/**4a** isomer mixture ($n = 3$) in high yields (85 and 80%, respectively). In the case of the isomer mixture, the amounts of both acrylic esters obtained were similar to those of the mixture of hydroxylated isomers used (i.e. 90% of linear compound and 10% of branched one) (Table 1).

The Fisher esterification (method 1) led to surprising results that varied according to the nature of the alcohols (Table 2). The yields remained constant (ca. 80–85% after purification) but according to the alcohols used (pure or as an isomer mixture), the nature of the compounds obtained was different.

Although esterification reactions of **1b** and **1f** alcohols and **1e**/**2e** mixture led to desired acrylic monomers, pure **3b** and **3f** acrylates and **3e**/**4e** isomer mixture, respectively, in expected amounts (95 and 5% of linear and branched compounds, respectively), esterification of **1a**/**2a** and **1d**/**2d** isomer mixtures led to more surprising and unexpected linear (**3**) and branched (**5**) isomers (Scheme 1).

In the case of **1d**/**2d** mixture, a careful study of the ^{13}C NMR spectrum of the acrylic monomer mixture compared to those of pure compounds **3d**, **4d** and **5d** enabled us to characterize without ambiguity the nature of the obtained mixture; the relative amounts of isomers were assessed by ^{1}H NMR spectroscopy.

To understand the formation of isomer **5** instead of that of expected isomer **4** (obtained in traces), we found it worth while to carry out the esterification reaction under the same conditions as those used for alcohol **1c** containing two methylene groups located between the hydroxyl function and the sulfur atom. Indeed, that reaction led to a mixture still containing a non-negligible amount of the starting alcohol and various by-products. Rondestvedt and Thayer [51] also noted such unexpected low yields (19%) in a similar study and reported that an uncontrolled polymerization occurred. In the same way, Cerf et al. [61] also observed a decrease in the yield of the esterification reaction, in an acidic medium, of several non-fluorinated-β-hydroxyl sulfides. Furthermore, Schies et al. [62] investigated the behavior, in acidic medium, of certain functionalized sulfur-containing compounds possessing two methylenic groups between the sulfur atom and a nucleophobic group. The formation of a thiiranium ion was assumed. This can be explained by the high nucleophilicity and polarizability of the sulfur atom and, in the case of alcohols, by the ability of protonation of the hydroxyl function, leading to an elimination of intramolecular water (Scheme 6) [62].

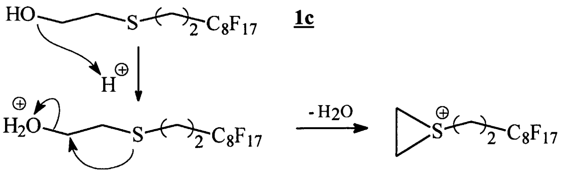
The formation of by-products can also be explained by the high electropositivity of the sulfur atom of the thiiranium

Table 1
Adducts from the reaction of alcohols with acryloyl chloride (method 2)

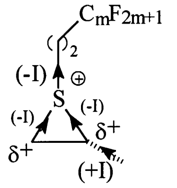
n	*m*	Alcohols		Esters	
3	6	**1a**, 90%	**2a**, 10%	**3a**, 90%	**4a**, 10%
11	6	**1b**	–	**1b**	–

Table 2
Adducts from the reaction of alcohols with acrylic acid (method 1)

n	*m*	Alcohols		Esters		
3	6	**1a**, 90%	**2a**, 10%	**3a**, 90%	–	**5a**, 10%
11	6	**1b**	–	**3b**	–	–
3	8	**1d**, 90%	**2d**, 10%	**3d**, 90%	**4d**, traces	**5d**, 10%
4	8	**1e**, 95%	**2e**, 5%	**3e**, 95%	**4e**, 5%	–
11	8	**1f**	–	**3f**	–	–



Scheme 6.



Scheme 7.

ion, generating two possible attack sites by nucleophilic species present in the medium (i.e. sulfide, acid, alcohol) [63] on both carbon atoms adjacent to the thiirane ring.

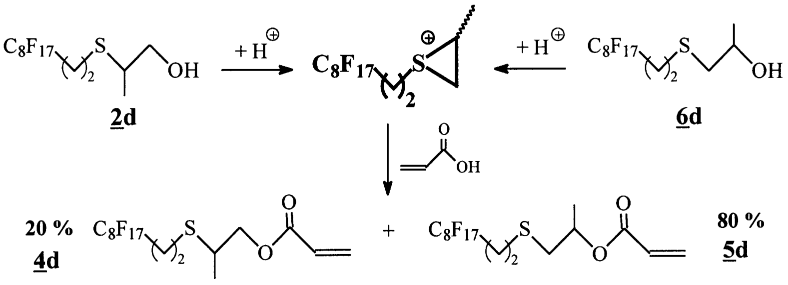
The synthesis of the corresponding acrylic monomer can thus be performed in neutral (or alkaline) medium, only, to avoid the formation of the thiiranium ion. Hence, esterification reaction of alcohol **1c** was achieved by acryloyl chloride in the presence of triethylamine leading to pure monomer **3c** in 80% yield. This clearly shows the influence of thiiranium ion on the esterification of a β-hydroxylated sulfide. Furthermore, esterification by acrylic acid of alcohol **1d** gave compound **3d** specifically, in 78% yield after purification. In the case of the isomers mixture, alcohol **2d** led mainly to acrylate **5d**. Similarly, for the esterification of the **1e**/**2e** isomer mixture, branched isomer **2e** yielded expected ester **4e**: this clearly shows that the branched structure of alcohol **2d** does not influence the rearrangement allowing formation of the product **5d**. Next, acylation reaction in the presence of acryloyl chloride of alcohol **2d** enabled us to obtain expected branched monomer **4d** selectively, in 78% yield. This reaction was carried out in an alkali medium and shows that isomer **5d** is formed when the reaction occurs in acid medium.

It can also be expected that in the course of the esterification of **1d**/**2d** mixture from method 1, branched isomer **2d**, because of both its β-hydroxyl-containing sulfide structure and the experimental conditions in acidic media, led to a thiiranium ion that produced ester **5d** by reacting with acrylic acid. The traces of product **4d** of direct esterification can be explained by the presence of both sites of nucleophilic attack (Scheme 7) on the thiiranium ion. The main attack of acrylic acid onto the more substituted carbon atom of the sulfur-containing ring confirms both Mueller's [64] and, Baig and Owen's [65] results for the ring opening of the asymmetric thiiranium ring by a chloride ion or by acetate salts, respectively. Comparing these studies, we suggest the following structure of the intermediate that may explain the major formation of **5d** above about that of **4d** in the Fisher esterification of alcohols **2d** and **5d** (Scheme 7). A $C_mF_{2m+1}C_2H_4$-group linked to the sulfur atom has a slightly electron-withdrawing behavior. This latter with a weaker electronic effect, can attract the electrons of both carbon atoms of the ring. The more branched carbon atom is stabilized by the donor inductive effect of the methyl group. The charge of this carbon atom is thus more stabilized and consequently this atom is the major site of attack. That hypothesis has been confirmed by esterifying alcohol **6d** by acrylic acid (method 1) that led to the same mixture (**4d**/**5d**, 80/20) as that obtained when the esterification was carried out with alcohol **2d** (Scheme 8).

The study, dealing with compounds containing a perfluorooctyl end-group can also be performed for those bearing a perfluorohexyl group. We have also noted the formation of ester **5a** in the course of the esterification of the **1a**/**2a** isomer mixture.

4. Conclusion

This work reports ways of preparation of various 2-(perfluoroalkyl)-ethyl alkyl thioether acrylic monomers from alcohols containing a reactive double bond. The wide range of commercially available unsaturated alcohols enabled us to obtain numerous monomers. However, several issues inherent to the different ways of synthesis, may lead to an isomer mixture of variable composition, according to the nature of the alcohol. It has also been possible to investigate the influence of the formation of the thiiranium ion when the esterification of β-sulfur-containing alcohol occurred in acidic medium.



Scheme 8.

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