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Synthesis of fluoro-substituted monomers bearing a functionalised lateral chain
Part 2. Preparation of sulfoxides and sulfones containing monomers

B. Pées[a], J.M. Paul[b], N. Oget[c], M. Sindt[c,*], J.L. Mieloszynski[c]

[a]*Atofina, Centre d'étude de Recherche et de Développement, 27470 Serquigny, France*
[b]*Atofina, Centre de Recherches et Développement de l'Est, B.P. 61005, 57501 Saint-Avold Cedex, France*
[c]*Laboratoire de Chimie et Applications (LCA), Groupe Synthèse Organique EA-3471, Université de Metz, Ile du Saulcy, 57012 Metz Cedex 01, France*

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Abstract

The oxidation of ω-(ω-perfluoroalkylalkyl-sulfanyl)-alkyl acrylates to corresponding sulfoxides and sulfones is described in this paper.

Keywords: Fluoroalkyl; Acrylic monomers; Sulfoxides; Sulfones

1. Introduction

The synthesis of sulfoxide or sulfone compounds is of interest because of a wide range of applications—medical and industrial. Industrially, it is of great interest to associate the properties of these functions with others. We have therefore synthesised a new series of fluorinated acrylate-containing sulfoxide and sulfone functions as a spacer link between the fluorinated chain and the acrylic group (Fig. 1).

It is well known that the homopolymers and copolymers substituted with a fluorinated function are used in textile treatment to endow them with oil and water repellency [1–4]; these characteristics are enhanced by the introduction of SO or SO_2 functions.

2. Results and discussion

Initially, we considered the synthesis of these compounds in two steps: (1) oxidation of sulfide alcohols to sulfoxides or sulfones, followed by (2) acid-catalysed esterification by acrylic acid. For example, oxidation of alcohol **4** with 4-chloro-peroxybenzoic acid (mCPBA) [5] gave the corresponding sulfone **5** (Fig. 2).

Nevertheless, the product is still difficult to obtain because of the formation of a very stable emulsion during the work-up. Moreover, the product is soluble only in acetone, and insoluble in chloroform, dichloromethane, cyclohexane or toluene. Thus, this alcohol cannot be esterified by traditional methods because of its non-miscibility in the solvent used for the reaction.

Therefore, it was decided to develop another sequence involving the oxidation of different ω-(ω-perfluoroalkylalkyl-sulfanyl)-alkyl acrylates. The corresponding sulfoxides or sulfones are then obtained without any purification before their use for polymer synthesis. The procedure used must be selective enough to isolate sulfoxide not contaminated by sulfone and vice versa, and to avoid the oxidation of the acrylic double bond.

2.1. Oxidation of sulfides to sulfoxides: synthesis of ω-(ω-perfluoroalkyl-sulfinyl)-alkyl acrylates

Many reactions in which sulfides are oxidised selectively to sulfoxides [6] are reported in the literature. They are divided into two broad classes depending on whether the oxidant is acting as an electrophile or a nucleophile: those selected to synthesise sulfoxide or sulfone with no

* Corresponding author. Tel.: +33-3-87-31-52-65; fax: +33-3-87-54-73-13.
E-mail address: sindt@sciences.univ-metz.fr (M. Sindt).

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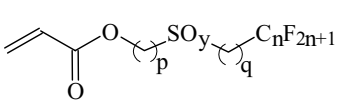


Fig. 1. ω-(ω-Perfluoroalkylalkyl-sulfinyl)-alkyl acrylates ($y = 1$) and ω-(ω-perfluoroalkylalkyl-sulfonyl)-alkyl acrylates ($y = 2$). (∗) means the value $n = 6-8$ corresponds to a mixture (industrial) which is high in perfluorohexyl radical: the average number of carbon's atoms is 7.5.

by-products [7–9] and the others for which the proportions of each reagent [10,11] must be adjusted accurately. We focused our attention on two reagents: cerium ammonium nitrate [12,13] and sodium periodate [14].

Ali et al. [12] have recently described the oxidation of various sulfides by cerium(IV) ammonium nitrate (CAN) with very good yields (80–100%) and a good selectivity. The very mild operating conditions (CH_2Cl_2, Rt, 0.25–2 h) would have allowed oxidation of perfluoroalkylalkyl-sulfanyl acrylates without disturbing the acrylic double bond (oxidation, polymerisation . . .). However, the oxidation of sulfides under these conditions did not enable us to obtain the corresponding sulfoxides despite a 24 h reaction time.

The poor reactivity of CAN towards fluorinated sulfides can be explained by its poor solubility in the reaction medium. Indeed, in the first step CAN is impregnated onto silica gel, then the mixture is suspended in dichloromethane and the reaction must take place on the silica gel surface. However, the fluorinated compounds do not absorb on the silica gel where CAN is supported.

With sodium periodate [14], the oxidation of compounds **1c** and **1f** was carried out successfully. Methanol allows the solubilisation of fluorinated sulfide and sodium periodate (diluted in a minimum of water). Then, with a temperature maintained strictly lower than 0 °C for 12 h, this reagent allows the synthesis of ω-(2-perfluorooctylethyl-sulfinyl)-alkyl acrylate; all of the thioether is consumed and only sulfoxide is obtained (Fig. 3).

2.2. Oxidation of sulfides to sulfones: synthesis of ω-(ω-perfluoroalkylalkyl-sulfonyl)-alkyl acrylates

In the case of sulfone, the use of an excess of oxidant often leads to the desired sulfone without sulfoxide traces. However, in the case of ω-(ω-perfluorooctylalkyl-sulfanyl)-alkyl acrylates, the oxidant must be sufficiently selective and used in such an amount as to prevent a reaction with the acrylic double bond.

The first reagent tested was Oxone® persulfate. Indeed, many reactions in which non-fluorinated sulfides are oxidised selectively to sulfones [8] are reported in the literature. However, when **1c** is treated with Oxone®, the product obtained is a mixture of sulfoxide **2c** (70%) and sulfone **3c** (30%), despite a greater reaction time (24 h) compared with those described in the literature (1–4 h). The reaction occurs in the presence of alumina as a catalyst which permits the reaction between an aqueous soluble product (Oxone®) and an insoluble one (sulfide). In our case, as mentioned for CAN, the poor reactivity of fluorinated sulfides towards Oxone® can be explained by its poor solubility in the reaction medium. However, the use of Oxone® tetra-*n*-butylammonium [15] leads to the same results (sulfoxide: 70% and sulfone: 30%), in spite of an anhydrous and homogeneous medium.

Another oxidising reagent 4-chloro-peroxybenzoic acid which is commonly used was tested. mCPBA can oxidise sulfides to sulfones when its proportion is 2 eq. compared with sulfide [16]. Thus, mCPBA provides various ω-(ω-perfluoroalkylalkyl-sulfonyl)-alkyl acrylates without reacting with the double bond present (Fig. 4).

The following mechanism involving β-elimination from 2-(2-perfluorooctylethyl-sulfonyl)-ethyl **3a** acrylate is proposed (Fig. 5).

In order to check this assumption, the pure sulfone **3a** was stirred in EtOH at 50 °C for 12 h; 10% of 2-perfluorooctyl-ethyl vinyl sulfone was formed. This result clearly suggests elimination from the synthesised sulfone. So ethanol

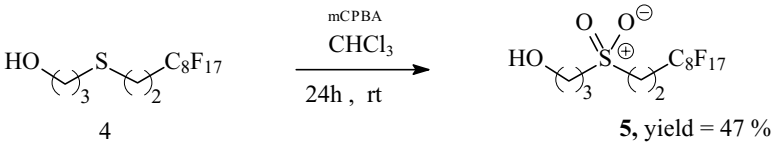


Fig. 2. Oxidation of 2-perfluorooctyl-ethyl 3-hydroxy-propyl sulfide.

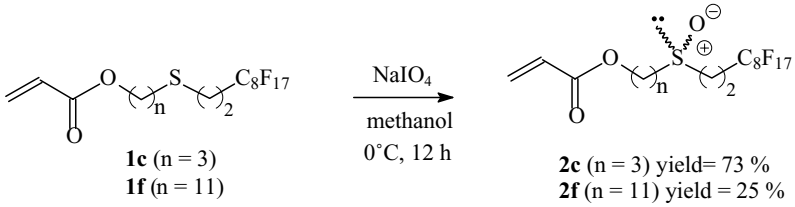
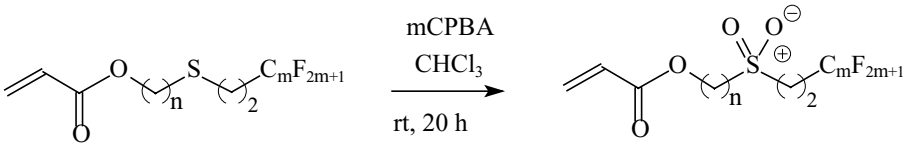


Fig. 3. Oxidation of ω-(ω-perfluorooctylalkyl-sulfanyl)-alkyl acrylates with sodium periodate.



Sample	n	m
1a	2	8
1b	3	6
1c	3	8
1e	11	6
1f	11	8

Sample	n	m	Yield(%)
3a	2	8	Mixture*
3b	3	6	66
3c	3	8	54
3e	11	6	87
3f	11	8	73

Fig. 4. Oxidation of ω-(ω-perfluoroalkylalkyl-sulfanyl)-alkyl acrylates with *m*-chloro-peroxybenzoic acid. (∗) means the oxidation of compound **1a** provides a mixture comprising sulfone **3a** (75%) and 2-perfluorooctyl-ethyl vinyl sulfone (25%).

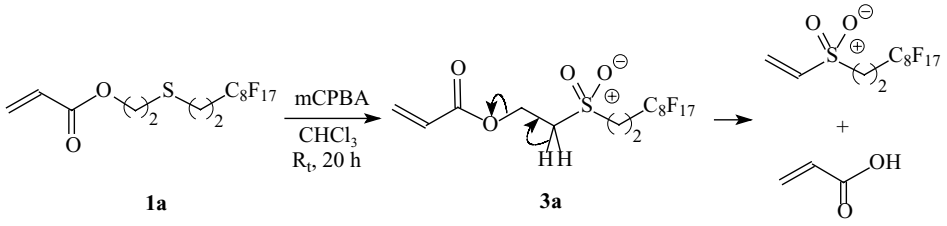


Fig. 5. Formation of 2-perfluorooctyl-ethyl vinyl sulfone.

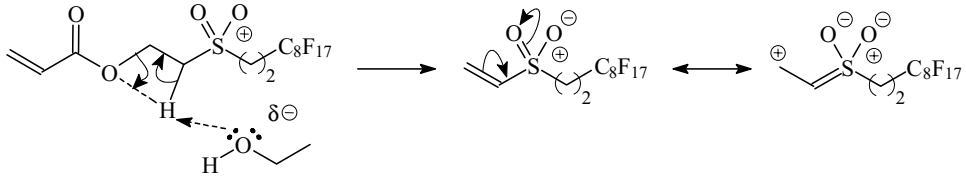


Fig. 6. Reaction between ethanol and sulfone **3a**.

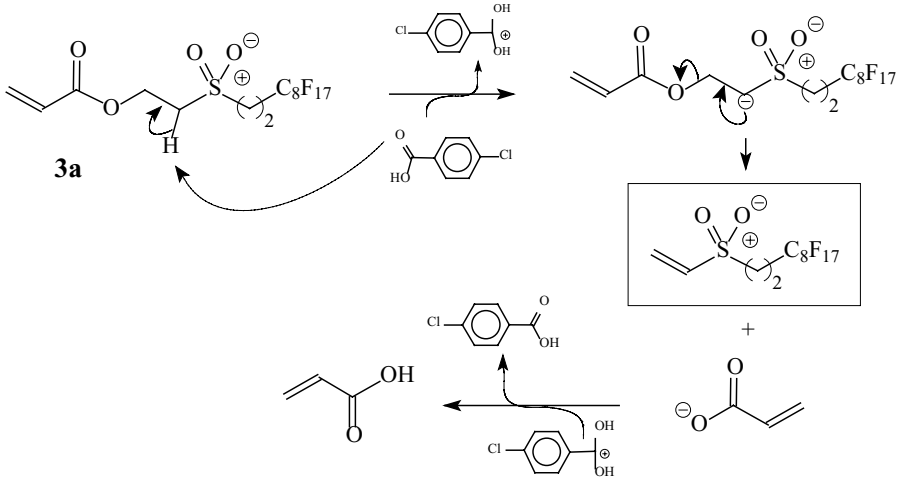
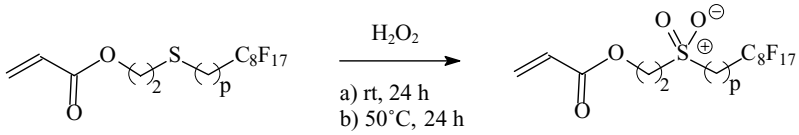


Fig. 7. Reaction between *m*-chloroperbenzoic acid and sulfone **3a**.



1a (p = 2)
1g (p = 11)

3a (p = 3) yield = 85 %
3g (p = 11) yield = 82 %

Fig. 8. Oxidation of ω-(ω-perfluorooctylalkyl-sulfanyl)-alkyl acrylate with hydrogen peroxide.

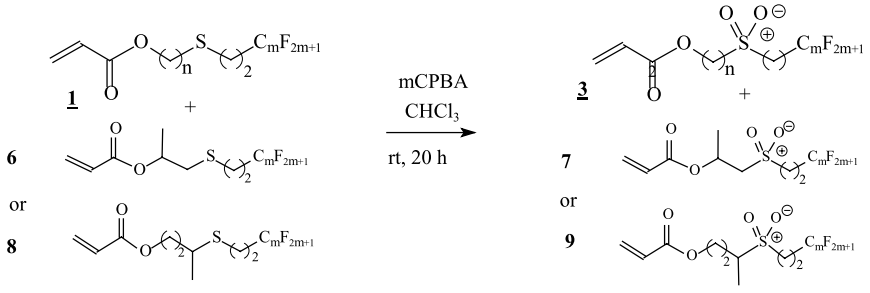
provides a base-catalysed reaction; it attacks the acidic α-sulfonyl hydrogen and liberates the stabilised vinylsulfone (Fig. 6).

In a similar way, we can suppose that *m*-chloroperbenzoic acid, attacking the acidic α-sulfonyl hydrogen, allows β-elimination from 2-(2-perfluorooctylethyl-sulfonyl)-ethyl **3a** (Fig. 7).

The pure sulfone **3a** was obtained with hydrogen peroxide: the oxidation of sulfides by H_2O_2 is a simple one-step reaction and its use in the case of fluorinated compounds has been described by Nemoto et al. [17]. The oxidation of sulfide **1a** therefore occurs under neutral conditions with an excess of H_2O_2 (basic or acidic catalysis was avoided because of the presence of the ester function). Nevertheless, the hydrolysis of the acrylate occurs, liberating the 2-perfluorooctyl-ethyl 2-hydroxy-ethyl sulfone. If the temperature is maintained at 50 °C for 24 h, this by-product is limited (10%) and sulfone **3a** is obtained at an acceptable yield (61%).

The same experiment was carried out for the synthesis of sulfone **3g** from sulfide **1g** which exhibits a structure similar to that of sulfide **1a** (Fig. 8).

In our previous work [18], we described the synthesis of sulfide mixtures (a typical case for an industrial use). Then we oxidised these mixtures with mCPBA to obtain the corresponding sulfones. Mixtures **A**–**D** provided mixtures **E**–**H**. The percents of isomeric sulfones in such a mixture and those of the corresponding isomeric sulfides in the initial mixture are exactly the same (Fig. 9).



Sulfide mixture		Sulfone mixture		yield
A	**1b** (n=3, m = 6), 90% **6a** (m = 6), 10%	**E**	**3b** (n=3, m = 6), 90% **7a** (m = 6), 10%	87
B	**1h** (n=3, m = 6-8), 90% **6b** (m = 6-8), 10%	**F**	**3h** (n=3, m = 6-8), 90% **7b** (m = 6-8), 10%	46
C	**1c** (n=3, m = 8), 90% **6c** (m = 8), 10%	**G**	**3c** (n=3, m = 8), 90% **7c** (m = 8), 10%	49
D	**1d** (n=4, m = 8), 95% **8a** (m = 8), 5%	**H**	**3d** (n=4, m = 8), 95% **9a** (m = 8), 5%	62

Fig. 9. Oxidation of ω-(ω-perfluoroalkylalkyl-sulfanyl)-alkyl acrylates (mixture of isomers) with *m*-chloroperbenzoic acid.

3. Conclusion

This work reports ways of preparing various ω-(ω-perfluoroalkylalkyl-sulfinyl)-alkyl and ω-(ω-perfluoroalkylalkyl-sulfonyl)-alkyl acrylates from sulfides which have been described in a previous paper. The synthetic method must be chosen to avoid reaction with the acrylic double bond. Sodium periodate readily permits the synthesis of sulfoxide. In the case of sulfones, the spacer between the ester function and the sulfur function is of great importance and directs the choice of the oxidant. When the spacer comprises more than two carbon atoms the *m*-chloroperbenzoic acid is sufficient. When the spacer comprises two carbon atoms, hydrogen peroxide must be used to avoid β-elimination. In the case of oxidation of sulfide mixtures with mCPBA to the corresponding sulfones, the reaction reflects the different percents of the starting sulfides in the initial mixture; this is of great interest for industrial application.

4. Experimental

4.1. General comments

The sufides are described in a previous work [18].

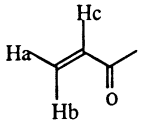
Cerium(IV) ammonium nitrate, sodium periodate, *m*-chloroperbenzoic acid, hydrogen peroxide and hydroquinone monomethylether (HQME) were supplied from Aldrich and used as received. Anhydrous sodium sulfate, and sodium hydroxide, calcium chloride, sodium hydrogenocarbonate were purchased from Fluka. Oxone® persulfate is a DuPont product. Solvents as dichloromethane, chloroform and methanol were purchased from Carlo-Erba. After reaction the monomers were stabilised with 250 ppm of HQME.

The ^{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, $C\bar{F}_3$, 3F); −113.7 (m, $C\bar{F}_2CH_2$, 2F); −122.4 (m, $C\bar{F}_2C\bar{F}_2$-CF_2CH_2, 4F); −123.5 (m, $C_2F_5C\bar{F}_2$, 2F); −126.6 (m, $CF_3C\bar{F}_2$, 2F).

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

The letters a, b, c were used to described the ethylenic system:



After reaction, some compounds were analysed 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). The IR spectra were obtained on a Perkin-Elmer 881 spectrometer. Some products were not soluble enough in the solvents or decomposed on heating. For these products the analyses were not complete.

4.2. Synthesis

4.2.1. Preparation of sulfoxides with sodium periodate

The acrylate (1 eq.) in methanol (30 ml $mmol^{-1}$ of sulfur) was placed in a four-necked round bottom flask fitted with a stirrer, a dropping funnel, a thermometer and a condenser. The solution was cooled to 0 °C. Aqueous $NaIO_4$ (0.5 ml H_2O $mmol^{-1}$ $NaIO_4$) was added dropwise to the reaction mixture. During the addition, the temperature was maintained at −5 to 0 °C with continuous stirring. The reaction mixture was stirred further for 12 h. The solution was filtered and concentrated under vacuum. The oily organic layer was extracted with chloroform, washed with water, dried over Na_2SO_4, and evaporated under reduced pressure in the presence of hydroquinone monomethylether (250 ppm HMEQ).

*4.2.1.1. 3-(2-Perfluorooctylethyl-sulfinyl)-propyl acrylate (**2c**). Yield*: 73%. NMR ^{1}H ($CDCl_3$) (δ, ppm): 6.43 (dd, $J_{AB} = 1.3$ Hz, $J_{AC} = 17.2$ Hz, CH^a); 6.12 (dd, $J_{AC} = 17.2$ Hz, $J_{BC} = 10.4$ Hz, CH^c); 5.87 (dd, $J_{BC} = 10.4$ Hz, $J_{AB} = 1.3$ Hz, CH^b); 4.32 (m, OCH_2); 2.87 (m, CH_2SO and $SOC\bar{H}_2CH_2CF_2$); 2.64 (m, $CH_2C\bar{H}_2CF_2$); 2.21 (m, CH_2). NMR ^{13}C ($CDCl_3$) (δ, ppm): 165.9 (s, C=O); 131.3 (s, $CH_2^{a,b}$); 128.0 (s, CH^c); 105–125 (m, $7CF_2$ and CF_3); 62.6 (s, OCH_2); 49.6 (s, CH_2SO); 43.0 (m, $SO\bar{C}H_2CH_2CF_2$); 24.9 (t, $^{2}J_{CF} = 22.8$ Hz, $\bar{C}H_2CF_2$); 22.3 (s, CH_2). IR (cm^{-1}) (KBr): 1731.5 (νCO); 1636.4 (νCH_2=CH–).

*4.2.1.2. 11-(2-Perfluorooctylethyl-sulfinyl)-undecyl acrylate (**2f**). Yield*: 25%. NMR ^{1}H ($CDCl_3$) (δ, ppm): 6.40 (dd, $J_{AB} = 1.2$ Hz, $J_{AC} = 17.1$ Hz, CH^a); 6.12 (dd, $J_{AC} = 17.1$ Hz, $J_{BC} = 10.4$ Hz, CH^c); 5.81 (dd, $J_{BC} = 10.4$ Hz, $J_{AB} = 1.2$ Hz, CH^b); 4.15 (t, $J = 6.7$ Hz, OCH_2); 2.81 (m, CH_2SO and $SOC\bar{H}_2CH_2CF_2$); 2.68 (m, $CH_2C\bar{H}_2CF_2$); 1.79 (m, CH_2); 1.65 (m, CH_2); 1.45 (m, CH_2); 1.29 (m, 6 CH_2). NMR ^{13}C ($CDCl_3$) (δ, ppm): 166.3 (s, C=O); 130.3 (s, $CH_2^{a,b}$); 128.6 (s, CH^c); 105–125 (m, 7 CF_2 and CF_3); 64.6 (s, OCH_2); 52.9 (s, CH_2SO); 42.6 (m, $SO\bar{C}H_2CH_2CF_2$); 28.3–29.4 (m, $7CH_2$); 25.8 (s, CH_2); 24.9 (t, $^{2}J_{CF} = 22.3$ Hz, $\bar{C}H_2CF_2$); 22.6 (s, CH_2). ĈG/SM (*m*/*z* (%)): 552); 69(15); 77(100); 100(5); 119(6); 131(8);

169(3); 181(2); 381(1); 446(1). IR (cm^{-1}): 1727.9 (νCO); 1637.6 (νCH_2=CH–).

4.2.2. Preparation of sulfones with m-chloroperbenzoic acid

The acrylate (1 eq.) in chloroform (3 ml $mmol^{-1}$ of sulfur) was placed in a four-necked round bottom flask fitted with a stirrer, a dropping funnel, a thermometer and a condenser. The solution was cooled to 0 °C. The 2.5 eq. of *m*-chloroperbenzoic acid, diluted in chloroform (2 ml $mmol^{-1}$ oxidant) were added dropwise to the reaction mixture. The temperature is maintained at 0 °C for 1% with continuous stirring. The reaction mixture was then stirred further for 20 h. The solution was filtered, washed with a 10% sodium hydrogenocarbonate, with water, dried over Na_2SO_4, and evaporated under reduced pressure in the presence of hydroquinone monomethylether (250 ppm HMEQ). A white solid was obtained.

*4.2.2.1. 2-Perfluorooctyl-ethyl 3-hydroxy-propyl sulfone (**5**). Yield*: 47%. NMR ^{1}H (acetone d_6) (δ, ppm): 3.66 (t, J = 5.9 Hz, OCH_2); 3.45 (tt, ($^4J_{HF}$), J_{HH} = 8.2 Hz, $SO_2C\bar{H}_2$-CH_2CF_2); 3.31 (t, J = 7.8 Hz, CH_2SO_2); 2.81 (tt, J_{HH} = 8.2 Hz, $^3J_{HF}$ = 16.4 Hz, $CH_2C\bar{H}_2CF_2$); 2.04 (m, CH_2).

*4.2.2.2. 2-(2-Perfluorooctylethyl-sulfonyl)-ethyl acrylate (**3a**). Yield*: 85%. NMR ^{1}H ($CDCl_3$) (δ, ppm): 6.48 (dd, J_{AB} = 1.0 Hz, J_{AC} = 17.1 Hz, CH^a); 6.08 (dd, J_{AC} = 17.1 Hz, J_{BC} = 10.3 Hz, CH^c); 5.94 (dd, J_{BC} = 10.3 Hz, J_{AB} = 1.0 Hz, CH^b); 4.65 (t, J = 5.5 Hz, OCH_2); 3.42 (t, J = 5.5 Hz, CH_2SO_2); 3.31 (tt, ($^4J_{HF}$), J_{HH} = 8.5 Hz, $SO_2C\bar{H}_2CH_2CF_2$); 2.69 (tt, J_{HH} = 8.5 Hz, $^3J_{HF}$ = 17.0 Hz, $CH_2C\bar{H}_2CF_2$). NMR ^{13}C ($CDCl_3$) (δ, ppm): 165.1 (s, C=O); 132.6 (s, $CH_2^{a,b}$); 127.0 (s, CH^c); 105–125 (m, 7 CF_2 and CF_3); 57.8 (s, OCH_2); 52.9 (s, CH_2SO_2); 46.2 (t, $^3J_{CF}$ = 3.8 Hz, $SO_2\bar{C}H_2CH_2CF_2$); 24.3 (t, $^2J_{CF}$ = 22.5 Hz, $\bar{C}H_2CF_2$). C̄G/SM (*m/z* (%)): 43(21); 69(52); 73(48); 91(100); 119(25); 131(32); 169(15); 231(3); 281(2); 381(5); 427(6); 480(7); 495(20); 520(6).

*4.2.2.3. 3-(2-Perfluorohexylethyl-sulfonyl)-propyl acrylate (**3b**). Yield*: 66%. NMR ^{1}H ($CDCl_3$) (δ, ppm): 6.45 (dd, J_{AB} = 1.0 Hz, J_{AC} = 17.2 Hz, CH^a); 6.13 (dd, J_{AC} = 17.2 Hz, J_{BC} = 10.3 Hz, CH^c); 5.89 (dd, J_{BC} = 10.3 Hz, J_{AB} = 1.0 Hz, CH^b); 4.33 (t, J = 6.1 Hz, OCH_2); 3.26 (tt, ($^4J_{HF}$), J_{HH} = 8.5, $SO_2C\bar{H}_2CH_2CF_2$); 3.18 (t, J = 8.0 Hz, CH_2SO_2); 2.69 (tt, J_{HH} = 8.5 Hz, $^3J_{HF}$ = 17.2 Hz, $CH_2C\bar{H}_2CF_2$); 2.28 (m, CH_2). NMR ^{13}C ($CDCl_3$) (δ, ppm): 166.0 (s, C=O); 131.6 (s, $CH_2^{a,b}$); 128.0 (s, CH^c); 105–125 (m, 5CF_2 and CF_3); 62.0 (s, OCH_2); 50.7 (s, CH_2SO_2); 44.7 (t, $^3J_{CF}$ = 3.5 Hz, $SO_2\bar{C}H_2CH_2CF_2$); 24.2 (t, $^2J_{CF}$ = 22.7 Hz, $\bar{C}H_2CF_2$); 21.7 (s, CH_2).

*4.2.2.4. 3-(2-Perfluorooctylethyl-sulfonyl)-propyl acrylate (**3c**). Yield*: 54%. NMR ^{1}H ($CDCl_3$) (δ, ppm): 6.44 (dd, J_{AB} = 1.0 Hz, J_{AC} = 17.2 Hz, CH^a); 6.12 (dd, J_{AC} = 17.2 Hz, J_{BC} = 10.3 Hz, CH^c); 5.88 (dd, J_{BC} = 10.3 Hz, J_{AB} = 1.0 Hz, CH^b); 4.33 (t, J = 6.0 Hz, OCH_2); 3.25 (tt, ($^4J_{HF}$), J_{HH} = 8.3, $SO_2C\bar{H}_2CH_2CF_2$); 3.19 (t, J = 8.0 Hz, CH_2SO_2); 2.66 (tt, J_{HH} = 8.3 Hz, $^3J_{HF}$ = 16.6 Hz, $CH_2C\bar{H}_2CF_2$); 2.28 (m, CH_2). NMR ^{13}C ($CDCl_3$) (δ, ppm): 165.7 (s, C=O); 131.5 (s, $CH_2^{a,b}$); 127.7 (s, CH^c); 105–125 (m, 5CF_2 and CF_3); 61.9 (s, OCH_2); 50.5 (s, CH_2SO_2); 44.6 (t, $^3J_{CF}$ = 3.4 Hz, $SO_2\bar{C}H_2CH_2CF_2$); 24.0 (t, $^2J_{CF}$ = 22.7 Hz, $\bar{C}H_2CF_2$); 21.6 (s, CH_2). C̄G/SM (*m/z* (%)): 41(19); 55(100); 69(9); 85(7); 113(36); 131(2); 169(1); 231(1); 281(1); 381(1); 513(5). IR (cm^{-1}): 1732.2 (νCO); 1637.3 (νCH_2=CH–).

*4.2.2.5. 11-(2-Perfluorohexylethyl-sulfonyl)-undecyl acrylate (**3e**). Yield*: 87%. NMR ^{1}H ($CDCl_3$) (δ, ppm): 6.40 (dd, J_{AB} = 1.5 Hz, J_{AC} = 17.1 Hz, CH^a); 6.12 (dd, J_{AC} = 17.1 Hz, J_{BC} = 10.3 Hz, CH^c); 5.81 (dd, J_{BC} = 10.3 Hz, J_{AB} = 1.5 Hz, CH^b); 4.15 (t, J = 6.7 Hz, OCH_2); 3.20 (tt, ($^4J_{HF}$), J_{HH} = 8.2 Hz, $SO_2C\bar{H}_2CH_2CF_2$); 3.05 (t, J = 8.1 Hz, CH_2SO_2); 2.70 (tt, J_{HH} = 8.2 Hz, $^3J_{HF}$ = 17.0 Hz, $CH_2C\bar{H}_2CF_2$); 1.87 (m, CH_2); 1.66 (m, CH_2); 1.46 (m, CH_2); 1.29 (m, 6CH_2). NMR ^{13}C ($CDCl_3$) (δ, ppm): 166.3 (s, C=O); 130.3 (s, $CH_2^{a,b}$); 128.6 (s, CH^c); 105–125 (m, 5CF_2 and CF_3); 64.6 (s, OCH_2); 53.7 (s, CH_2SO_2); 44.2 (t, $^3J_{CF}$ = 3.3 Hz, $SO_2\bar{C}H_2CH_2CF_2$); 28.4–29.4 (m, 7CH_2); 25.9 (s, CH_2); 24.1 (t, $^2J_{CF}$ = 22.6 Hz, $\bar{C}H_2CF_2$); 21.9 (s, CH_2). C̄G/SM (*m/z* (%)): 41(21); 55(100); 69(40); 85(28); 97(28); 152(17); 169(1); 281(1); 381(1); 513(4). IR (cm^{-1}): 1724.5 (νCO); 1637.5 (νCH_2=CH–).

*4.2.2.6. 11-(2-Perfluorooctylethyl-sulfonyl)-undecyl acrylate (**3f**). Yield*: 73%. NMR ^{1}H ($CDCl_3$) (δ, ppm): 6.40 (dd, J_{AB} = 1.4 Hz, J_{AC} = 17.3 Hz, CH^a); 6.10 (dd, J_{AC} = 17.3 Hz, J_{BC} = 10.3 Hz, CH^c); 5.81 (dd, J_{BC} = 10.3 Hz, J_{AB} = 1.4 Hz, CH^b); 4.15 (t, J = 6.7 Hz, OCH_2); 3.21 (tt, ($^4J_{HF}$), J_{HH} = 8.3 Hz, $SO_2C\bar{H}_2CH_2CF_2$); 3.05 (t, J = 8.1 Hz, CH_2SO_2); 2.70 (tt, J_{HH} = 8.3 Hz, $^3J_{HF}$ = 16.6 Hz, $CH_2C\bar{H}_2CF_2$); 1.87 (m, CH_2); 1.66 (m, CH_2); 1.46 (m,CH_2); 1.29 (m, 6CH_2). NMR ^{13}C ($CDCl_3$) (δ, ppm): 166.3 (s, C=O); 130.3 (s, $CH_2^{a,b}$); 128.6 (s, CH^c); 105–125 (m, 5CF_2 and CF_3); 64.6 (s, OCH_2); 53.7 (s, CH_2SO_2); 44.2 (t, $^3J_{CF}$ = 3.4 Hz, $SO_2\bar{C}H_2CH_2CF_2$); 28.4–29.4 (m, 7CH_2); 25.9 (s, CH_2); 24.1 (t, $^2J_{CF}$ = 22.6 Hz, $\bar{C}H_2CF_2$); 21.9 (s, CH_2). C̄G/SM (*m/z* (%)): 41(21); 55(100); 69(40); 85(28); 97(28); 152(17); 169(1); 281(1); 381(1); 513(4). IR (cm^{-1}): 1724.5 (νCO); 1637.5 (νCH_2=CH–).

*4.2.2.7. 3-(2-Perfluorohexylethyl-sulfonyl)-propyle (isomer mixture) (mixture **E**). Yield*: 87%.

3-(2-Perfluorohexylethyl-sulfonyl)-propyl acrylate (isomer **3b** *(90%))*. NMR ^{1}H ($CDCl_3$) (δ, ppm): 6.44 (dd, J_{AB} = 1.0 Hz, J_{AC} = 17.2 Hz, CH^a); 6.12 (dd, J_{AC} = 17.2 Hz, J_{BC} = 10.4 Hz, CH^c); 5.88 (dd, J_{BC} = 10.4 Hz, J_{AB} = 1.0 Hz, CH^b); 4.32 (t, J = 6.0 Hz, OCH_2); 3.24 (tt, ($^4J_{HF}$), J_{HH} = 8.6, $SO_2C\bar{H}_2CH_2CF_2$); 3.18 (t, J = 7.9 Hz,

CH_2SO_2); 2.69 (tt, $J_{HH} = 8.6$ Hz, $^3J_{HF} = 17.2$ Hz, CH_2-$C\bar{H}_2CF_2$); 2.28 (m, CH_2). NMR ^{13}C ($CDCl_3$) (δ, ppm): 165.8 (s, C=O); 131.6 (s, $CH_2^{a,b}$); 127.8 (s, CH^c); 105–125 (m, xCF_2 and CF_3); 62.0 (s, OCH_2); 50.7 (s, CH_2SO_2); 44.8 (m, $SO_2\bar{C}H_2CH_2CF_2$); 24.2 (t, $^2J_{CF} = 22.6$ Hz, $\bar{C}H_2CF_2$); 21.7 (s, CH_2).

2-(2-Perfluorohexylethyl-sulfonyl)-propyl acrylate (isomer **7a** *(10%))*. NMR ^1H ($CDCl_3$) (δ, ppm): 6.44 (dd, $J_{AB} = 1.0$ Hz, $J_{AC} = 17.3$ Hz, CH^a); 6.11 (dd, $J_{AC} = 17.3$ Hz, $J_{BC} = 10.4$ Hz, CH^c); 5.89 (dd, $J_{BC} = 10.4$ Hz, $J_{AB} = 1.0$ Hz, CH^b); 5.45 (m, $OCH^{X'}$); 3.45 (m, $CH_2^{a',b'}SO_2$ and $SO_2C\bar{H}_2CH_2CF_2$); 2.69 (tt, $J_{HH} = 8.5$ Hz, $^3J_{HF} = 17.1$ Hz, $CH_2C\bar{H}_2CF_2$); 1.48 (d, $J_{M'X'} = 7.0$ Hz, $CH_3^{m'}$).

4.2.2.8. 3-(2-Perfluoroalkylethyl-sulfonyl)-propyle (isomer mixture: mixture ***F****) (m = 6–8). Yield*: 46%.

3-(2-Perfluoroalkyl-ethyl-sulfonyl)-propyl acrylate (isomer **3h** *(90%))*. NMR ^1H ($CDCl_3$) (δ, ppm): 6.44 (dd, $J_{AB} = 1.0$ Hz, $J_{AC} = 17.2$ Hz, CH^a); 6.12 (dd, $J_{AC} = 17.2$ Hz, $J_{BC} = 10.4$ Hz, CH^c); 5.88 (dd, $J_{BC} = 10.4$ Hz, $J_{AB} = 1.0$ Hz, CH^b); 4.32 (t, $J = 6.0$ Hz, OCH_2); 3.24 (tt, ($^4J_{HF}$), $J_{HH} = 8.6$, $SO_2C\bar{H}_2CH_2CF_2$); 3.18 (t, $J = 7.9$ Hz, CH_2SO_2); 2.69 (tt, $J_{HH} = 8.6$ Hz, $^3J_{HF} = 17.2$ Hz, CH_2-$C\bar{H}_2CF_2$); 2.28 (m, CH_2). NMR ^{13}C ($CDCl_3$) (δ, ppm): 165.8 (s, C=O); 131.6 (s, $CH_2^{a,b}$); 127.8 (s, CH^c); 105–125 (m, xCF_2 and CF_3); 62.0 (s, OCH_2); 50.7 (s, CH_2SO_2); 44.8 (m, $SO_2\bar{C}H_2CH_2CF_2$); 24.2 (t, $^2J_{CF} = 22.6$ Hz, $\bar{C}H_2CF_2$); 21.7 (s, CH_2).

2-(2-Perfluoroalkylethyl-sulfonyl)-propyl acrylate (isomer **7b** *(10%))*. NMR ^1H ($CDCl_3$) (δ, ppm): 6.44 (dd, $J_{AB} = 1.0$ Hz, $J_{AC} = 17.2$ Hz, CH^a); 6.13 (dd, $J_{AC} = 17.2$ Hz, $J_{BC} = 10.4$ Hz, CH^c); 5.88 (dd, $J_{BC} = 10.4$ Hz, $J_{AB} = 1.0$ Hz, CH^b); 5.45 (m, $OCH^{X'}$); 3.40 (m, $CH_2^{a',b'}$-SO_2 and $SO_2C\bar{H}_2CH_2CF_2$); 2.69 (tt, $J_{HH} = 8.6$, Hz, $^3J_{HF} = 17.2$ Hz, $CH_2C\bar{H}_2CF_2$); 1.48 (d, $J_{M'X'} = 7.0$ Hz, $CH_3^{m'}$). NMR ^{13}C ($CDCl_3$) (δ, ppm): 165.8 (s, C=O); 131.6 (s, $CH_2^{a,b}$); 127.8 (s, CH^c); 105–125 (m, xCF_2 and CF_3); 65.8 (s, OCH); 58.6 (s, CH_2SO_2); 46.0 (m, $SO_2\bar{C}H_2CH_2CF_2$); 24.2 (t, $^2J_{CF} = 22.6$ Hz, $\bar{C}H_2CF_2$); 20.1 (s, CH_3).

4.2.2.9. 3-(2-Perfluorooctylethyl-sulfonyl)-propyl acrylate (isomer mixture: mixture ***G****). Yield*: 49%. IR (cm^{-1}): 1732.2 (νCO); 1637.3 (νCH_2=CH–).

3-(2-Perfluorooctylethyl-sulfonyl)-propyl acrylate (isomer **3c** *(90%))*. See above.

2-(2-Perfluorooctylethyl-sulfonyl)-propyl acrylate (isomer **7c** *(10%))*. NMR ^1H ($CDCl_3$) (δ, ppm): 6.44 (dd, $J_{AB} = 1.2$ Hz, $J_{AC} = 17.2$ Hz, CH^a); 6.13 (dd, $J_{AC} = 17.2$ Hz, $J_{BC} = 10.4$ Hz, CH^c); 5.89 (dd, $J_{BC} = 10.4$ Hz, $J_{AB} = 1.2$ Hz, CH^b); 5.45 (m, $OCH^{X'}$); 3.45 (m, $CH_2^{a',b'}SO_2$ and $SO_2C\bar{H}_2CH_2CF_2$); 2.69 (tt, $J_{HH} = 8.4$, Hz, $^3J_{HF} = 16.7$ Hz, $CH_2C\bar{H}_2CF_2$); 1.48 (d, $J_{M'X'} = 7.0$ Hz, $CH_3^{m'}$). NMR ^{13}C ($CDCl_3$) (δ, ppm): 165.7 (s, C=O); 131.5 (s, $CH_2^{a,b}$); 127.8 (s, CH^c); 105–125 (m, $7CF_2$ and CF_3); 65.7 (s, OCH); 58.3 (s, CH_2SO_2); 46.0 (m, $SO_2\bar{C}H_2CH_2CF_2$); 24.0 (t, $^2J_{CF} = 22.4$ Hz, $\bar{C}H_2CF_2$); 20.0 (s, CH_3).

4.2.2.10. 4-(2-Perfluorooctylethyl-sulfonyl)-butyl acrylate (isomer mixture: mixture ***H****). Yield*: 62%.

4-(2-Perfluorooctylethyl-sulfonyl)-butyl acrylate (isomer **3d** *(95%))*. NMR ^1H ($CDCl_3$) (δ, ppm): 6.41 (dd, $J_{AB} = 1.6$ Hz, $J_{AC} = 17.3$ Hz, CH^a); 6.11 (dd, $J_{AC} = 17.3$ Hz, $J_{BC} = 10.3$ Hz, CH^c); 5.84 (dd, $J_{BC} = 10.3$ Hz, $J_{AB} = 1.6$ Hz, CH^b); 4.22 (t, $J = 6.0$ Hz, OCH_2); 3.22 (tt, ($^4J_{HF}$), $J_{HH} = 8.6$ Hz, $SO_2C\bar{H}_2CH_2CF_2$); 3.12 (t, $J = 7.7$ Hz, CH_2SO_2); 2.67 (tt, $J_{HH} = 8.6$ Hz, $^3J_{HF} = 17.2$ Hz, $CH_2C\bar{H}_2CF_2$); 2.01 (m, CH_2); 1.87 (m, CH_2). NMR ^{13}C ($CDCl_3$) (δ, ppm): 166.0 (s, C=O); 131.1 (s, $CH_2^{a,b}$); 128.1 (s, CH^c); 105–125 (m, $7CF_2$ and CF_3); 63.0 (s, OCH_2); 53.0 (s, CH_2SO_2); 44.4 (m, $SO_2\bar{C}H_2CH_2CF_2$); 27.4 (s, CH_2); 24.1 (t, $^2J_{CF} = 22.7$ Hz, $\bar{C}H_2CF_2$); 18.8 (s, CH_2).

3-(2-Perfluorooctylethyl-sulfonyl)-butyl acrylate (isomer **9a** *(5%))*. NMR ^1H ($CDCl_3$) (δ, ppm): 6.41 (dd, $J_{AB} = 1.6$ Hz, $J_{AC} = 17.3$ Hz, CH^a); 6.11 (dd, $J_{AC} = 17.3$ Hz, $J_{BC} = 10.3$ Hz, CH^c); 5.84 (dd, $J_{BC} = 10.3$ Hz, $J_{AB} = 1.6$ Hz, CH^b); 4.40 (m, OCH_2); 3.50 (m, $CHSO_2$); 3.20 (m, $SO_2C\bar{H}_2CH_2CF_2$); 24.10 (t, $^2J_{CF} = 22.7$ Hz, $\bar{C}H_2CF_2$); 2.00 (m, CH_2); 1.55 (d, J=7.0 Hz, CH_3).

4.2.3. Preparation of sulfones with hydrogen peroxide

The acrylate (1 eq.) was placed in a four-necked round bottom flask fitted with a stirrer, a dropping funnel, a thermometer and a condenser. At room temperature, 6 eq. of 15% hydrogen peroxide were added dropwise to the reaction mixture. The temperature was maintained at room temperature for 24 h with continuous stirring. The reaction mixture was then stirred further for 24% at 45 °C. The milky organic layer was extracted three times with dichloromethane, dried over Na_2SO_4, and evaporated under reduced pressure in the presence of hydroquinone monomethylether (250 ppm HMEQ).

*4.2.3.1. 2-(2-Perfluorooctylethyl-sulfonyl)-ethyl acrylate (**1a**). Yield*: 85%, see above.

*4.2.3.2. 2-(11-Perfluorooctylundecylsulfonyl)-ethyl acrylate (**1g**). Yield*: 82% NMR ^1H ($CDCl_3$) (δ, ppm): 6.47 (dd, $J_{AB} = 1.6$ Hz, $J_{AC} = 17.4$ Hz, CH^a); 6.13 (dd, $J_{AC} = 17.4$ Hz, $J_{BC} = 10.4$ Hz, CH^c); 5.92 (dd, $J_{BC} = 10.4$ Hz, $J_{AB} = 1.6$ Hz, CH^b); 4.61 (t, $J = 6.0$ Hz, OCH_2); 3.33 (t, $J = 6.0$ Hz, $SO_2C\bar{H}_2CH_2O$); 3.03 (t, $J = 8.0$ Hz, CH_2SO_2); 2.05 (m, $CH_2C\bar{H}_2CF_2$); 1.84 (m, CH_2); 1.60 (m, CH_2); 1.29 (m, $7CH_2$). NMR ^{13}C ($CDCl_3$) (δ, ppm): 165.3 (s, C=O); 132.1 (s, $CH_2^{a,b}$); 128.6 (s, CH^c); 105–125 (m, 5 CF_2 and CF_3); 57.8 (s, OCH_2); 54.4 (s, $SO_2\bar{C}H_2CH_2O$);

51.8 (s, $SO_2\bar{C}H_2$); 30.9 (t, $^2J_{CF} = 22.2$ Hz, $\bar{C}H_2CF_2$); 28.2–30.5 (m, $7CH_2$); 22.6 (s, CH_2); 21.9 (t, $^3J_{CF} = 3.6$ Hz, $\bar{C}H_2CH_2CF_2$).

Solutions of various acrylates of ω-(2-perfluoroalkylethyl-sulfonyl)-alkyl acrylates concentrated in chloroform or dichloromethane look like a transparent colloid which liquefies quickly after heating or mechanical agitation. This property, already highlighted by Tschierske [19], is characteristic of compounds which, in solution, are like ''liquid crystals'' by forming a thixotropic gel. Since sulfonic perfluorinated acrylic monomers have such properties, the corresponding polymers should present very interesting properties.

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