

Synthesis and polymerization of fluorinated monomers bearing a reactive lateral group¹

Part 4. Preparation of functional perfluorovinyl monomers by radical addition of functional mercaptans to 1,1,2-trifluoro-1,4-pentadiene

B. Améduri^{a,*}, B. Boutevin^a, G.K. Kostov^b, P. Petrova^b

^aESA 5076, Ecole Nationale Supérieure de Chimie, 8 Rue de l'École Normale 34296, Montpellier Cedex 5, France

^bUniversity of Bourgas, Center for Electron Beam Technology and Polymers, 8010, Bourgas, Bulgaria

Received 4 June 1998; accepted 13 July 1998

Abstract

The synthesis of novel perfluorovinyl monomers $\text{CF}_2=\text{CFC}_3\text{H}_6\text{S}-\text{G}$ **1** bearing hydroxyl or carboxyl as G end-groups from 1,1,2-trifluoro-1,4-pentadiene **2** is presented. They were obtained by radical addition of ω -hydroxy and carboxy mercaptans to **2**. These addition reactions were performed either photochemically or in the presence of various radical initiators used at different temperatures. The nature of the functional group of the mercaptan and the way of initiation enabled these additions to occur either on both double bonds of **2** or on the hydrogenated or fluorinated one leading to telechelic $\text{G}-\text{SCF}_2\text{CFHC}_3\text{H}_6\text{S}-\text{G}$ diacid or diol, to **1** or to $\text{G}-\text{SCF}_2\text{CFHCH}_2\text{CH}=\text{CH}_2$, respectively. The amounts of these products were determined by ¹H and ¹⁹F NMR spectroscopy, and the reactivity of both mercaptans was also discussed. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Fluorinated 1,4-diene; Functional mercaptan; Thiylation; Radical addition; UV radiation; Trifluorovinyl monomers

1. Introduction

Perfluorovinyl functional monomers have already been shown to be of great utility in copolymerization with fluorinated or non-fluorinated commercially available comonomers [1–5]. The functional group which is subsequently introduced in a lateral position about the backbone of the copolymer brings specific and complementary properties: adhesion from a carboxylic function [6], solubility from a cyclohexyl group [7], curability from hydroxy or epoxide functions [8–11], surface properties from a perfluorinated group [12] or good hydrophilicity, and heat and chemical resistance brought by the phosphonate function [13]. Various functional monomers which exhibit a ω -trifluorovinyl group have already been synthesized. In 1963, Tarrant et al. [14] reacted trifluorovinyl lithium with trifluoroacetone to produce a perfluorovinyl tertiary alcohol. Later, the Daikin Company [9–11] achieved the preparation of a series of various monomers having the formulae $\text{F}_2\text{C}=\text{CF}(\text{CF}_2)_n(\text{CH}_2)_m-\text{G}$ where $n=0, 1, 2$; $m=1, 2$ and

G represents $-\text{OH}$ or $-\text{CH}(\text{O})\text{CH}_2$ functions. Chvatal et al. [15] prepared $\text{F}_2\text{C}=\text{CFC}_2\text{H}_4\text{OH}$ from the monoadduct of bromine to chlorotrifluoroethylene (CTFE), followed by a substitution of one bromine atom by a hydroxy group and then dehalogenation. Recently, we have optimised the synthesis of $\text{F}_2\text{C}=\text{CFC}_3\text{H}_6\text{OH}$ by a four-step scheme, starting from the radical addition of iodine monochloride to CTFE. The corresponding acetate was also obtained [16]. Further work was done by Hu et al. [17] who isolated in high yield perfluorovinyl monomers terminated with ester, amide, nitrile or ketone groups. In the same way, Yang et al. [18] obtained interesting ω -acetoxo, epoxide, furan, trimethylsilyl or phosphonate fluoromonomers by the redox addition of 1,1,2,3,3-pentafluoro-3-iodo propene (or perfluoroallyl iodide) to functional olefins in the presence of copper metal. The preparation of perfluorovinyl fluoroethylether was described by Guglielmo [19], and intensive research was carried out by the Du Pont Company to obtain functional perfluorovinyl ethers useful for the synthesis of fluorinated copolymers [20,21], fluorinated crown ethers [22] or fluorinated telechelic polyethers [22]. In addition, a two-step reaction enabled Nguyen and Wakselman [23] to synthesize the fluorinated alcohol $\text{CF}_2=\text{CF}-\text{CH}_2\text{OH}$ by addition of

*Corresponding author. Fax: +33-4-67-14-7220.

¹Part 3, see [16]

butyl lithium to 2,2,3,3-tetrafluoropropanol. This trifluoroallyl alcohol could also be obtained by dehydrofluorination of 2,3,3,3-tetrafluoropropanol. This latter alcohol was prepared from hexafluoropropene in three steps [24].

In addition, we have recently synthesized 1,1,2-trifluoro-1,4-pentadiene **1** from dechlorination and then deiodoacetylation of $\text{ClCF}_2\text{CFCICH}_2\text{CHXCH}_2\text{Y}$ with (X, Y)=(I, OAc) or (OAc, I) produced from the radical addition of $\text{Cl}(\text{C}_2\text{F}_3\text{Cl})\text{I}$ to allyl acetate [25,26]. Such a diene appears quite interesting since it can behave as a precursor of original functional trifluorovinyl monomers because hydrogenated double bonds are reactive with transfer agents [27] under radical conditions.

Among these telogens, functional mercaptans have been chosen and the objective of the present paper is the addition of these thiols to the hydrogenated double bond of $\text{CF}_2=\text{CFCH}_2\text{CH}=\text{CH}_2$ in order to obtain novel functional perfluorovinyl monomers.

2. Experimental details

2.1. General comments

Thioglycolic acid, 2-mercapto ethanol and benzophenone were provided by Aldrich, AIBN by Merck, whereas *tert*-butylcyclohexyl peroxy carbonate (Perkadox-16) was kindly donated by Akzo. 1,1,2-trifluoro-1,4-pentadiene was synthesized as before [25].

Several reactions were carried out at atmospheric pressure in classical round bottom flasks whereas others were done in borosilicate Carius tubes (thickness: 3 mm, outside diameter: 40 mm and length: 30 mm). Photochemical-induced reactions required a mercury lamp Philips HPK 125 W.

After reaction, the products were worked-up and analyzed by gas chromatography (GC) using a Delsi apparatus (model 330) equipped with an SE 30 column, 1 m × 1/8 in (3.13 mm) (i.d.). Nitrogen pressure at the entrance to the column was maintained at 0.6 bar and the detector and injector temperatures were 260°C and 255°C, respectively. The temperature programme started from 50°C and attained 250°C at a heating rate of 15°C min⁻¹. The GC apparatus was connected to a Hewlett Packard integrator (model 3390) which automatically calculated the area of each peak on the chromatogram.

The products were characterized by ¹H, ¹³C and ¹⁹F NMR spectroscopy all undertaken at room temperature. ¹H and ¹³C NMR spectra were recorded on Bruker AC 200 or 250 instruments, using deuterated chloroform as the solvent and lock, and TMS as the internal reference. The letters s, d, t, q, qi and m designate singlet, doublet, triplet, quartet, quintet and multiplet, respectively. ¹⁹F NMR spectra were also recorded on Bruker AC 200 or 250 instruments with deuterated chloroform as lock and CFCl_3 as the internal refer-

ence. Coupling constants and chemical shifts are given in hertz (Hz) and ppm, respectively.

2.2. Model reaction: Radical addition of thioglycolic acid to 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro undecane

2.2.1. In the presence of AIBN

In a two-necked round-bottom flask equipped with a condenser and a device for nitrogen flow were reacted 18.25 g (198 mmol) thioglycolic acid, 90.75 g (200 mmol) fluoroalkene synthesized as previously [36], 40.0 g acetonitrile and 1.37 g (8.4 mmol) AIBN. The reaction was carried out at 80°C for 7 h. Then, acetonitrile was evaporated from the homogeneous and clear liquid and fluorinated acid was added dropwise into vigorously stirred water (150 ml). The precipitate was filtered off and dried to constant weight at 60°C under vacuum (ca. 10 mm Hg). 78.1 g (yield=71%) of a yellow wax was obtained.

7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-Heptadecafluoro-3-thia-tetradecanoic acid: ¹H NMR (CDCl_3 , ppm) δ : 1.90 (qi, ³J_{HH}=6.9 Hz, $\text{CH}_2\text{CH}_2\text{S}$, 2H); 2.3 (m, $\text{R}_\text{F}\text{CH}_2$, 2H); 2.80 (t, ³J_{HH}=7.0 Hz, CH_2S , 2H); 3.25 (s, $\text{HO}_2\text{C}-\text{CH}_2\text{S}$, 2H); 11.7 (broad s, HO_2C , 1H).

¹⁹F NMR (CDCl_3 , ppm) δ : -82.6 (tt, CF_3 , 3F); -115.1 (m, CF_2CH_2 , 2F); -122.3 (m, $\text{C F}_2\text{CF}_2\text{CH}_2$, 2F); -123.5 (m, $\text{C}_3\text{F}_7\text{CF}_2\text{CF}_2\text{CF}_2$, 6F); -124.5 (m, $\text{C}_2\text{F}_5\text{CF}_2$, 2F); -127.1 (m, CF_3CF_2 , 2F).

2.2.2. By photochemical initiation

A similar reaction as above was carried out at 25–30°C in the presence of 0.32 g (1.7 mmol) benzophenone as the photoinitiator, 10.42 g (113.1 mmol) thioglycolic acid and 53.2 g (115.6 mmol) fluoroolefin. The mixture was UV-irradiated for 12 h and after a similar work-up, 51.2 g (92.7 mmol) fluorinated acid (yellow wax) were obtained (yield=82%). ¹H and ¹⁹F NMR characteristics were identical to those described above.

2.3. Radical addition of functional thiols to 1,1,2-trifluoro-1,4-pentadiene

2.3.1. Use of thioglycolic acid

2.3.1.1. Photochemical initiation (excess of diene: experiment 4). A Carius tube containing 0.055 g (0.3 mmol) benzophenone, 1.84 g (20 mmol) thioglycolic acid, 5.00 g (41 mmol) 1,1,2-trifluoro-1,4-pentadiene and 9.0 g acetonitrile was cooled in an acetone/liquid nitrogen mixture and degassed under vacuum by 5 thaw-freeze cycles to remove oxygen. Then, it was sealed and irradiated by a UV lamp for 16 h. After reaction, the tube was frozen in liquid nitrogen, opened and the solvent and volatiles were evaporated under vacuum (0.01 mm Hg). **1a** was first distilled yielding a 1.9 g yellow pale liquid, b.p.=87–90°C/0.15 mm Hg (yield =44%).

1,1,2-Trifluoro-6-thia-octenoic-8-acid (1a): ^1H NMR (CDCl_3 , ppm) δ : 1.81 (qi, $^3J_{\text{HH}}=7.2$ Hz, $\text{CH}_2\text{CH}_2\text{S}$, 2H); 2.32 (md, CFCH_2 , $^3J_{\text{HH}}=22.1$ Hz, 2H); 2.70 (t, $\text{CH}_2\text{CH}_2\text{S}$, $^3J_{\text{HH}}=7.2$ Hz, 2H); 3.21 (s, $\text{CH}_2\text{CO}_2\text{H}$, 2H). ^{19}F NMR (CDCl_3 , ppm) δ : -105.5 (ddt, $^2J_{\text{FFgem}}=87.7$ Hz; $^3J_{\text{FFcis}}=32.0$ Hz; $^4J_{\text{FH}}=2.7$ Hz, 1F); -124.5 (ddt, Fa, $^2J_{\text{FFgem}}=87.7$ Hz, $^3J_{\text{FFtr}}=113.8$ Hz; $^4J_{\text{Fah}}=3.7$ Hz, 1F); -175.0 (ddt, Fc, $^3J_{\text{FFcis}}=113.8$ Hz, $^3J_{\text{FFbvic}}=32.1$ Hz, $^3J_{\text{FH}}=22.1$ Hz, 1F). ^{13}C NMR (CDCl_3 , ppm) δ : 24.16 (dd, $^2J_{\text{CF}}=21.4$ Hz, $^3J_{\text{CF}}=2.3$ Hz, CF-CH_2); 24.59 (d, $^3J_{\text{CF}}=3.3$ Hz, $\text{CH}_2\text{CH}_2\text{CF}$); 31.44 (s, $\text{CH}_2\text{SCH}_2\text{CO}_2\text{H}$); 33.18 (s, $\text{SCH}_2\text{CO}_2\text{H}$); 126.8 (ddd, $^1J_{\text{CF}}=235.8$ Hz, $^2J_{\text{CF}}=53.3$ Hz, $^2J_{\text{CF}}=15.5$ Hz, CF); 153.1 (ddd, $^1J_{\text{CF}}=286.0$ Hz, $^1J_{\text{CF}}=272.7$ Hz, $^2J_{\text{CF}}=46.9$ Hz, CF_2); 177.02 (s, CO).

2.3.1.2. Photochemical initiation (three fold excess of mercaptan: experiment 7). A similar experiment as above was performed in the presence of 0.083 g (0.46 mmol) benzophenone, 8.42 g (91.5 mmol) thioglycolic acid, 3.72 g (30.5 mmol) 1,1,2-trifluoro-1,4-pentadiene and 10.0 g acetonitrile. After the same work-up and distillation of the excess of thioglycolic acid, 5.29 g of a yellow wax were obtained (yield=81%).

3,3,4-Trifluoro-2,8-dithia-1,9-nonane diacid (2a). ^1H NMR (CDCl_3 , ppm) δ : 1.8 (qi, $^3J_{\text{HH}}=7.2$ Hz, $\text{CH}_2\text{CH}_2\text{S}$, 2H); 1.95 (AB syst., CFHCH_2 , 2H); 2.7 (t, $^3J_{\text{HH}}=7.2$ Hz, $\text{C}_2\text{H}_4\text{CH}_2\text{S}$, 2H); 3.2 (s, $\text{C}_3\text{H}_6\text{SCH}_2$, 2H); 3.3 (s, CF_2SCH_2 , 2H); 4.65 (md, $^2J_{\text{HF}}=48.0$ Hz, $^3J_{\text{HH}}=3.9$ Hz, 1H); 10.3 (broad s, CO_2H , 2H). ^{19}F NMR (CDCl_3 , ppm) δ : AB system at -84.3 (Fa, $^2J_{\text{FaFb}}=217.5$ Hz) and -87.8 (Fb, $^2J_{\text{FaFb}}=217.5$ Hz, $^3J_{\text{FF}}=7.7$ Hz, $^3J_{\text{FH}}=16.5$ Hz, 1F); -193.1 (complex multiplet, X part, CFH, 1F).

2.3.1.3. Addition in the presence of radical initiator (a) in the presence of AIBN: experiment 1). A sealed Carius tube was heated at 80°C for 7 h containing a stirred mixture of 0.049 g (0.3 mmol) AIBN, 1.5 g (16.3 mmol) thioglycolic acid, 1.99 g (16.3 mmol) diene and 10 g acetonitrile. After reaction and opening of the tube, the solvent and the unreacted starting materials were evaporated. The brown residue was flash-chromatographed over a silica bed with diethyl ether leading to an orange oil. The overall yield was 46%. According to the integration of the characteristic signals in the ^1H and ^{19}F NMR spectra, the amounts of **1a**, **2a** and **3a** were 26%, 37% and 37%, respectively.

A similar experiment initiated by *t*-butyl cyclohexyl peroxycarbonate at 60°C for 5 h led to 68% of **1a**, 7% of **2a** and 25% of **3a** with an overall yield of 67%.

4,5,5-Trifluoro-6-thia-octanoic-8-acid (3a). ^1H NMR (CDCl_3 , ppm) δ : 3.7 (m, $\text{CH}_2\text{CH}=\text{CH}_2$, 2H); 4.7 (dm, CFH, $^2J_{\text{FH}}=48.3$ Hz, $^3J_{\text{FH}}=22.1$ Hz, 1H); 5.2 (m, $=\text{CH}_2$, 2H); 5.8 (m, CH=, 1H). ^{19}F NMR (CDCl_3 , ppm) δ : AB system at -83.7 ($^2J_{\text{FF}}=217.3$ Hz, $^3J_{\text{FF}}=7.8$ Hz, $^3J_{\text{FH}}=17.8$ Hz) and -87.2 ($^2J_{\text{FF}}=217.4$ Hz, $^3J_{\text{FF}}=9.1$ Hz, $^3J_{\text{FH}}=16.1$ Hz); -193 (X part of ABX system, m).

(b) In the presence of di-*t*-butyl peroxide: (experiment 3): In similar conditions as above, 5.00 g (0.04 mol) diene, 3.80 g (0.04 mol) thioglycolic acid, 0.117 g (0.8 mmol) di-*t*-butylperoxide and 10 ml acetonitrile reacted together. After stirring at 140°C for 6 h and opening the tube, the solvent was evaporated and the residue was dried at 55°C under 0.1 mm Hg until constant weight. A brown viscous liquid was obtained (4.3 g) which is insoluble in chloroform, acetone, DMF, dimethylacetamide, THF and 1,2,2-trifluoroethane. The total yield was 49%.

2.3.2. Use of 2-mercapto ethanol (experiment 9)

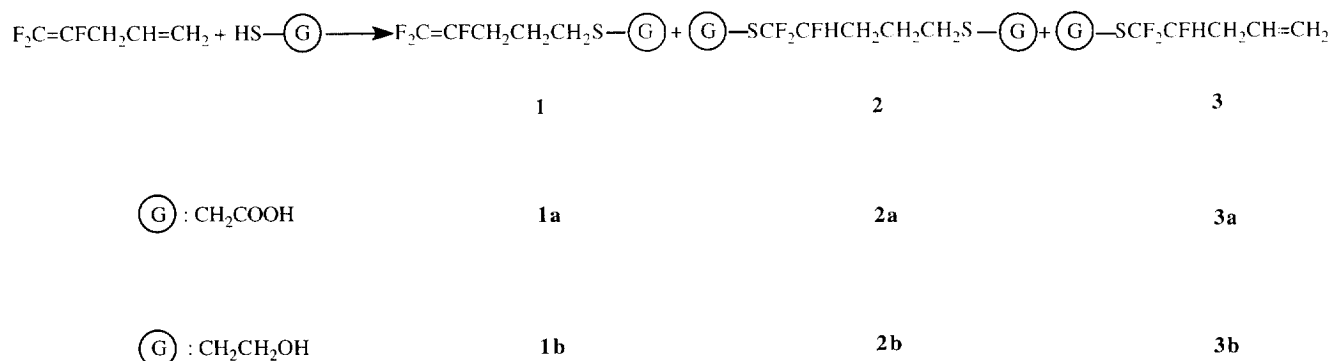
The reaction took place in a Carius tube containing a stirred mixture of 0.19 g (1.0 mmol) benzophenone, 2.70 g (34 mmol) 2-mercapto ethanol, 5.01 g (41 mmol) diene and 9.5 g acetonitrile. After six thaw-freeze cycles, the tube was exposed to UV light at room temperature (ca. 25°C) for 14 h. After similar work-up, the gross was purified and product **1b** was distilled. 2.03 g of a colourless liquid (yield=29%) was obtained; b.p.=65–66°C/1 mm Hg.

1,1,2-Trifluoro-6-thia-8-octanol (1b). ^1H NMR (CDCl_3 , ppm) δ : 1.80 (qi, $^3J_{\text{HH}}=7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$, 2H); 2.35 (ddd, $^3J_{\text{FH}}=22.1$ Hz, $^3J_{\text{HH}}=7.2$ Hz, $^4J_{\text{FH}}=4.2$ Hz, $^4J_{\text{FH}}=2.5$ Hz, $=\text{CFCH}_2$, 2H); 2.55 (t, $^3J_{\text{HH}}=7.2$ Hz, $\text{C}_2\text{H}_4\text{CH}_2\text{S}$, 2H); 2.65 (t, $^3J_{\text{HH}}=6.1$ Hz, $\text{CH}_2\text{CH}_2\text{OH}$, 2H); 2.85 (broad s shifted with CCl_3NCO , OH, 1H); 3.68 (t, $^3J_{\text{HH}}=6.1$ Hz, 2H, CH_2OH). ^{19}F NMR (CDCl_3 , ppm) δ : -105.55 (ddt, $^2J_{\text{FFgem}}=88.2$ Hz, $^2J_{\text{FFcis}}=31.8$ Hz, $^4J_{\text{FH}}=2.3$ Hz, 1F); -124.5 (ddt, $^2J_{\text{FFgem}}=88.5$ Hz, $^3J_{\text{FFtr}}=112.9$ Hz, $^4J_{\text{FH}}=3.8$ Hz, 1F); -175.15 (ddt, $^3J_{\text{FFtr}}=113.3$ Hz, $^3J_{\text{FFcis}}=33.0$ Hz, $^3J_{\text{FH}}=22.2$ Hz, 1F). ^{13}C NMR (CDCl_3 , ppm) δ : 24.2 (dd, $^2J_{\text{CF}}=21.9$ Hz, $^3J_{\text{CF}}=2.2$ Hz, CCH_2CF , 1C); 25.4 (d, $^3J_{\text{CF}}=2.3$ Hz, $\text{CH}_2\text{CH}_2\text{CF}$, 1C); 30.5 (s, $\text{C}_2\text{H}_4\text{CH}_2\text{S}$, 1C); 34.5 (s, S $\text{CH}_2\text{CH}_2\text{OH}$, 1C); 60.7 (s, CH_2OH , 1C); 128.0 (ddd, $^1J_{\text{CF}}=234.5$ Hz, $^2J_{\text{CF}}=53.4$ Hz, $^2J_{\text{CF}}=15.4$ Hz, $=\text{CF}$, 1C); 153.1 (ddd, $^1J_{\text{CF}}=285.9$ Hz, $^1J_{\text{CF}}=272.6$ Hz, $^2J_{\text{CF}}=47.2$ Hz).

Diol **2b** was purified by flash chromatography over a 1 cm layer of silica using diethyl ether as eluent (yellow oil).

4,4,5-Trifluoro-3,9-dithia undecane-1,11-diol (2b). ^1H NMR (CDCl_3 , ppm) δ : 1.82 (CH_2 , $^3J_{\text{HH}}=7.2$ Hz, $\text{CH}_2\text{CH}_2\text{S}$, 2H); 2.52 (m, CFH_2 , 2H); 2.57 (t, $^3J_{\text{HH}}=7.0$ Hz, $\text{C}_2\text{H}_4\text{CH}_2\text{SH}$, 2H); 2.65 (broad s shifted with Cl_3CNCO [40], OH, 2H); 2.71 (t, $^3J_{\text{HH}}=7.2$ Hz, $\text{C}_3\text{H}_6\text{SCH}_2$, 2H); 3.05 (t, $^3J_{\text{HH}}=7.2$ Hz, CH_2SCF_2 , 2H); 3.70 (t, $^3J_{\text{HH}}=7.1$ Hz, $\text{C}_3\text{H}_6\text{SCH}_2\text{CH}_2\text{OH}$, 2H); 3.82 (t, $^3J_{\text{HH}}=7.2$ Hz, $\text{HOCH}_2\text{-CH}_2\text{SCF}_2$, 2H); 4.55 (dm, $^2J_{\text{FH}}=48.1$ Hz). ^{19}F NMR (CDCl_3 , ppm) δ : AB system centred at -83.5 (A part, $^2J_{\text{FaFb}}=217.9$ Hz, $^3J_{\text{Fah}}=18.2$ Hz, $^3J_{\text{Fafx}}=7.9$ Hz, 1F) and -86.5 (B part, $^2J_{\text{FaFb}}=217.8$ Hz, $^3J_{\text{Fbfx}}=6.8$ Hz, $^3J_{\text{Fbh}}=11.8$ Hz, 1F); X part centred at -193.0 (complex multiplet).

4,5,5-Trifluoro-6-thia octene-8-ol (3b). ^1H NMR (CDCl_3 , ppm) δ : 2.65 (m, $\text{CH}_2\text{CH}=\text{CH}_2$, 2H); 2.75 (broad s shifted with CCl_3NCO , OH, 1H); 3.01 (t, $^3J_{\text{HH}}=6.1$ Hz, $\text{HOCH}_2\text{CH}_2\text{S}$, 2H); 3.75 (t, $^3J_{\text{HH}}=6.1$ Hz, HOCH_2 , 2H); 4.6 (dm,



Scheme 1. Radical addition of functional thiols to 1,1,2-trifluoro-1, 4-pentadiene.

$^2J_{\text{FH}}=49.3$ Hz, CFH, 1H); 5.15 (m, =CH₂, 2H); 5.80 (m, =CH, 1H). ¹⁹F NMR (CDCl₃, ppm) δ: AB system at -86.9 ($^2J_{\text{FF}}=212.9$ Hz, $^3J_{\text{FH}}=17.2$ Hz, $^3J_{\text{FF}}=9.0$ Hz) and -83.5 ($^2J_{\text{FF}}=200.4$ Hz, $^3J_{\text{FF}}=9.1$ Hz and $^3J_{\text{FH}}=17.9$ Hz, CF₂, 2F); -192.3 (m, CFH, 1F). ¹³C NMR (CDCl₃, ppm) δ: 32.5 (s, HOCH₂CH₂S); 41.7 (dt, $^2J_{\text{CF}}=26.5$ Hz, $^3J_{\text{CF}}=2.5$ Hz, CFHCH₂); 61.4 (s, CH₂OH); 91.8 (dt, $^1J_{\text{CF}}=186.1$ Hz, $^2J_{\text{CF}}=29.3$ Hz, CFH); 118.8 (s, =CH₂); 128.1 (td, $^1J_{\text{CF}}=282.3$ Hz, $^2J_{\text{CF}}=26.0$ Hz, CF₂); 131.0 (d, $^3J_{\text{CF}}=3.0$ Hz, HC=CH₂).

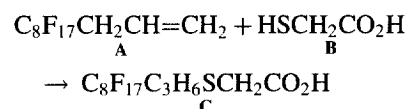
3. Results and discussion

The radical addition of two functional mercaptans (thioglycolic acid, 2-mercapto ethanol) to 1,1,2-trifluoro-1,4-pentadiene was attempted via two different initiation ways. Indeed, this addition can be promoted either photochemically or in the presence of radical initiators. For each reaction, three different telechelic derivatives can be expected coming from the radical addition of mercaptan to either the hydrogenated or the fluorinated double bonds, or both, as shown in Scheme 1.

The radical addition of thiols to fluorinated alkenes has already led to interesting results [28–35]; however, to our knowledge, the literature is rather poor for similar addition of mercaptans to fluorinated allyl olefins. Hence, a model reaction was first performed by adding thioglycolic acid to an allylic fluorinated olefin.

3.1. Model reaction

The model reaction concerned the radical addition of thioglycolic acid to 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro undecene since it can be assumed that the perfluorooctyl group has a similar electron-withdrawing effect as a trifluorovinyl group. The reaction is as follows:



The fluorinated monomer was previously obtained from the radical addition of perfluorooctyl iodide to allyl acetate followed by a deiodoacetatization in the presence of zinc [36]. The addition of this carboxylic mercaptan to that olefin was carried out either photochemically or in the presence of AIBN as the radical initiator, using an equimolar amount of thioglycolic acid and fluoroalkene. After purification, the original fluorinated acid was characterized by ¹⁹F and ¹H NMR. The ¹H NMR spectrum of fluoro acid C shows the absence of the triplet centred at 2.0 ppm and that of the complex system in the 5.0–6.0 ppm range assigned to the SH group of the thiol and to the ethylenic protons of the fluorinated allylic reactant, respectively. The fluorinated acid was easily characterized by the various expected signals and especially its quintet centred at 1.90 ppm assigned to the methylene group between two CH₂ groups.

The yields of the synthesis of fluorinated acid C were 71% and 82% from the allylic olefin A, and 48% and 55% from the perfluorooctyl iodide B, by radical or photochemical initiations, respectively.

The successful synthesis was thus applied to the radical addition of mercaptan to 1,1,2-trifluoro-1,4-pentadiene (Scheme 1). The results are listed in Table 1 and are commented on hereafter, by considering the reactions involving both different thiols, step by step.

3.2. Radical addition of functional mercaptans to 1,1,2-trifluoro-1,4-pentadiene

3.2.1. Use of thioglycolic acid

As above, two methods of initiation have been chosen: photochemical or chemical initiation (use of radical initiators) (Table 1).

3.2.1.1. Photoinduced reaction. Knowing that mercaptans can be added to fluorinated double bonds [28–35], three products of addition can be expected (1a, 2a and 3a) (Scheme 1). Our strategy is based on the preparation of one compound selectively in order to know its NMR characteristics. Hence, a first attempt was performed to synthesize fluorinated α, ω-diacid 2a by a three fold

Table 1

Experimental conditions and overall yield for the radical addition of mercaptan G-SH to 1,1,2-trifluoro-1,4-pentadiene (CHPC, DTBP and benz., mean initial *t*-butyl cyclohexyl peroxy carbonate, di-*t*-butylperoxide and benzophenone, respectively)

Experiment No.	G of thiol	$\frac{FUNC[\text{thiol}]_0}{FUNC[\text{diene}]_0}$	Initiator	<i>T</i> (°C)	<i>t</i> (h)	Overall yield (%)	1 (%)	2 (%)	3 (%)
1	CH ₂ CO ₂ H	1.0	AIBN	80	7	46	45	18	37
2	CH ₂ CO ₂ H	1.0	CHPC	60	5	67	68	7	25
3	CH ₂ CO ₂ H	1.0	DTBP	140	6	49 (wt)	Insoluble product		
4	CH ₂ CO ₂ H	0.5	UV, benzene	25	16	83	89(44 ^a)	7	4
5	CH ₂ CO ₂ H	0.8	UV, benzene	25	24	85	85	5	10
6	CH ₂ CO ₂ H	1.5	UV, benzene	25	15	80	42	35	23
7	CH ₂ CO ₂ H	3.0	UV, benzene	25	19	81	0	100	0
8	C ₂ H ₄ OH	0.1	CHPC	60	6	68	65	17	18
9	C ₂ H ₄ OH	0.8	UV, benzene	25	14	67	71(29 ^a)	15	24

^{initial} [initiator]₀/[diene]₀ = 0.02 for each case.

^ayield calculated from distilled product.

excess of thioglycolic acid to 1,1,2-trifluoro-1,4-pentadiene (experiment 7).

After 19 h-reaction at 25°C and elimination of unreacted starting materials, the **2a** telechelic product was characterized by NMR spectroscopy. GC analysis and ¹H and ¹⁹F NMR showed the absence of the mercaptan and that of the fluorinated diene (absence of signals at -106.3, -125.1 and -174.3 ppm in the ¹⁹F NMR spectrum and that of the signals centred at 3.0, 5.2 and 5.8 ppm from ¹H NMR).

The presence of diacid **2a** was proved by ¹H and ¹⁹F NMR spectroscopy. First, its ¹⁹F NMR spectrum shows an ABX system, the AB part being centred at -86 ppm while the X part shows a complex signal centred at -193 ppm. The AB part is easily identified by its eight characteristic bands assigned to both fluorine atoms and centred at -84.3 and -87.7 ppm, with large coupling constants: ²J_{FF} = 216.8 Hz. Such a behaviour confirms the results observed by Harris and Stacey [28] when they characterised telomers of trifluoroethylene with mercaptans.

In the ¹H NMR spectrum, the most interesting feature is the doublet (²J_{FH} = 48.5 Hz) of multiplets centred at 4.65 ppm, assigned to the CFH group. It is also noteworthy that the thiol radical attacked the CH₂ end-group of the diene selectively and not the =CH because of the absence of a doublet in the 0.8–1.9 ppm range assigned to the methyl groups of β-adducts HO₂CCH₂SCH(CH₃)CH₂-CF=CF₂ and HO₂CCH₂SCH(CH₃)CH₂CFHCF₂SCH₂CO₂H.

After having ascribed the different chemical shifts of the diacid **2a**, it was easier to deduce those of products **1a** and **3a** in order to calculate the amounts of these three products, given in Table 1 (experiments 1–6).

The percentages of each product **1a**, **2a** and **3a** can be determined by considering the integration of the characteristic signals from the ¹H and ¹⁹F NMR spectra of the grosses of the reactions, dried at reduced pressure (2–5 mm Hg) at 40°C to constant weight (i.e. after total evaporation of 1,1,2-trifluoro-1,4-pentadiene (b.p. = 38°C/760 mm Hg) and thioglycolic acid (bp = 96°C/5 mm Hg)). For instance,

the ¹⁹F NMR spectrum (Fig. 1) allows calculation of the amount of compound **1a**: in practice, from the integrations of peaks centered at -105.0 ppm (*I*₁), -124.0 ppm (*I*₂) and -175.0 ppm (*I*₃) assigned to the fluorine atoms born by both ethylenic carbons of **1a**, and from that (*I*₄) of the multiplied doublet centred at -192.0 ppm corresponding to the CFH group of **2a** and **3a**, the percentage of product **1a** is:

$$\%1\mathbf{a} = \frac{\alpha}{\alpha + I_4} \quad \text{where } \alpha = \frac{I_1 + I_2 + I_3}{3}$$

The amounts of **2a** and **3a** were determined from the ¹H NMR spectrum which shows a doublet of multiplets centred at 4.65 ppm assigned to the CFH group of **2a** and **3a** (integration *I*₅) and two multiplets centred at 5.2 and 5.8 (*I*₆) ascribed to ethylenic protons of **3a** (=CH₂ and =CH groups, respectively). Hence, the relative amount of **3a** is $\frac{I_6}{I_5}$ leading to the percentages of **3a** and **2a**:

$$\%3\mathbf{a} = (100 - \%1\mathbf{a}) \times \frac{I_6}{I_5} \quad \%2\mathbf{a} = (100 - \%1\mathbf{a}) \left(1 - \frac{I_6}{I_5}\right)$$

In addition to these characteristic signals, is noted the distinct and interesting AB part of the ABX system of products **2a** and **3a**, in the ¹⁹F NMR spectrum assigned to the CF₂CFH group. The eight bands ascribed to each anisochronous fluorine atom are meat for both products (chemical shifts at about -84 and -87 ppm). The coupling constants are the following:

$${}^2J_{FF} = 217.4 \text{ Hz} \quad {}^3J_{FF} = 7.8 \text{ Hz} \quad {}^3J_{FH} = 16.5 \text{ Hz}$$

Several experimental conditions were chosen by modifying the reaction time and the initial [mercaptan]₀/[diene]₀ molar ratio and the results are listed in Table 1. Interestingly, an excess of diene was necessary to make negligible the amounts of telechelic **2a** and **3a** products. The expected trifluorovinyl ω-carboxylic acid was thus produced in good yield and purified by distillation. Beside unambiguous ¹H and ¹⁹F NMR spectra, the ¹³C NMR spectrum confirmed the purity of **1a**. It shows the expected doublets of doublets of

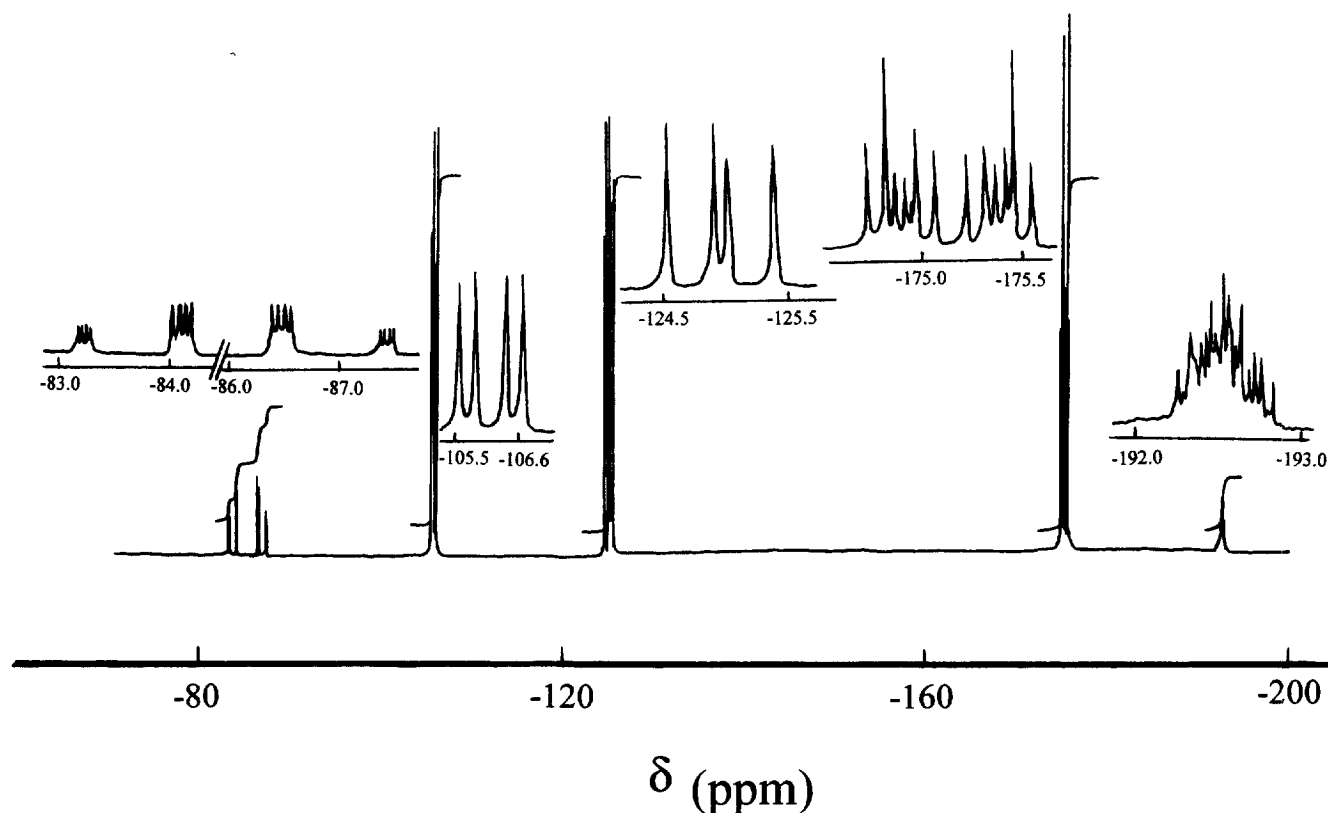


Fig. 1. ^{19}F NMR spectrum of the crude product of experiment 1 after drying under reduced pressure.

doublets centred at 126.8 and 153.1 ppm attributed to $=\text{CF}$ and $\text{F}_2\text{C}=\text{}$ groups, respectively. In addition, are noted two close signals: that centred at 24.16 ppm is a doublet ($^2J_{\text{CF}} = 21.4$ Hz) of doublets ($^3J_{\text{CF}} = 2.4$ Hz) assigned to the methylene group adjacent to the trifluorovinyl extremity, high field shifted about its adjacent CH_2 group centred at 24.59 ppm. Such an observation is not surprising since it was already noted in the ^{13}C NMR assignments of $\text{F}_2\text{C}=\text{CFCH}_2\text{CH}_2\text{CH}_2\text{OH}$ when compared to those of $\text{F}_2\text{C}=\text{CFCH}_2\text{OH}$ [16].

It is noted that the selective preparation of the perfluorovinyl compound was almost possible by UV initiation, and that a two fold excess of diene was necessary. The overall yields were high and in the best conditions, 80% yield of **1a** was obtained.

To try to improve the yields, the reaction was performed by radical addition of mercaptan in the presence of initiators.

3.2.1.2. Radical initiation. Three radical initiators were chosen and used at a temperature for which their half life was 1 h: AIBN, *t*-Bu cyclohexyl-peroxycarbonate (CHPC) and di-*t*-butyl peroxide (DTBP) used at 80, 60 and 140°C, respectively.

Initially, the overall yields were worse than those obtained for a photochemical initiation, with poor percentage of perfluorovinyl compound (Table 1).

Interestingly, when the reaction temperature was lowered, a higher overall yield was obtained and a better selectivity of synthesis of product **1a** was observed. This may be due to an increase of by-products with a higher temperature when radical reactions are performed, especially when a transfer reaction occurs. Such behaviour is likely since mercaptans are known to act as efficient transfer agents and thus it is not surprising to observe an increase of formation of diacid by raising the temperature from experiment 2 to experiment 1.

Further, such selectivity decreases and more side reactions seem to occur when the reaction was carried out at 140°C (experiment 3). At this temperature, no improvement was noted, and a product insoluble in usual organic solvents (acetone, DMF, THF, DMAC, 1,1,2-trifluoro-1,2,2-trichloroethane, chloroform) was obtained. A polymer was probably produced by polythioesterification, polycondensation or a transfer reaction creating a cross-linking network.

Hence, to increase the 1:1 selectivity, it was necessary to use a two-fold excess of diene; this diene being easily recovered by distillation.

According to the above results for the addition of thio-glycolic acid to 1,1,2-trifluoro-1,4-diene, we have shown that the photochemical initiation led to higher overall yields with a high amount of $\text{CF}_2=\text{CFC}_3\text{H}_6\text{SCH}_2\text{CO}_2\text{H}$ (**1a**). This seems to confirm previous investigations on the grafting of fluorinated thiols to the double bonds of hydroxyl telechelic polybutadienes. These reactions showed higher reactivity

and selectivity of the mercaptans from photoinduced addition [37] than from initiation in the presence of various radical initiators [38].

Hence, the photochemical method was applied for similar reactions involving other functional thiols such as 2-mercapto ethanol, 3-mercaptopropyl trimethoxysilane and thiol-acetic acid. The reactions involving the two last products will be described in a forthcoming article [39].

3.2.2. Radical addition of 2-mercapto ethanol to fluorinated diene

3.2.2.1. In the presence of initiator. An equimolar mixture composed of this thiol and the 1,1,2-trifluoro-1,4-pentadiene initiated by *t*-butyl cyclohexyl peroxy-carbonate for 6 h led to an overall yield of 68% with poor yield of perfluorovinyl ω -hydroxyl monomer (experiment 8). A similar calculation from ^1H and ^{19}F NMR integrations as above was required to determine the amounts of each product.

3.2.2.2. Photochemical-induced addition. The photochemical initiation of a mixture containing an excess of diene led to a higher percentage of perfluorovinyl **1b** monomer (experiment 9). After distillation, this hydroxyl monomer was characterized by ^1H and ^{19}F NMR spectroscopy. The ^1H NMR spectrum clearly shows the absence of the hydrogenated double bond and the presence of the characteristic triplets assigned to the methylene groups adjacent to sulfur and oxygen atoms. However, the complex signal (doublet of doublets of doublets of triplets) centred at 2.35 is ascribed to the methylene group adjacent to the trifluorovinyl end-group.

The ^{19}F NMR spectrum was simpler and rather similar to that of the diene precursor or acid **1a**.

The unsaturated **3b** compound was distilled and characterized without any ambiguity. Its ^1H NMR spectrum shows the presence of the hydrogenated double bond proved by both complex signals centred at 5.15 and 5.80 ppm and the doubled signal centred at 4.60 ppm assigned to the CFH group. The ^{19}F NMR spectrum exhibits the expected ABX system; its AB part is assigned to the CF₂ group centred at -86.9 ppm whereas the X part gives a complex signal at -192.3 ppm.

The residue was chromatographed over a silica column and led to the fluorinated diol **2b**. It was easily characterized by ^1H and ^{19}F NMR showing similar signals to those observed for the unsaturated compound **3b** without any signal in the 4.8–6.0 ppm range.

4. Conclusions

The synthesis of new perfluorovinyl functional monomers containing a thioether bridge can be simply achieved from the photochemical addition of functional thiols to an excess

of 1,1,2-trifluoro-1,4-pentadiene. Such a reaction is simple, quick, performed at room temperature and this addition seems more selective on the hydrogenated double bond, contrary to that induced by radical initiators. This reaction is also influenced by the electron-withdrawing group of the mercaptan that directs the overall yield and selectivity of the addition, showing that thioglycolic acid was more efficient than 2-mercaptoethanol.

These fluorovinyl derivatives are interesting comonomers for the copolymerization of commercially available fluoro-olefins leading to a possible new generation of fluorinated functional elastomers, now under investigation.

Acknowledgements

The authors would like to express their gratitude to the Ministère Français de l'Enseignement Supérieur et de la Recherche for an associate professor's position at ENSC Montpellier (to GK) and for a grant administrated by the Centre International des Etudiants et Stagiaires (to PP). Gifts of chlorotrifluoroethylene from Elf Atochem and Solvay were also greatly appreciated. Professor Fruchier (Head for NMR of ENSCM) is also acknowledged for fruitful discussions.

References

- [1] M.Y. Yamabe, *Makromol. Chem. Macromol. Symp.* 64 (1992) 11.
- [2] R.E. Banks, *Preparation, Properties and Industrial Applications of Organofluorine Compounds*, Wiley, Chichester, 1982.
- [3] B. Boutevin, B. Améduri, 34th Int. Microsymp., Prague Meeting on Macromolecules, Fluorinated Monomers and Polymers, 19–22 July 1993; *Makromol Chem. Macro. Symp.* 82 (1994) 1.
- [4] G.K. Kostov, O. Matsuda, S. Machi, Y. Tabata, *J. Poly. Sci. Part A, Poly. Chem.* 17 (1979) 3991.
- [5] G.K. Kostov, P.Ch. Petrov, *J. Poly. Sci. Part A, Poly. Chem.* 30 (1992) 10836.
- [6] T. Uchino, M. Hisasue, H. Kojima, *Asahi Glass*, U.S. Patent 4151342 (24/04/79); *Chem. Abstr.* 91 (1979) 58473.
- [7] H. Nishimura, M. Ichimura, M. Hisasue, *Asahi Glass*, *Jap. Patent* 54046286 (12/04/79); *Chem. Abstr.* 91 (1979) 75333.
- [8] Y. Nakano, H. Miyazaki, K. Watanabe, *Asahi Glass Co., Ltd.*, *Jap. Patent* 62073944 (27/09/85) 107 (1987) 98345.
- [9] A. Ohmori, N. Tomihashi, H. Inukai, Y. Shimizu, *Daikin Kogyo*, *Eur. Patent* 0135917 (16/03/88); *Chem. Abstr.* 103 (1985) 38796.
- [10] A.I. Ohmori, N. Tomihashi, H. Inukai, Y. Shimizu, *Eur. Patent Appl.* 0138091 to Daikin, Kogyo, (20/08/84).
- [11] I. Ohmori, N. Tomihashi, H. Inukai, Y. Shimizu, *US Patent* 4564717 to Daikin Kogyo, (14/01/86).
- [12] Daikin Kogyo, *Jap. Patent* 60/067,518 (21/09/83); (*Chem. Abstr.* 103 (1985) 55550).
- [13] M. Tatemoto, T. Nakamura, *Eur. Pat. Appl.* EP 398,250 (to Daikin) 22/11/90; (*Chem. Abstr.* 114:103040).
- [14] P. Tarrant, P. Johncock, J. Savory, *J. Org. Chem.* 28 (1963) 839.
- [15] Z. Chvatal, J. Muzac, V. Marousek, 34th Int. Microsymp. Prague Meetings on Macromolecules Fluorinated Monomers and Polymers, 19–22 July 1993.
- [16] B. Améduri, B. Boutevin, G. Kostov, P. Petrova, *J. Fluor. Chem.*, in press.

- [17] C.M. Hu, Q.S. Hu, Y.L. Qui, J. Chen, *J. Fluor. Chem.* 66 (1994) 171.
- [18] Z.Y. Yang, B.V. Nguyen, D.J. Burton, *Synth. Lett.* 2 (1992) 141.
- [19] G. Guglielmo, G. Gambaretto, *Eur. Pat. Appl. EP 201871* (20/11/86), (Chem. Abstr., 106 (1987) 66747n).
- [20] S.V. Kotov, S.D. Pederson, W. Qiu, Z.M. Qiu, D.J. Burton, *J. Fluor. Chem.* 82 (1997) 13.
- [21] J.B. Marshall, Kalrez[®]-type perfluoroelastomers: synthesis, properties and applications, in: J. Scheirs, (Ed.), *Modern Fluoropolymers*, Wiley, New York, 1997, Chap. 19, p. 349.
- [22] A.E. Fiering, *J.M.S. Pure Appl. Chem.* A31 (1994) 1657.
- [23] T. Nguyen, C. Wakselman, *J. Org. Chem.* 54 (1989) 5640.
- [24] T. Nguyen, C. Wakselman, *J. Fluor. Chem.* 74 (1995) 273.
- [25] B. Améduri, B. Boutevin, A. Fruchier, G. Kostov, P. Petrova, *J. Fluor. Chem.* 89 (1998) 167.
- [26] T.I. Gorbunova, M.I. Kodess, A.V. Podol'Skii, V.I. Saloutin, *Zh. Obshch Khim.* 61 (1991) 2364 (Chem. Abstr. 116 (1991) 151082).
- [27] B. Améduri, B. Boutevin, Telomerization, in: D. Bloor, R.J. Brooke, R.D. Flemings, S. Mahajan, (Eds.), *Encyclopedia Advance Materials*, Pergamon Press, Oxford, p. 2767.
- [28] J.F. Harris, F.W. Stacey, *J. Am. Chem. Soc.* 85 (1963) 749.
- [29] B. Boutevin, Y. Furet, Y. Hervaud, G. Rigal, *J. Fluor. Chem.* 69 (1994) 11.
- [30] J.F. Harris, F.W. Stacey, *J. Am. Chem. Soc.* 83 (1961) 840.
- [31] B. Boutevin, Y. Furet, Y. Hervaud, G. Rigal, *J. Fluor. Chem.* 74 (1995) 37.
- [32] B.A. Shainyan, *Sulfur Lett.* 11 (1990) 109.
- [33] O. Beaune, J.M. Bessière, B. Boutevin, A. El Bachiri, *J. Fluor. Chem.* 73 (1995) 27.
- [34] B. Boutevin, F. Cersosimo, B. Youssef, P. Kappler, *J. Fluor. Chem.* 52 (1991) 403.
- [35] H.P. Guan, B.H. Luo, C.M. Hu, *J. Fluor. Chem.* 85 (1997) 141.
- [36] B. Améduri, B. Boutevin, M. Nouri, M. Talbi, *J. Fluor. Chem.* 74 (1995) 191.
- [37] B. Boutevin, Y. Hervaud, M. Nouri, *Eur. Polym. J.* 26 (1990) 877.
- [38] B. Améduri, B. Boutevin, M. Nouri, *J. Polym. Sci., Part A, Polym. Chem.* 31 (1993) 2069.
- [39] B. Améduri, B. Boutevin, G. Kostov, P. Petrova, *J. Appl. Polym. Sci.*, submitted.
- [40] M. Duc, B. Améduri, B. Boutevin, M. Kharroubi, *Macromol. Chem. Phys.*, 199 (1998).