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New polyfluoroalkoxysulfonyl fluorides. Part IX. A new fluoroacrylate ester – monomer and polymer

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Abstract

The synthesis and characterization of a novel fluoroacrylate ester containing the fluorosulfonyl group (SO_2F) has been carried out. This ester, $H_2C{=}CHC(O)O(CH_2)_2(CF_2)_2O(CF_2)_2SO_2F$ (1), was successfully polymerized in bulk and as a film. Infrared, mass and NMR spectra are presented in order to support the assigned structures.

Keywords: Polyfluoroalkoxysulfonyl fluorides; Fluoroacrylate ester monomer; Fluoroacrylate ester polymer; NMR spectroscopy; IR spectroscopy; Mass spectrometry

1. Introduction

For a number of years we have been interested in preparing novel monomeric and polymeric systems containing the fluorosulfonyl group [1–6]. Fluorosulfonyl molecular systems containing double bonds [1–3], a triple bond [2], aromatic groups [4], the epoxide group [5] and the alcohol group [6] have been prepared. The utilization of fluorocarbons containing the fluorosulfonyl group as ion-exchange resins, fuel cell electrolytes, surface-active agents and in the preparation of strong sulfonic acids continues to make them a subject of considerable interest [7–10]. Fluoroalkylacrylate esters are useful in preparing a number of useful polymeric coatings and films [11–14]. Therefore, it was of interest to incorporate into the acrylate system the fluorosulfonyl group by treatment of $HO(CH_2)_2(CF_2)_2O(CF_2)_2SO_2F$ [2] with acrylic acid.

2. Experimental details

2.1. Materials

The alcohol $HOCH_2CH_2CF_2CF_2OCF_2CF_2SO_2F$ was prepared according to the literature method [2]. The acrylic acid (Aldrich) and trifluoroacetic anhydride (PCR, Inc.) and all other chemicals were used as received.

2.2. General procedures

Infrared spectra were obtained as capillary films on sodium chloride windows for liquid samples and as thin films for solid samples using a Nicolet 20DX spectrometer. NMR spectra were recorded with a Varian EM390 spectrometer operating at 90 MHz for proton and 84.7 MHz for fluorine resonances or with a Bruker AMX-400 spectrometer operating at 400, 376.5 and 100.6 MHz for proton, fluorine and carbon resonances; $(CH_3)_4Si$, $CFCl_3$, CD_3Cl and CD_3CN were used as internal standards. In ^{19}F spectra, chemical shifts upfield from $CFCl_3$ are assigned negative values. ^{13}C NMR data are for proton-decoupled spectra, except where noted. Mass spectra were obtained using a Hewlett Packard HP5890 series II gas chromatograph with a 5970 mass selective detector utilizing a 15 m DB-5 column.

Elemental analyses were determined by Beller Microanalytical Laboratory in Göttingen, Germany.

2.3. Preparation of $H_2C{=}CHC(O)OCH_2CH_2CF_2CF_2OCF_2CF_2SO_2F$ (1)

To a 10 ml two-neck round-bottomed flask, containing a Teflon-coated stirring bar and fitted with a rubber septum, was attached a Claisen adaptor with a thermometer reaching to the bottom of the flask and a reflux condenser with a calcium chloride drying tube. The flask was placed in an ice bath and 8.8 mmol of freshly distilled acrylic acid added along with a trace of hydroquinone. Trifluoroacetic anhydride (8.7

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mmol) was added slowly with stirring at a rate that kept the solution temperature below 15 °C. The ice bath was removed and the solution stirred for an additional 15 min. Addition of 8.7 mmol of $HOCH_2CH_2CF_2CF_2OCF_2CF_2SO_2F$ over 15 min caused the mixture to reach 25 °C. The solution was stirred an additional 90 min and then washed twice with 5 ml of water, twice with 5% sodium bicarbonate solution and then again with water containing a trace of hydroquinone. Distillation under dynamic vacuum (0.5 Torr/35 °C) resulted in 1.02 g of product containing unreacted $HOCH_2CH_2CF_2CF_2OCF_2CF_2SO_2F$, $H_2C{=}CHC(O)OCH_2CH_2CF_2CF_2OCF_2CF_2SO_2F$ and polymerized product. Separation by column chromatography using SiO_2 and diethyl ether resulted in 0.5 mmol of $H_2C{=}CHC(O)OCH_2CH_2CF_2CF_2OCF_2CF_2SO_2F$ (6% yield).

IR (cm^{-1}): 3044 (vw); 2974 (w); 2925 (w); 2859 (w); 1797 (w); 1735 (s); 1639 (w); 1622 (w); 1464 (vs); 1411 (m); 1352 (m); 1326 (m); 1299 (s); 1273 (s); 1247 (vs); 1210 (vs); 1190 (vs); 1151 (vs); 1115 (vs); 1082 (s); 989 (s); 973 (m); 910 (w); 821 (s); 811 (s); 778 (m); 706 (w); 646 (m); 606 (s). ^1H NMR ($CDCl_3$, int. TMS): relative integration areas $H_2C{=}CH$ (3.0), $C(O)CH_2$ (1.9), CH_2CF_2 (2.1). ^{19}F NMR ($CDCl_3$, ext. $CFCl_3$): relative integration areas CH_2CF_2 (2.1), CF_2O (2.1), OCF_2 (2.1), CF_2S (2.1), SO_2F (1.0). MS (*m/e*, species) EI^+: 398 $(M)^+$; 127 $(C_4H_3F_4)^+$; 113 $(C_3H_4F_2O)^+$; 105 $(C_4H_3F_2O)^+$; 100 $(CF_2CF_2)^+$; 99 $(CH_2CHCO_2CH_2CH_2)^+$; 85 $(CH_2CHCO_2CH_2)^+$; 78 $(C_3H_4F_2)^+$; 73 $(CH_2CHCO_2H_2)^+$; 64 $(C_2H_2F_2)^+$; 55 $(CH_2CHCO)^+$; 44 $(CO_2)^+$. Analysis: Calc. for $C_9H_7F_9SO_5$: C, 27.15; H, 1.77; F, 42.9; S, 8.05%. Found: C, 26.69; H, 1.99; F, 43.1; S, 7.83%.

2.4. Preparation of polymer 2

Solution polymerization

Into a 5 ml round-bottomed flask, fitted with a septum cap and a reflux condenser topped by a calcium chloride drying tube, was placed a Teflon-coated stirring bar and 2 ml of distilled acetone containing 0.72 mmol (0.29 g) of the acrylate monomer **1**. Half of the initiator (AIBN) solution, 0.06 mmol (0.01 g) in 1 ml of acetone, was added to the solution with stirring. After heating to reflux for 2 h, the remainder of the initiator was added and the solution again heated for 2 h. Removal of the solvent via vacuum-transfer resulted in 0.27 g (93% yield) of a glassy honey-colored solid, $[-CH_2-CH-(CO_2CH_2CH_2CF_2CF_2OCF_2CF_2SO_2F)]_n$ (**2**). IR (cm^{-1}): 2966 (w); 2931 (w); 1795 (w); 1742 (s); 1463 (vs); 1351 (m); 1325 (m); 1304 (m); 12246 (vs); 12202 (vs); 1149 (vs); 1116 (vs); 1078 (s); 1008 (m); 987 (m); 905 (w); 823 (s); 779 (m); 705 (w); 646 (m). ^1H NMR (acetone-d_6, int. TMS): relative integration area $-CH_2-CH-$(3.0), CO_2CH_2 (1.7), CH_2CF_2 (1.9). ^{19}F NMR (acetone-d_6, ext. $CFCl_3$): relative integration area CH_2CF_2 (2.1), CF_2O (1.9), OCF_2 (2.0), CF_2S (2.0), SO_2F (1.0).

Bulk photopolymerization

A 0.0377g portion of a solution prepared from 0.096 mmol (0.0383 g) of acrylate monomer and 0.0012 mmol (0.0002 g, 0.5 wt.%) of azo(bis)isobutyronitrile was placed in a 5 ml Teflon cup and irradiated with a horizontal 450 W Hanovia mercury lamp for 5 min. A small quantity of the viscous liquid removed for infrared analysis revealed a spectrum identical to that above. Further irradiation for a total of 30 min resulted in 0.0347 g (99% yield) of a light-brown viscous product.

Film-forming photopolymerization

A single drop of the monomer (**1**) solution was placed between two sodium chloride infrared windows. The windows were placed under a horizontal 450 W Hanovia mercury lamp for 5 min, after which the windows were found to be well adhered. The infrared spectrum was identical to that given above.

3. Results and discussion

Several methods are available for preparing acrylate esters from fluoroalcohols: for example, (1) treatment of acryloyl chloride with an amine; and (2) use of equimolar amounts of trifluoroacetic anhydride and acrylic acid. The latter method proved successful.

$$(CF_3CO)_2O + H_2C{=}CHC(O)OH + HOCH_2CH_2CF_2CF_2OCF_2CF_2SO_2F \longrightarrow \underset{(\mathbf{1})}{H_2C{=}CHC(O)OCH_2CH_2CF_2CF_2OCF_2CF_2SO_2F} + 2CF_3C(O)OH \quad (1)$$

The first method used acryloyl chloride and pyridine; the expected acrylate ester was not produced but loss of the fluorosulfonyl group occurred instead.

The infrared spectrum of **1** was similar to that of the starting alcohol with the exception that no O–H stretching or bending motions were observed. The carbon–oxygen stretching motion seen as a medium band at 1051 cm^{-1} in the alcohol was also absent; no new band attributable to a similar motion in the ester could be assigned due to many intense bands in this region. Very weak and medium bands at 3044 and 1411 cm^{-1} were assigned to olefinic carbon–hydrogen stretching and scissoring motions, respectively. The conjugated carbon–oxygen and carbon–carbon stretchings were seen at 1735 and 1639 cm^{-1}. The characteristic features of the tetrafluoroethylsulfonyl fluoride group ($-OCF_2CF_2SO_2F$) include: the SO_2 asymmetric and symmetric stretching frequencies found at 1464 and 1247 cm^{-1}; the S–F absorption at 811 cm^{-1}; and the strong carbon fluorine absorption bands at 1210–1082 cm^{-1} attributed to the CF_2 groups [1–6].

The NMR spectra of **1** are consistent with the structure. In the ^1H NMR spectrum (Table 1), the olefinic protons appeared in the range 6.2–7.0 ppm as an unresolved second-order multiplet. The remaining signals showed similar chemical shifts and coupling constants compared with the starting alcohol; a notable shift for the $C(O)OCH_2$ protons to 4.8

Table 1
^1H and ^{19}F NMR data for $H_2C{=}CHC(O)OCH_2CH_2CF_2CF_2OCF_2CF_2SO_2F$ (δ, ppm; J, Hz)

$H_2{}^aC{=}CH^b$	$OCH_2{}^c$	$CH_2{}^d$	$CF_2{}^e$	$CF_2{}^fO$	$CF_2{}^g$	$CF_2{}^hS$	SO_2F^i
7.0–6.2 (m)	4.8 (t) $J_{H^d}=6.6$	2.8 (t,t) $J_{F^c}=18.2$	−118.7 (t,t) $J_{F^f}=17.8$	−89.1 (t,t) $J_{F^g}=6.2$	−83.5 (m)	−113.5 (d,t) $J_{F^g}=5.1$	45.7 (t,t) $J_{F^g}=6.3$ $J_{F^i}=6.3$

Table 2
^{13}C NMR data for $H_2C{=}CHC(O)OCH_2CH_2CF_2CF_2OCF_2CF_2SO_2F$ (δ, ppm; J, Hz) *

$H_2{}^aC{=}$	$=CH^b$	$C(O)$	$OCH_2{}^c$	$CH_2{}^d$	$CF_2{}^e$	$CF_2{}^fO$	$CF_2{}^g$	$CF_2{}^hSO_2F^i$
131.1 (s)	127.7 (s)	164.6 (s)	55.9 (s)	30.0 (t) $J_{F^c}=21.7$	114.9 (t,t) $J_{F^e}=270.8$ $J_{F^f}=34.0$	117.4 (t,t) $J_{F^f}=289.3$ $J_{F^e}=35.0$	114.8 (t,t) $J_{F^g}=289.1$ $J_{F^h}=31.0$	112.4 (t,t,d) $J_{F^h}=302.8$ $J_{F^g}=38.1$ $J_{F^i}=38.1$

* Splitting patterns listed are for the proton-decoupled spectrum. In the proton-coupled spectrum, the ^1J_H splitting patterns and coupling constants were $H_2C{=}$ (t), 155.9; $=CH_2$, 161.1; OCH_2 (t), 150.4; CH_2 (t), 130.9.

Table 3
^1H and ^{19}F NMR data for $[(-CH_2{-}CH{-})C(O)OCH_2CH_2CF_2CF_2OCF_2CF_2SO_2F]_n$ (δ, ppm; J, Hz)

$-CH_2{}^a{-}CH^b-$	$OCH_2{}^c$	$CH_2{}^d$	$CF_2{}^e$	$CF_2{}^fO$	$CF_2{}^g$	$CF_2{}^hS$	SO_2F^i
2.5	4.5	1.8	−118.0 (t) $J_{F^e{-}H^d}=18.3$ *	−88.2	−83.0	−113.2	45.8

* All other resonances were broad and unresolved.

ppm in the ester as compared to 3.6 ppm for the $HOCH_2$ protons in the alcohol was observed. The ^{19}F spectrum was very similar to that reported for the alcohol and is also presented in Table 1. The ^{13}C NMR spectrum, listed in Table 2, revealed chemical shifts and coupling constants for the $-OCF_2CF_2SO_2F$ carbons similar to those reported for other compounds with this group [15]. The $H_2C{=}CHC(O)$-$OCH_2CH_2CF_2CF_2-$ portion showed the ^1J_H and ^1J_F splitting patterns expected for the structure; ^2J_F couplings were also found for the $-CH_2CF_2CF_2O-$ carbons.

Mass spectral data showed a molecular fragment. Other important fragments are listed under Experimental details (Section 2).

Another route towards the synthesis of a different acrylate ester ($H_2C{=}CHC(O)OCH_2CH_2OCF_2CF_2SO_2F$) was attempted. Pfeffer and Silbert have reported high yields by direct esterification of alkyl halides using sodium, mercury or silver carboxylates in a polar aprotic solvent [16]. Esterification of 5-bromo-1,1,2,2-tetrafluoro-3-oxa-1-1-sulfonyl fluoride with sodium acrylate was attempted using hexamethylphosphoramide as solvent:

$$H_2C{=}CHC(O)ONa + BrCH_2CH_2OCF_2CF_2SO_2F \xrightarrow{HMPA} H_2C{=}CHC(O)OCH_2CH_2OCF_2CF_2SO_2F + NaBr \quad (2)$$

No product was isolated. Instead a thick brown oily residue was formed. The loss of the ^{19}F NMR resonance for SO_2F suggests the possible formation of a sulfonamide-type product.

The free-radical polymerization of the acrylate ester **1** was investigated as a means of preparing a novel class of fluoroalkylacrylate polymers containing the fluorosulfonyl group. Polymerization of the monomer was successfully performed in solution, in bulk and as a film formed in situ using azo(bis)isobutyronitrile (AIBN) as a radical initiator.

Solution polymerization was thermally initiated in refluxing acetone while bulk and film-forming polymerizations were achieved using photoinitiation:

$$n\,(\mathbf{1}) \xrightarrow[\text{acetone, }\Delta \text{ or } h\nu]{\text{AIBN}} (-CH_2-CH-)_n \quad C(O)OCH_2CH_2CF_2CF_2OCF_2CF_2SO_2F \quad (\mathbf{2}) \quad (3)$$

Yields of all polymerizations were >95%; viscous liquids or a tacky film were formed.

The proton NMR spectrum of the product is consistent with the polymerized structure. Olefinic protons in the 6.2–7.0 ppm chemical shift region, present in the monomer, were not observed. Instead, a new broad unresolved resonance at 2.5 ppm, indicative of aliphatic protons, was present. Resonances for the other protons in the structure were broad and

also unresolved (Table 3). The chemical shifts in the ^{19}F NMR spectrum were essentially unchanged from those in the monomer. As in the ^{1}H spectrum, the signals were broad and unresolved, with the exception of the CH_2CF_2 fluorines for which a triplet splitting pattern was observed.

The bands characteristic of olefinic carbon–hydrogen and carbon–carbon stretching (3044 and 1639 cm^{-1}) present in the infrared spectrum of the monomer were not present in the spectra of the polymers, supporting the proposed structure.

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