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NEW FLUOROSULFONYL-CONTAINING MONOMERS/POLYMERS

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SUMMARY

New fluorinated monomers and polymers containing the fluorosulfonyl group have been prepared and characterized via the reaction of β-fluorosultones ($\overline{CF_2CF_2OSO_2}$, $CF_3\overline{CFCF_2OSO_2}$, $SF_5\overline{CFCF_2OSO_2}$, $SF_5\overline{CHCF_2OSO_2}$) with polyvinyl and allyl alcohols.

INTRODUCTION

Sulfonyl fluorides (RSO_2F) and their derivatives, where R = hydrocarbon and fluorocarbon moieties, continue to be subjects of considerable interest. It is known that incorporating a sulfonyl fluoride group (SO_2F) into molecular systems can lead to compounds useful as ion-exchange resins, surface-active agents and strong sulfonic acids[1-3]. Recently, it was found that reaction of fluorosultones, $X\overline{CFCF_2OSO_2}$ (X=F, CF_3) with fluorinated and non-fluorinated alcohols containing one or more hydroxy groups is an excellent pathway for

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preparing new sulfonyl fluoride derivatives[4,5]. Using this method, we wish to report our results in preparing new allyl monomeric/polymeric esters containing the sulfonyl fluoride group as well as new sulfonyl fluoride esters of polyvinyl alcohol.

RESULTS AND DISCUSSION

We have found that the following fluorosultones, $\overline{CF_2CF_2OSO_2}$, $SF_5\overline{CFCF_2OSO_2}$ and $SF_5\overline{CHCF_2OSO_2}$ react with allyl alcohol according to the following equations:

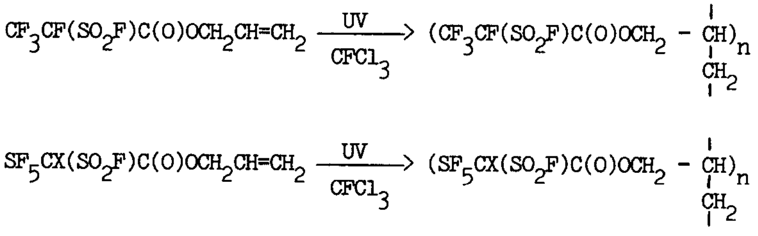
$$\overline{CF_2CF_2OSO_2} + CH_2{=}CHCH_2OH + NaF \longrightarrow FSO_2CF_2C(O)OCH_2CH{=}CH_2 + NaF{\cdot}HF$$

$$SF_5\overline{CXCF_2OSO_2} + CH_2{=}CHCH_2OH + NaF \longrightarrow SF_5CX(SO_2F)C(O)OCH_2CH{=}CH_2 + NaF{\cdot}HF$$

X = F, H

The new fluorosulfonyl allyl esters are stable water clear liquids.

While a number of non-fluorinated and fluorinated polyesters exist[6,7], there are no systems in which the SO_2F group and SF_5 group are incorporated into the polyester framework. We have found two ways to incorporate these groups into a polyester. The first way involves UV irradiation of the new allyl monomers in $CFCl_3$:

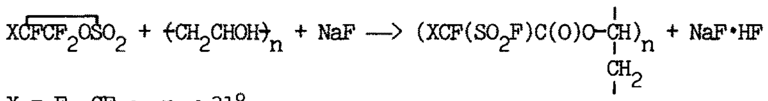


$$CF_3CF(SO_2F)C(O)OCH_2CH{=}CH_2 \xrightarrow[CFCl_3]{UV} (CF_3CF(SO_2F)C(O)OCH_2-\underset{\underset{|}{CH_2}}{\overset{|}{CH}})_n$$

$$SF_5CX(SO_2F)C(O)OCH_2CH{=}CH_2 \xrightarrow[CFCl_3]{UV} (SF_5CX(SO_2F)C(O)OCH_2-\underset{\underset{|}{CH_2}}{\overset{|}{CH}})_n$$

X = F, H

The second way, involves reacting β-sultones with polyvinyl alcohol (PVA). It was found that $\overline{\mathrm{CF_2CF_2OS}}\mathrm{O_2}$ and $\mathrm{CF_3}\overline{\mathrm{CFCF_2OS}}\mathrm{O_2}$ reacted with polyvinyl alcohol according to the following equation:



$$\mathrm{X}\overline{\mathrm{CFCF_2OS}}\mathrm{O_2} + \left(\mathrm{CH_2CHOH}\right)_n + \mathrm{NaF} \longrightarrow \Big(\mathrm{XCF(SO_2F)C(O)O{-}}\overset{|}{\underset{\underset{|}{\mathrm{CH_2}}}{\mathrm{CH}}}\Big)_n + \mathrm{NaF{\cdot}HF}$$

$X = F, CF_3$; $n \sim 318$

Under similar conditions SF_5 containing sultones produced little or no product. The decomposition and solubility characteristics are summarized in Table I; fluorosulfonyl polyesters appear to have limited thermal stability.

The infrared spectra of the new sulfonyl fluoride monomeric esters have several common features. The carbonyl stretching frequency is found in the 1764-1792 cm^{-1} region; the carbonyl bands for the new esters agree closely with those found for perfluoro/polyfluoro esters[8,9]. The asymmetric and symmetric $-SO_2-$ bands can be tentatively assigned to the regions 1440-1455 and 1222-1237 cm^{-1}, respectively. This assignment is complicated by the appearance of strong carbon-fluorine absorption bands usually found in the 1100-1300 cm^{-1} region, but in any case the above assignment for the SO_2 group agrees closely with that found for CF_3SO_2F and other fluorosulfuryl derivatives[10,3,4]. For the fluorosulfonyl group, the intense S-F absorption band is located in the 801-808 cm^{-1} region and is in the region found for other sulfonyl fluorides[11]. The C-H absorption bands for the hydrogen containing esters are located in the 2966-3100 cm^{-1} region. The C=C stretching frequency is located near 1650 cm^{-1}. The two SF_5 containing esters have as a common feature the SF_5 group and its characteristic infrared absorptions. Cross and coworkers[12] reported that for compounds containing the SF_5 group, the most intense bands should occur in the region of 850-920 cm^{-1} (S-F) stretching modes, and in the region of 600 cm^{-1} (S-F) deformation modes. For the SF_5 containing esters reported in this paper, absorption bands in the 850-934 cm^{-1} region are assigned to the S-F stretching vibrations. The S-F deformation modes are found near 600 cm^{-1}. For compounds containing a C-F group and a CF_2 group, the C-F stretching vibration is usually located in the 1000-1100 cm^{-1} region while marked absorption in the range 1050-1250 cm^{-1} can be correlated with the CF_2 group[13].

The infrared spectra of the polymers are similar to the results reported for the monomers with one notable exception; the C=C stretching frequency near 1650 cm^{-1} is absent in all polymers.

In the $(CI)^+$ mass spectra, parent peaks were found for $SF_5CF(SO_2F)CO_2C_3H_5$ and $FSO_2CF_2CO_2C_3H_5$; in the negative ion mass spectrum a parent peak for $SF_5CH(SO_2F)CO_2C_3H_5$ was found. The base peak for the allyl esters was $(C_3H_5)^+$. For all esters, a consistent cracking pattern was found and fragments were observed corresponding to $(C_3H_5)^+$, $(SO)^+$, $(SF)^+$, $(C_3H_5O)^+$, $(SO_2)^+$, $(SOF)^+$, $(SO_2F)^+$, $(CO_2C_3H_5)^+$; for the two SF_5 containing esters, the mass peaks corresponding to SF_5^+, SF_3^+, SF_2^+, SF^+ and SF_3C^+ were present. These results, except for the SF_5 peaks, are consistent with the spectra of previously reported fluorinated esters[4,5,8,9].

The ^1H nmr data (chemical shifts and coupling constants) for the new monomeric esters are reported in Table II. The chemical shifts and coupling constants for the $-CH_2CH=CH_2$ moiety are in agreement with values reported for allyl alcohol and $FO_2S(CF_2)_2O(CF_2)_2OCH_2CH=CH_2$[14,15]. The $C\underline{H}$ proton chemical shift in $SF_5C\underline{H}(SO_2F)CO_2C_3H_5$ was located at 6.24 ppm; in SF_5CFHSO_2F the corresponding shift was reported at 6.31 ppm[3]. The proton chemical shifts for polymeric materials obtained with ultraviólet irradiation showed, in general, broad peaks for the CH and CH_2 groups.

Table 1

Solid Polymers

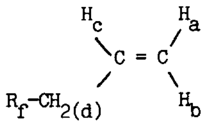
Composition	Decomp. (°C)	Solubility		
		H_2O	Acetone	$CFCl_3$
$(CF_3CF(SO_2F)CO_2CH_2CHCH_2{-})_n$	164	insol.	sl. sol.	insol.
$(SF_5CF(SO_2F)CO_2CH_2CHCH_2{-})_n$	150	insol.	sol.	insol.
$(SF_5CH(SO_2F)CO_2CH_2CHCH_2{-})_n$	170	insol.	sol.	insol.
$(FO_2SCF_2CO_2CHCH_2{-})_n$	120	insol.	sol.	insol.
$(CF_3CF(SO_2F)CO_2CHCH_2{-})_n$	170	insol.	sol.	insol.

Note: Average value of n is 318 for PVA based polymers; value is derived from average molecular weight of starting PVA.

Viscous polymers prepared from allyl esters were soluble in acetone and $CFCl_3$.

Table 2

^{1}H NMR Data



R_f	Chemical Shifts (ppm)*				Coupling Constants (Hz)			
	H_d	H_c	H_b	H_a	J_{ab}	J_{ac}	J_{bc}	J_{cd}
$SF_5CF(SO_2F)CO_2$	5.07	6.12	5.82	5.58	5.1	9.9	17.1	5.7
$SF_5CH'(SO_2F)CO_2$	4.90	6.04	5.72	5.54	4.5	10.5	18.0	5.7
$CF_3CF(SO_2F)CO_2$	4.95	5.96	5.66	5.42	4.8	10.5	17.1	5.4
$FSO_2CF_2CO_2$	4.95	6.02	5.72	5.43	3.0	10.8	18.0	6.0

CH' = Proton 6.24 ppm (multiplet, J_{SF_4CH} = 10.2 Hz)

* = H_d (doublet), H_c (doublet of triplet), H_b (doublet of doublet), H_a (doublet of doublet) Proton chemical shifts in ppm downfield from external TMS

The ^{19}F nmr spectral data are reported in Table III. The ^{19}F nmr spectra for the SF_5 group of $SF_5CF(SO_2F)CO_2C_3H_5$ consisted of the expected AB_4 pattern with the B_4 equatorial fluorines split into a complex doublet and the axial fluorine, A, into a nine-line pattern. The chemical shifts for the AB_4 pattern in $SF_5CF(SO_2F)CO_2C_3H_5$ were located at 64.3(A) and 56.3(B) ppm. In $SF_5CH(SO_2F)CO_2C_3H_5$, the expected AB_4 pattern is not observed but instead a complex multiplet centered at 70.7 ppm is found. The $C\underline{F}$ chemical shift in $SF_5C\underline{F}(SO_2F)CO_2C_3H_5$ was found at -121.9 ppm; in $SF_5C\underline{F}(SO_2F)COF$ the corresponding chemical shift was reported as -122 ppm[3]. The ^{19}F nmr spectrum of the allyl ester, prepared from $\overline{CF_2CF_2OSO_2}$, contained the CF_2 resonance at -104.9 ppm which is the region expected for a CF_2 group; for example, in $FSO_2CF_2CO_2CH_2CF_3$ the CF_2 resonance was found at -106.4[5]. In all allyl esters, the resonance bands for the FSO_2 are located in the region 39.9-58.5 ppm; in a number of sulfonyl fluoride derivatives CF_3CFHSO_2F, SF_5CFHSO_2F, $FSO_2CF_2CO_2CH_2CF_3$ the corresponding resonance band was located in the 40-52 ppm range[16,3,5]. The fluorine chemical shifts for polymeric materials obtained from ultraviolet irradiation were, in general, in agreement with values found for the corresponding monomers; as expected the peaks were significantly broadened.

The ^{19}F nmr results for PVA based polymers were in excellent agreement with corresponding group values reported above for the UV produced products. The ^{1}H nmr spectra for the PVA based polymers prepared from $\overline{CF_2CF_2OSO_2}$ and $CF_3\overline{CFCF_2OSO_2}$ contained a broadened singlet (CH-O) at δ 5.32-5.15 ppm and a broadened singlet (CH_2) at δ1.0-3.05 ppm, respectively. By comparison, it is reported that for polyvinyl chloride, the chemical shift values in the δ 1.9-2.3 ppm region are attributed to the β protons (CH_2) and the values at δ 4.2-4.5 ppm to the α (CH) protons[17].

Table 3

^{19}F NMR Data[a] - $R_fCH_2CH{=}CH_2$

R_f	Chemical Shifts (ppm)				Coupling Constants (Hz)
$FSF_4CF(SO_2F)CO_2$	$SF(64.3)$ (9-line)	$SF_4(56.3)$ (d)	$CF(-121.9)$ (s)	$SO_2F(48.6)$ (p)	$J_{SF-SF_4} = 141$, $J_{SF-CF} = 3.1$, $J_{SF_4-CF} = 3.1$ $J_{CF-SO_2F} < 1.0$, $J_{SF_4-SO_2F} = 11.6$
FSF_4[b]$CH(SO_2F)CO_2$	$SF_5(70.7)$ (multiplet)			$SO_2F(58.5)$ (multiplet)	$J_{SF_4-CH} = 4.5$, $J_{SF_4-SO_2F} = 11.6$
$CF_3CF(SO_2F)CO_2$	$CF_3(-74.3)$ (d of d)		$CF(-161.8)$ (q of d)	$SO_2F(50.1)$ (q of d)	$J_{CF_3-CF} = 8.3$, $J_{CF_3-SO_2F} = 9.6$, $J_{CF-SO_2F} = 4.2$
$CF_2(SO_2F)CO_2$	$CF_2(-104.9)$ (d)			$SO_2F(39.9)$ (t)	$J_{CF_2-SO_2F} = 5.3$

a = Fluorine chemical shifts in ppm from external $CFCl_3$, d = doublet, t = triplet, q = quartet, p = pentet, s = sextet

b = Complex multiplet observed in place of expected AB_4 (FSF_4) coupling.

EXPERIMENTAL

The fluorinated sultones and $CF_3CF(SO_2F)CO_2CH_2CH=CH_2$ were prepared according to literature methods [3,5,18]

Allyl alcohol (Mallinckrodt) was used as received. Polyvinyl alcohol (PVA) with an average molecular weight of 14,000 was obtained from Aldrich and dried in vacuo prior to use. Sodium fluoride (Baker) was dried under vacuum before use. Freon-11 (CCl_3F) was dried with silica gel prior to use. Carbon tetrachloride (Mallinckrodt Spectra grade) was dried over 4A molecular sieves.

General Procedure. Gases were manipulated in a conventional Pyrex-glass vacuum apparatus equipped with a Heise-Bourdon tube gauge and a Televac thermocouple gauge. Infrared spectra were obtained by using a Pyrex-glass cell with KBr windows or as solids between KBr disks on a Nicolet 20DX spectrometer. The nmr spectra were recorded with a Varian Model EM-390 spectrometer operating at 90.0 MHz for proton and 84.67 MHz for the fluorine resonance. TMS and F-11 were used as external standards. The melting/decomposition points were determined by using a Mel-Temp capillary melting point apparatus and are uncorrected. The mass spectra were taken on a VG 7070 HS mass spectrometer with an ionization potential of 70 eV. Perfluorokerosene was used as an internal standard.

Elemental analyses were determined by Beller Microanalytical Laboratory in Gottingen, F.R.G.

Synthesis of $SF_5CF(SO_2F)COOCH_2CH=CH_2$ Olefin

Into a 125 mL Pyrex-glass reaction vessel equipped with a Kontes Teflon valve and a Teflon stirring bar, were added 114.8 mmol of anhydrous sodium fluoride, 22.6 mmol allyl alcohol, and 21.4 mmol of $SF_5\overline{CFCF_2OS}O_2$. This mixture was magnetically stirred for 5 days at room temperature and 9 days at 40-50°C.

Distillation of the volatile material gave 15.0 mmol of $SF_5CF(SO_2F)COOCH_2CH=CH_2$ in 70% yield; b.p. 103±1°C/74 mm.

The infrared spectrum of the liquid had bands (cm^{-1}): 3100(vw), 2995(w), 2966(w), 1792(s), 1652(w), 1455(s), 1384(vw), 1363(w), 1279(s), 1258(m), 1230(s), 1166(s), 1082(w), 1019(w), 991(w), 934(m), 885(vs), 850(s), 808(m), 780(m), 674(m), 668(w), 618(m), 597(s), 576(s), 491(m), 456(w), 421(w).

The relative nmr band areas for SF, SF_4, SO_2F, CF were 1.0:4.2:1.1:1.1; theory 1.0:4.0:1.0:1.0. In addition to a molecular ion (326), other appropriate fragment ions were found: 243 $(M-SO_2F)^+$, 199 $(M-SF_5)^+$, 186 $(SF_5CFCO)^+$, 143 $(FSCO_2C_4)^+$, 127 $(SF_5)^+$, 116 $(M-SF_5SO_2F)^+$, 108 $(SF_4)^+$ 101 $(SF_3C)^+$, 91 $(SCFCO)^+$, 89 $(SF_3)^+$, 85 $(CO_2C_3H_5)^+$, 83 $(CO_2C_3H_3, SO_2F)^+$, 71 $(CFCOC)^+$, 70 $(SF_2)^+$, 69 $(C_3H_5CO)^+$, 67 $(SOF, C_4H_3O)^+$, 65 $(C_4HO)^+$, 64 $(C_4O, SO_2)^+$, 63 $(FSC)^+$, 59 $(CFCO)^+$, 57 $(C_3H_5O)^+$, 56 $(C_3H_4O)^+$, 55 $(C_3H_3O)^+$, 51 $(SF)^+$, 48 $(SO)^+$, 44 $(CS, CO_2)^+$, 42 $(C_2H_2O)^+$, 41 $(C_3H_5, 100\%)^+$.

Anal. Calcd for $C_5H_5F_7S_2O_4$: C, 18.41; H, 1.54; F, 40.77; S, 19.66. Found: C, 18.56; H, 1.41; F, 41.10; S, 19.48.

Synthesis of $FO_2SCF_2COOCH_2CH=CH_2$ Olefin

Into a 100 mL Pyrex-glass reaction vessel equipped with a Kontes Teflon valve and a Teflon stirring bar, were added 122.5 mmol of anhydrous sodium fluoride, 22.3 mmol of allyl alcohol, and 22.4 mmol of $\overline{CF_2CF_2OSO_2}$. This mixture was magnetically stirred for 6 days at room temperature and then heated at 40–50°C (18 d). Distillation of the volatile material gave 15.4 mmol of $FSO_2CF_2CO_2CH_2CH=CH_2$ in 69% yield; b.p. 141–142°C.

The infrared spectrum had bands (cm^{-1}): 3100(w), 3037(w), 2995(w), 1785(vs), 1652(w), 1448(s), 1370(m), 1314(s with sh. at 1293), 1237(s), 1195(s), 1152(s), 1082(w), 1040(wm), 1019(m), 991(m), 977(w), 941(m), 899(wm), 829(s), 801(s), 723(w), 680(w), 656(w), 646(m), 597(wm), 569(m), 526(w), 484(w), 456(w).

The relative nmr band area for $SO_2F:CF_2$ was 1.0:2.0, theor. 1.0:2.0.

The molecular ion was observed at 218 and other ion fragments were found: 135 $(M-SO_2F)^+$, 134 $(M-SO_2FH)^+$, 133 $(M-SO_2FH_2, M-CO_2C_3H_5)^+$, 106 $(CF_2COC_2H_4)^+$, 85 $(CO_2C_3H_5)^+$, 84 $(CO_2C_3H_4)^+$, 83 $(CO_2C_3H_3, SO_2F)^+$, 79 $(SOFC)^+$, 78 $(CF_2CO)^+$, 69 $(C_4H_5O)^+$, 67 $(C_4H_3O, SOF)^+$, 64 $(SO_2)^+$, 57 $(OC_3H_5)^+$, 56 $(C_3H_4O)^+$, 55 $(C_3H_3O)^+$, 51 $(SF)^+$, 48 $(SO)^+$, 44 $(CS, CO_2)^+$, 43 $(C_2H_3O)^+$, 42 $(OCH_2C)^+$, 41 $(C_3H_5, 100\%)^+$.

Anal. Calcd for $C_5H_5F_3SO_4$: C, 27.53; H, 2.31; F, 26.1; S, 14.69. Found: C, 27.58; H, 2.36; F, 26.5; S, 14.52.

Synthesis of $SF_5CH(SO_2F)COOCH_2CH=CH_2$ Olefin

Into a 125 mL Pyrex-glass reaction vessel equipped with a Kontes Teflon valve and a Teflon stirring bar, were added 73.55 mmol of dried sodium fluoride, 18.83 mmol of $SF_5\overline{CHCF_2OS}O_2$, and 18.58 mmol of allyl alcohol. The reaction mixture was stirred at 70°C for 170 hours. Distillation of the volatile material gave 8.97 mmol of $SF_5CH(SO_2F)COOCH_2CH=CH_2$ in 48% yield; b.p. 108.5±1.5°C/50 mm.

The infrared spectrum had bands (cm^{-1}): 2980(w), 1764(s), 1651(w), 1440(s), 1363(m), 1298(s), 1285(s), 1222(s), 1152(s), 1109(w), 1079(w), 1027(w), 988(w), 873(vs,b with sh, at 934), 802(m), 747(w), 689(m), 654(w), 610(m), 569(s), 489(m), 453(w).

In the $(CI)^-$ mass spectrum, the molecular ion was observed at $308(M)^-$; other negative ions found were 307 $(M-H)^-$, 223 $(SF_5CHSO_2F)^-$, 179 $(F_3S_2O_2C_2H_2)^-$, 150 $(F_3S_2OCH)^-$, 129 $(SC_2O_2C_3H_5)^-$, 127 $(SF_5)^-$, 108 $(SF_4)^-$, 85 $(CO_2C_3H_5)^-$, 83, $(SO_2F)^-$, 78 $(C_5H_2O)^-$. For the $(CI)^+$ spectrum, the fragment ions found were 253 $(M-HOF_2)^+$, 251 $(M-OC_3H_5)^+$, 231 $(S_2F_3C_5O_3H_2)^+$, 219 $(S_2F_3C_4O_3H_2)^+$, 209 $(S_2F_3C_2O_4)^+$, 181 $(S_2FC_4O_3H_2)^+$, 168 $(SF_5CHCO)^+$, 149 $(SF_4CHCO)^+$, 127 $(SF_5)^+$, 125 $(SC_5O_2H)^+$, 105 $(SC_2O_3H)^+$, 101 $(SF_3C)^+$, 100 $(SC_3O_2)^+$, 97 $(C_5O_2H_5)^+$, 91 $(FSC_2O)^+$, 89 $(SF_3)^+$, 85 $(CO_2C_3H_5)^+$, 83 $(CO_2C_3H_3, SO_2F)^+$, 81 $(CO_2C_3H, C_5H_5O)^+$, 80 $(FSOCH)^+$, 73 $(SOC_2H)^+$, 72 $(SOC_2)^+$, 70 $(SF_2)^+$, 69 $(C_4H_5O)^+$, 67 $(C_4H_3O, SOF)^+$, 65 $(C_4HO)^+$, 64 $(C_4O, SO_2)^+$, 63 $(FSC)^+$, 61 $(SCHO)^+$, 60 $(SCO)^+$, 57 $(C_3H_5O)^+$, 56 $(C_3H_4O)^+$, 55 $(C_3H_3O)^+$, 54 $(C_3H_2O)^+$, 53 $(C_3HO)^+$, 52 $(C_3O)^+$, 51 $(SF)^+$, 48 $(SO)^+$, 45 $(SCH)^+$, 44 $(SC, CO_2)^+$, 43 $(C_2H_3O)^+$, 42 $(C_2H_2O)^+$, 41 $(C_3H_5$, 100%$)^+$.

Anal. Calcd for $C_5H_6F_6S_2O_4$: C, 19.48; H, 1.96; F, 37.0; S, 20.80. Found: C, 19.67; H, 1.98; F, 37.7; S, 20.55.

Polymerization of $CF_3CF(SO_2F)COOCH_2CH{=}CH_2$ Olefin

In a 80 mL quartz reaction vessel, equipped with a Kontes Teflon valve and a Teflon stirring bar, a solution of 1.75 g (6.53 mmol) $CF_3CF(SO_2F)COOCH_2CH{=}CH_2$ olefin in 7.77 g (56.5 mmol) of trichlorofluoromethane was irradiated with an ultraviolet light from a 100 watt Hanovia lamp for 72 h. The resulting light yellow solution was filtered through a sintered funnel to remove discolored solid material. Removal of all volatile material left behind a viscous tan oil, 0.856 g of $(CF_3CF(SO_2F)COOCH_2CHCH_2\text{-})_n$ in 49% yield.

The infrared spectrum of the viscous liquid had bands (cm^{-1}): 2945(w), 2875(vw), 1792(s), 1454(s), 1393(vw), 1300(s), 1250(vs), 1166(s), 1068(w), 1018(m), 983(w), 835(s,b with sh at 824), 744(m), 688(m), 603(s), 547(w), 484(w), 456(w).

The ^{19}F nmr spectrum contained a broadened singlet at 50.5 ppm (SO_2F), a broadened singlet at −73.5 ppm (CF_3), and a broadened singlet at −161.4 ppm (CF). The relative band areas for SO_2F, CF_3, and CF were 1.0:3.2:1.0; theor. 1.0:3.0:1.0.

The proton nmr spectrum contained a broad singlet centered at 4.8 ppm (CH_2O) and a series of peaks in the 1.2-3.8 ppm range (CH_2, CH).

Anal. Calcd for $C_6H_5F_5SO_4$: C, 26.87; H, 1.88; F, 35.4; S, 11.96. Found: C, 26.79; H, 1.94; F, 35.6; S, 11.85.

In another run, 3.96 g (14.8 mmol) of $CF_3CF(SO_2F)COOCH_2CH{=}CH_2$ was placed in a quartz reaction vessel with 1.99 g (14.5 mmol) of $CFCl_3$ and irradiated (56 h). The liquid was drained from the reaction vessel, and the $CFCl_3$ removed under vacuum to give a brown highly viscous liquid, 3.19 g, in 80% yield. Left behind in the reaction vessel was a tan waxy solid, 0.376 g, formed in 9.4% yield. The waxy solid did not soften and melt prior to decomposition at 164°C.

The infrared and nmr spectra for both products agreed with that found in the previous run.

Polymerization of $SF_5CF(SO_2F)COOCH_2CH{=}CH_2$ Olefin

In a 80 mL quartz reaction vessel, equipped with a Kontes Teflon valve and a Teflon stirring bar, 2.07 g (6.30 mmol) of $SF_5CF(SO_2F)COOCH_2CH{=}CH_2$ in 7.77 g (56.5 mmol) of trichlorofluoromethane was irradiated with a 100 watt ultraviolet Hanovia lamp for 78 h. The fraction soluble in F-11 was transferred from the reaction flask; the F-11 was removed under vacuo yielding a brownish viscous oil of 0.917 g $(SF_5CF(SO_2F)CO_2CH_2CHCH_2)_n$, 44% yield.

The infrared spectrum of the viscous liquid had bands (cm^{-1}): 2973(w,b), 1792(s), 1454(s), 1384(w), 1365(w), 1278(s), 1228(s), 1171(s), 1090(vw), 1018(w), 990(w), 934(w), 882(vs), 856(w), 812(s), 784(s), 678(m), 618(s), 587(s), 575(s), 487(m), 453(w).

The proton nmr spectrum contained a broad singlet centered at 4.8 ppm (CH_2O) and a series of peaks in the range of 1.0-3.5 ppm (CH_2, CH).

The ^{19}F spectrum contained a broadened multiplet at 65.2 ppm (axial SF), a broadened doublet at 57.4 ppm (SF_4), a broadened singlet at 48.8 ppm, and a broadened singlet at -121.5 ppm (CF). The relative band areas for $SF:SF_4:CF:SO_2F$ were: 1.4:4.0:1.0:1.0; theor. 1.0:4.0:1.0:1.0.

Anal. Calcd. for $C_5H_5F_7S_2O_4$: C, 18.41; H, 1.54; F, 40.8; S, 19.66. Found: C, 18.86; H, 1.50; F, 40.0; S, 19.30.

In another run, 0.602 g (1.84 mmol) of $SF_5CF(SO_2F)COOCH_2CH{=}CH_2$ was placed in a quartz reaction vessel with 2.45 g (17.8 mmol) of $CFCl_3$ and was irradiated for 39 h. The $CFCl_3$ was removed under vacuum leaving a light tan waxy solid with some viscous oil on the sides of the vessel; $(SF_5CF(SO_2F)COOCH_2CHCH_2)_n$ was formed in 95% yield. The softening temperature of the solid was ∿52°C. The IR and nmr spectra agreed with that found for the viscous oil reported in the first run.

Polymerization of $SF_5CH(SO_2F)COOCH_2CH{=}CH_2$ Olefin

In a 80 mL quartz reaction vessel, equipped with a Kontes Teflon valve and a Teflon stirring bar, 1.89 g (6.10 mmol) of $SF_5CH(SO_2F)COOCH_2CH{=}CH_2$ in 6.21 g (45.2 mmol) of trichlorofluoromethane was irradiated with a 100 watt ultraviolet Hanovia lamp for 26 h. After this time period, an insoluble oil had formed on the walls of the quartz vessel. The trichlorofluoromethane solution was decanted and the remaining oil was extracted with acetone. The acetone soluble solution was evaporated in vacuo to yield a viscous clear dark brown oil of 0.9523 g (3.09 mmol) $(SF_5CH(SO_2F)COOCH_2CHCH_2)_n$, 51% yield.

The infrared spectrum of the viscous liquid had bands (cm^{-1}): 2973(w), 1764(s), 1440(s with sh at 1384), 1293(s), 1222(s), 1159(s), 1068(w), 990(w), 871(vs,b), 800(s), 772(m), 750(m), 690(m), 644(m), 612(m), 569(s), 489(m), 457(m), 415(w).

The proton nmr spectrum contained a broad singlet at 7.24 ppm (SF_5CH), a broad singlet at 4.4 ppm (CH_2O) and a series of peaks in the range of 1.2-3.3 ppm (CH_2, CH).

The ^{19}F spectrum contained a broadened singlet at 71.3 ppm (SF_5), and a broadened singlet at 58.5 ppm (SO_2F).

Anal. Calcd. for $C_5H_6F_6S_2O_4$: C, 19.48; H, 1.96; F, 37.0; S, 20.80. Found: C, 19.76; H, 2.09; F, 36.4; S, 20.54.

In another run, 0.440 g (1.43 mmol) of $SF_5CH(SO_2F)COOCH_2CH{=}CH_2$ was placed in the 80 mL quartz vessel with 1.39 g (10.1 mmol) $CFCl_3$ and irradiated for 26 h. The $CFCl_3$ was removed under vacuum leaving a tan waxy solid along with some viscous oil, $(SF_5CH(SO_2F)CO_2CH_2CHCH_2-)_n$ was formed in 100% yield. The softening temperature of the solid was ∿45°C.

The above product exhibited the same infrared and nmr spectra as previously reported.

Reaction of $CF_3\overline{CFCF_2OS}O_2$ with PVA

Into a 25 mL round bottom reaction vessel containing 80.56 mmol of sodium fluoride, 37.40 mmol of powdered PVA was added. To this solid mixture 42.10 mmol of $CF_3\overline{CFCF_2OS}O_2$ was added. This mixture was heated with stirring at 78°C (21 h). After this time, the resulting solid material was washed with water. The water insoluble material was dried under vacuo (12 h). The water insoluble material, 10.94 mmol of $(CF_3CF(SO_2F)CO_2CHCH_2)_n$, was formed in 29% yield; partial melting at 120° with decomposition at 170°C.

The infrared spectrum of the solid had bands (cm^{-1}): 2938(w), 1790(s), 1781(s), 1456(s), 1293(s), 1250(vs), 1225(s), 1165(s with sh at 1080), 1068(w), 1018(m), 971(w), 903(w), 834(m), 803(m), 746(m), 690(w), 600(s), 546(w), 490(w), 462(w).

The proton nmr spectrum contained a very broad singlet centered at 5.15 ppm (CHO) and a series of peaks in the range of 1.3-2.9 ppm (CH_2).

The ^{19}F spectrum contained a broadened singlet at 50.7 ppm (SO_2F), a broadened singlet at -73.7 ppm (CF_3), and a broadened singlet at -161.5 ppm (CF); relative band area for CF_3:SO_2F:CF was 3.2:1.0:1.0; theor. 3.0:1.0:1.0.

Anal. Calcd. for $C_5H_3F_5SO_4$: C, 23.63; H, 1.19; F, 37.4; S, 12.62. Found: C, 25.57; H, 1.50; F, 37.2; S, 12.50.

Reaction of $\overline{CF_2CF_2OS}O_2$ with PVA

Into a 25 mL round bottom reaction vessel containing 16.0 mmol of anhydrous sodium fluoride and 11.0 mmol of polyvinyl alcohol, 9.30 mmol of $\overline{CF_2CF_2OS}O_2$ and 20.6 mmol of CCl_4 were added.

This reaction mixture was heated to 90°C (62 h) under a nitrogen atmosphere. A gray solid material was recovered after removing all volatile material at room temperature. The solid material was extracted with acetone and the acetone extract was evaporated to dryness under vacuo, leaving behind a brown clear solid, 2.80 mmol $(FSO_2CF_2C(O)OCHCH_2)_n$ in 30% yield; partial melting at 90°C with decomposition at 123°C.

The infrared spectrum of the solid had bands (cm^{-1}): 2973(w), 2945(w), 1785(s), 1686(w), 1447(s), 1314(s), 1236(s), 1208(s), 1159(s with sh at 1087), 1004(m), 899(vw), 850(m), 807(m), 723(m), 646(m with sh at 661), 603(w), 561(m), 534(w), 523(w), 485(m), 459(w).

The proton nmr spectrum contained a broadened singlet centered at 5.32 ppm (CHO) and a series of peaks in the range of 1.0-3.0 ppm.

The ^{19}F nmr spectrum contained a singlet at 40.4 ppm (SO_2F) and a singlet at -104.9 ppm (CF_2); relative band area for CF_2:SO_2F was 2.0:1.0; theor. 2.0:1.0.

Anal. Calcd. for $C_4H_3F_3SO_4$: C, 23.54; H, 1.48; F, 27.9; S, 15.71. Found: C, 24.41; H, 1.76; F, 29.1; S, 13.54.

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