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**Feiring et al.**

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[54] **FLUORINATED ION-EXCHANGE  
POLYMERS AND INTERMEDIATES  
THEREFOR**  
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[\*] Notice: The term of this patent shall not extend  
beyond the expiration date of Pat. No.  
5,536,754.

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**Related U.S. Application Data**

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Pat. No. 5,668,233, which is a continuation-in-part of Ser.  
No. 534,525, Sep. 27, 1995, Pat. No. 5,536,754, which is a  
continuation-in-part of Ser. No. 388,789, Feb. 15, 1995, Pat.  
No. 5,475,143.  
[51] **Int. Cl.<sup>6</sup>** ..... **C08F 14/26**  
[52] **U.S. Cl.** ..... **526/243; 526/274; 526/253**  
[58] **Field of Search** ..... **526/247, 243,  
526/253**

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*Primary Examiner*—Fred Zitomer

[57] **ABSTRACT**

Disclosed herein are partially fluorinated (co)polymers con-  
taining sulfonic acid or sulfonate salt groups, processes for  
making those polymers, and intermediates for those (co)  
polymers. The (co)polymers are useful as ion-exchange  
resins and (in the sulfonic acid form) acid catalysts.

**4 Claims, No Drawings**

**FLUORINATED ION-EXCHANGE  
POLYMERS AND INTERMEDIATES  
THEREFOR**

This application is filed as a continuation-in-part of pending Ser. No. 08/652,733, filed on May 23, 1996, which issued as U.S. Pat. No. 5,668,233 on Sep. 16, 1997, which is a continuation in part of Ser. No. 08/534,525, filed on Sep. 27, 1995, which issued as U.S. Pat. No. 5,536,754 on Jul. 16, 1996, which is a continuation-in-part of Ser. No. 08/388,789, filed on Feb. 15, 1995, and which issued as U.S. Pat. No. 5,475,143 on Dec. 12, 1995.

**FIELD OF THE INVENTION**

This invention concerns partially fluorinated sulfonic acid containing polymers suitable as ion-exchange resins and strong acid catalysts, and novel intermediates thereto. Also disclosed are novel processes for making such polymers.

**TECHNICAL BACKGROUND**

Polymers containing strongly acidic or basic groups are useful as ion-exchange resins, and for other uses. Sulfonic acid containing polymers are useful as ion-exchange resins and as strong acid catalysts. Polymers which are fluorinated may also be more thermally and/or chemically resistant than unfluorinated polymers, so fluorinated sulfonic acid containing polymers may be particularly useful. Such polymers are useful in the form of films, coatings, membranes, other shaped articles and particles.

For use as an ion exchange resin or strong acid catalyst resin, it is generally preferred if the resin contains as many active sites as possible. It is known in the art (see, for instance, U.S. Pat. No. 4,948,844) that it is difficult to (co)polymerize perfluorinated (alkyl vinyl ethers), while fluorinated alkyl vinyl ethers which contain some hydrogen in the alkyl group, particularly alpha to the ether oxygen, are more readily polymerizable, and can be (co)polymerized to give polymers with high vinyl ether contents.

Yu. E. Kirsh, et al., Russian Chemical Rev., vol. 59, p. 560-574 (1990) have reviewed the literature of perfluorinated cation exchange membranes.

U.S. Pat. No. 4,597,913 describes the synthesis of certain perfluorinated (with the exception of the "R" group on the sulfur) sulfide containing vinyl ethers, (co)polymers containing those vinyl ethers as repeat units, and oxidation of the (co)polymers to obtain the analogous sulfonic acid containing perfluorinated polymers. No mention is made of partially fluorinated sulfonic acid containing polymers.

T. Nguyen, et al., Eur. Polym. J., vol. 27, p. 435-438 (1991) describe the preparation of certain perfluorinated (with the exception of the "R" group on sulfur) sulfide containing vinyl ethers and their conversion to sulfonyl chlorides. No mention is made of the novel compounds described herein.

U.S. Pat. No. 5,206,440 describes the oxidation of organofluorine containing sulfides to sulfones using a fluorine/acetonitrile/water reagent. S. Rozen, et al., J. Chem. Soc., Chem. Commun., p. 1959 (1994) describes the oxidation of thiophenes to S,S-dioxides using a fluorine/acetonitrile/water reagent.

**SUMMARY OF THE INVENTION**

This invention concerns a copolymer consisting essentially of the repeat units



wherein:

Q is  $-\text{SO}_3\text{M}$ ,  $-\text{SCl}$ ,  $-\text{SO}_2\text{Cl}$  or  $-\text{SR}^1$ ;

n is an integer of 1 to 10;

M is hydrogen, an alkali metal cation or an ammonium ion; and

$\text{R}^1$  is an alkyl group containing 1 to 10 carbon atoms; and provided that the molar ratio of (I):(II) is 0:100 to about 99:1.

This invention also provides a compound of the formula



wherein  $\text{R}^1$  is an alkyl group containing 1 to 10 carbon atoms; and n is an integer of 1 to 10.

Also disclosed herein is a process to make a partially fluorinated polymer, comprising:

reacting tetrafluoroethylene, carbon dioxide, and an alkali metal thioalkoxide to obtain the alkali metal salt of a thio-containing partially fluorinated alkali metal carboxylate, and reacting said carboxylate with a dialkyl sulfate to obtain an ester of a thio-containing partially fluorinated carboxylic acid; or

reacting tetrafluoroethylene, an alkali metal thioalkoxide and a dialkyl carbonate to obtain said ester;

reducing said ester with a suitable reducing agent to the corresponding thio-containing partially fluorinated alcohol;

reacting said alcohol with a base capable of forming an alkoxide anion from said alcohol, and tetrafluoroethylene, to form a monomer of the formula  $\text{CF}_2=\text{CFOCH}_2\text{CF}_2\text{CF}_2\text{SR}^1$ ;

free radically polymerizing said monomer, optionally with tetrafluoroethylene comonomer, to form a thio-containing polymer;

reacting said thio-containing polymer with a sufficient amount of chlorine at a temperature of about 80° C. to about 140° C. for a period of time sufficient to form a sulfenyl chloride containing polymer; and

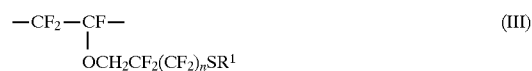
reacting said sulfenyl chloride containing polymer with a sufficient amount of chlorine and water, or with an alkali metal hypochlorite, at a temperature of about 25° C. to about 140° C., for a period of time sufficient to form a sulfonyl chloride containing polymer; and

converting said sulfonyl chloride containing polymer to a sulfonic acid, alkali metal sulfonate, or ammonium sulfonate by reaction with water, an alkali metal base or an amine, respectively;

and wherein  $\text{R}^1$  is alkyl containing 1 to 10 carbon atoms.

Described herein is a process for producing a sulfonyl chloride or sulfonic acid containing polymer, comprising,

(a) contacting at 80° C. to about 140° C., a sufficient amount of chlorine with a polymer consisting essentially of the repeat units



for a period of time sufficient to produce a polymer consisting essentially of the repeat units



(b) contacting at 80° C. to about 140° C., a sufficient amount of chlorine and water with a polymer consisting essentially of repeat units (I) and (IV) for a period of time sufficient to produce a polymer consisting essentially of the repeat units



or carrying (a) and (b) simultaneously on a polymer consisting essentially of repeat units (I) and (III) to produce a polymer consisting essentially of repeat units (I) and (VI);

wherein n is an integer of 1 to 10; R<sup>1</sup> is an alkyl group containing 1 to 10 carbon atoms; and T is SO<sub>2</sub>Cl or SO<sub>3</sub>H; and provided that the molar ratio of (I):(III) is 0:100 to about 99:1.

Described herein is a compound of the formula CF<sub>2</sub>=CFOCH<sub>2</sub>CF<sub>2</sub>(CF<sub>2</sub>)<sub>n</sub>SO<sub>2</sub>CR<sup>2</sup>R<sup>3</sup>R<sup>4</sup>, (VI) wherein n is 1 to 10, and each of R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently alkyl containing 1 to 10 carbon atoms.

This invention concerns a copolymer consisting essentially of the repeat units



wherein:

each of R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently alkyl containing 1 to 10 carbon atoms;

n is an integer of 1 to 10;

X is —SO<sub>2</sub>F or —SO<sub>2</sub>CR<sup>2</sup>R<sup>3</sup>R<sup>4</sup>;

and provided that the molar ratio of (I):(II) is 0:100 to about 99:1.

Described herein is a process for producing a sulfonyl fluoride containing polymer, comprising,

(a) contacting, a mixture of fluorine, acetonitrile and water, or BrF<sub>3</sub>, with a polymer consisting essentially of the repeat units



for a period of time sufficient to produce a polymer consisting essentially of the repeat units



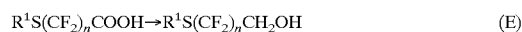
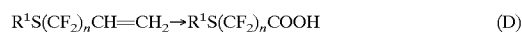
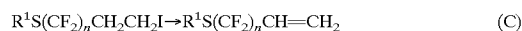
Y is —Cl or —CR<sup>2</sup>R<sup>3</sup>R<sup>4</sup>;

each of R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently alkyl containing 1 to 10 carbon atoms; and

provided that when BrF<sub>3</sub> is used, Y is —CR<sup>2</sup>R<sup>3</sup>R<sup>4</sup>.

#### DETAILS OF THE INVENTION

The synthesis of the final partially fluorinated sulfonic acid (or sulfonate) containing polymers described herein can be done by a series of reactions. Some of these reactions are known. For instance the following reactions would be applicable when n is >1.



Once the product of E is obtained, the synthesis can proceed similarly to that shown in (5a) and (5b), below. The following papers contain information on the above reactions:

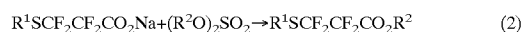
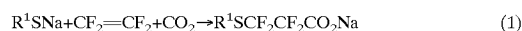
(A) C. Wakselman, et al., in "Organofluorine Chemistry. Principles and Commercial Applications", R. E. Banks, et al., (ed.), Plenum Press, New York, 1994, p. 182.

(B) and (C) *Ibid.*, p. 189.

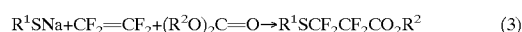
(D) M. Hudlicky, "Chemistry of Organic Fluorine Compounds", Ellis Horwood, Ltd., 1976, p. 210, using potassium permanganate as the oxidant.

(E) *Ibid.*, p. 180, using LiAlH<sub>4</sub> or NaBH<sub>4</sub> as the reducing agents.

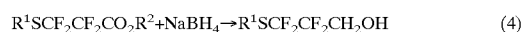
One method to obtain the vinyl ether monomer (V) is to first prepare an alcohol of the formula HOCH<sub>2</sub>CF<sub>2</sub>(CF<sub>2</sub>)<sub>n</sub>SR<sup>1</sup> (VI), wherein n and R<sup>1</sup> are as defined above. For instance, when n is 1, (VI) can be obtained by either of the following reaction sequences:



or

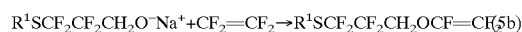


then



Reactions similar to (1) and (2) are described in U.S. Pat. No. 4,474,700, col. 4, line 67 to col. 5, line 3 (which is hereby included by reference), while reactions similar to (3) are described in U.S. Pat. Nos. 4,597,913 and 4,555,369 (which are hereby included by reference). While not critical, reaction (3) may be carried out at about 0° C. to about 100° C., and reaction (4) at about 0° C. to about 50° C. The same solvents for (1) and (2), as recited in U.S. Pat. No. 4,474,700 may be used for (3). For (4), it is preferred to run the reaction in water or a lower alcohol, such as ethanol, or a mixture of the two. In reaction (4) alkali metal borohydrides are suitable reducing agents, but LiAlH<sub>4</sub> or hydrogen in the presence of a suitable catalyst may also be used under conditions known to the artisan.

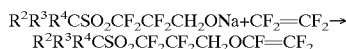
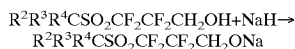
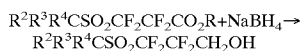
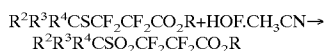
The alcohol formed in reaction (4) may be converted to the vinyl ether by



Reactions (5a) and (5b) may be carried out in sequence in a single reactor. Any suitable base that will produce the appropriate alkoxide anion in a reaction such as (5a) may be

used, such as an alkali metal hydride or metal alkyl. Reaction (5a) may be carried out at a temperature of about 0° C. to about 50° C., which reaction (5b) can be carried out at about 25° C. to about 100° C. The pressure range and solvents which are useful for (5b) include those listed in U.S. Pat. No. 4,474,700, supra. Dioxane is also a useful solvent.

Compound (VI) can be made, for instance by the following sequence of reactions:



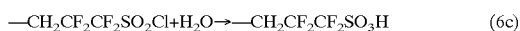
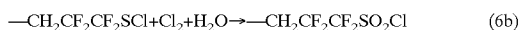
These reactions are illustrated in the Examples.

Compounds of formula (V) or (VI), such as the product of reaction (5b) may be homopolymerized or copolymerized with TFE, using standard free radical polymerization techniques, see for instance U.S. Pat. Nos. 4,273,728, 4,273,729 and 4,275,225, which are hereby included by reference. The polymerizations may be conducted neat, in the presence of an organic liquid (which may or may not be solvent for any of the starting materials and/or product polymer, and which preferably does not cause appreciable chain transfer), or in aqueous suspension or emulsion. For instance, a polymerization may be run in 1,1,2-trichlorotrifluoroethane using perfluoropropionyl peroxide as the free radical initiator. Polymerization temperature is chosen depending on the type of initiator and is generally in the range of 0° C. to about 150° C. Preferred temperatures are from about 25° C. to about 100° C. Polymerizations are generally run in a closed pressure vessel so as to minimize loss of volatile or gaseous monomers, in the absence of oxygen and at autogenous pressures.

The (co)polymer produced by the (co)polymerization of (V) or (VI) is soluble in organic solvents, and so is useful as a chemically resistant coating or encapsulant. The coating may be made by applying the solution to the surface to be coated by brushing, spraying or rolling etc., of a solution of the polymer, and the solvent allowed to evaporate. An article may be encapsulated by dipping or otherwise completely coating the article with a polymer solution and allowing the solvent to evaporate.

The (co)polymers of (V) or (VI) are also useful as intermediates for the preparation of a sulfonic acid containing (co)polymer which is useful as an ion-exchange resin or an acid catalyst. In (co)polymers of (V) the sulfonic acid is produced by oxidation of thio group present in the (co) polymer. When this oxidation is carried out it is important that the reactions used to produce the sulfonic acid group are selective so that the —CH<sub>2</sub>— group in the polymer is not oxidized or otherwise chemically changed. This is somewhat different from the analogous thio-containing perfluorinated polymers, which are overall much more resistant to such oxidations or other side reactions.

Continuing with the polymer of the product of reaction (5b), this oxidation may be accomplished by the following reactions (only the appropriate sulfur group is shown on the polymer—the remainder of the polymer is chemically unaffected)



The product of reaction (6c) may be converted to an alkali metal or ammonium sulfonate by reaction with an appropriate base, such as sodium hydroxide, potassium carbonate, or ammonium hydroxide.

For reaction (6a) the minimum amount of chlorine desired is the stoichiometric amount but it is preferred if there is a 2 to 5 fold excess of chlorine present. For reaction (6b) it is desirable to have at least the stoichiometric amounts of water and chlorine present, but it is preferred if the water is present in 2 to 20 fold excess, and the chlorine is present in 2 to 5 fold excess. Reaction (6b) may also be carried out by using an alkali metal hypochlorite, such as sodium hypochlorite, in place of chlorine. Reaction (6b) may also be conducted in the presence of an organic acid, such as acetic acid or trifluoroacetic acid, or in an inert organic solvent such as 1,1,2-trichloro-1,2,2-trifluoroethane. Reaction (6a) and (6b) are preferably done in a closed pressure vessel so as to minimize the loss of volatile reagents, and under autogenous pressure. Reaction (6b) is preferably done in a vessel constructed of glass or an inert polymeric material such as polytetrafluoroethylene, to minimize formation of corrosion products which may be formed in metal reactors. In both reactions, having at least a stoichiometric amount of each reagent present ensures at least the possibility that all of the thio groups will be converted to sulfonyl chloride groups. Reactions (6a) and (6b) may be carried out "simultaneously", that is the sulfide starting material of equation (6a) is placed in a reactor with water and a sufficient amount of chlorine to carry out both (6a) and (6b) and the two reactions carried out by heating for a sufficient period of time to convert the starting sulfide directly to the desired sulfonyl chloride (see Example 30).

For reaction (6c), typical hydrolysis conditions for sulfonyl chlorides are used, which involves contact of the sulfonyl chloride with water and a base such as sodium, potassium or ammonium hydroxide. Ambient temperatures are convenient, although temperatures up to 75° C. may be used to accelerate the hydrolysis reaction. If sufficient base is used to form the sulfonate salt, the sulfonic acid may be made by addition of a strong acid.

The resulting sulfonyl chloride containing polymer consists essentially of repeat unit repeat unit (IV), and optionally repeat unit (I). The polymer wherein corresponding unit is a sulfonic acid or sulfonate group consists essentially of the repeat unit (II), and optionally repeat unit (I). In both instances "consisting essentially of" includes polymers with small amounts of residual (unconverted) thio, sulfenyl chloride, and/or sulfonyl chloride groups.

In some preferred polymers containing repeat unit (II) or (VII), repeat unit (I) is also present. In these polymers it is preferred that the molar ratio of (I):(II) or (I):(VII) in the polymer is about 1:99 to about 99:1, more preferably about 1:10 to about 10:1. In another preferred polymer, the ratio of (I):(II) or (VII) is 0:100.

When the repeat unit derived from (VI) is included in a polymer, the sulfone containing side chain, —OCH<sub>2</sub>CF<sub>2</sub>(CF<sub>2</sub>)<sub>n</sub>SO<sub>2</sub>CR<sup>2</sup>R<sup>3</sup>R<sup>4</sup> is present in the polymer. As noted above a —OCH<sub>2</sub>CF<sub>2</sub>(CF<sub>2</sub>)<sub>n</sub>SCL side chain may also be present in the polymer, derived from the monomer (V), and subsequently converted to this side chain. Both of these may be converted to a sulfonyl fluoride containing side chain —OCH<sub>2</sub>CF<sub>2</sub>(CF<sub>2</sub>)<sub>n</sub>SO<sub>2</sub>F by reaction of the polymer (actually the sulfone or sulfenyl chloride of the side chain) with a reagent derived from fluorine, acetonitrile and water. This combination is known in the art, and sometimes has been formulated as HOF·CH<sub>3</sub>CN, see for instance S. Rozen, et al., Tetrahedron, vol. 49, p. 8169 (1993). The sulfonyl fluoride may be converted to a sulfonic acid or a sulfonic acid salt by methods similar to those described for converting the analogous sulfonyl chlorides. However, sulfonyl fluorides have the advantage of being more stable than

sulfonyl chlorides, see for instance Oudrhiri-Hassani, et al., *J. Fluorine Chem.*, vol. 25, p. 491-504 (1984). By starting with the sulfone group  $-\text{OCH}_2\text{CF}_2(\text{CF}_2)_n\text{SO}_2\text{CR}^2\text{R}^3\text{R}^4$ , and the fluorine/acetonitrile/water reagent, the side chain can be converted to sulfonyl fluoride in one step, another advantage. It is preferred that, in all compounds and processes in which they appear,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are all methyl.

It is preferred that the reaction with the fluorine/acetonitrile/water combination be carried out in solution at a temperature of about  $0^\circ\text{C}$ . to about  $25^\circ\text{C}$ . As with most reactions that use or produce very reactive substances, it is preferred to carry out the reaction in the presence of an inert gas such as nitrogen or argon. It is also preferred that an approximately stoichiometric amount of the fluorine/acetonitrile/water reagent be used in the reaction. It is noted that the sulfone or sulfonyl chloride is usually cleanly converted to the sulfonyl fluoride without fluorination of any carbon-hydrogen bonds in the polymer.

Alternatively, polymers containing an  $-\text{OCH}_2\text{CF}_2(\text{CF}_2)_n\text{SO}_2\text{CR}^2\text{R}^3\text{R}^4$  can be converted to the sulfonyl fluoride by reaction with  $\text{BrF}_3$ . It is preferred that the reaction with the  $\text{BrF}_3$  be carried out in solution at a temperature of about  $50^\circ\text{C}$ . to about  $100^\circ\text{C}$ . It is preferred that an approximately 50% excess of the fluorine/acetonitrile/water reagent be used in the reaction.

In all of the compounds and polymers herein, as applicable: it is preferred that all alkyl or substituted alkyl groups contain 1 to 10 carbon atoms, and more preferred if such alkyl groups are methyl groups; it is also preferred if  $\text{R}^1$  is alkyl, especially methyl; and it is preferred if  $n$  is 1.

#### EXAMPLE 1

##### Synthesis of $\text{CH}_3\text{SCF}_2\text{CF}_2\text{CO}_2\text{CH}_3$

A 400 mL pressure vessel was charged with 34.1 g (0.49 mol) of sodium thiomethoxide and 150 mL of anhydrous dimethylsulfoxide (DMSO). The vessel was closed, cooled in dry ice, evacuated and charged with 32 g (0.73 mol) of carbon dioxide and 50 g (0.5 mol) of tetrafluoroethylene. The vessel contents were heated with agitation to  $50^\circ\text{C}$ . for 1 hr and  $100^\circ\text{C}$  for 5 hr. After cooling to room temperature, the vessel contents were transferred to a 500 mL round bottom flask using an additional 30 mL of DMSO to rinse. Dimethylsulfate (65 g, 0.52 mol) was added and the mixture was stirred for 3 hr at  $30^\circ\text{C}$ – $50^\circ\text{C}$ . Volatiles were removed by distillation at 1 mm into a dry ice cooled receiver with a maximum pot temperature of  $65^\circ\text{C}$ .

The volatiles collected from eight reactions were combined, washed with water and dried over anhydrous magnesium sulfate. Distillation through a 46 cm Vigreux column gave 547 g (80%) of colorless liquid, bp  $88^\circ\text{C}$ . at 8 kPa.  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 2.38 (s, 3H), 3.96 (s, 3H);  $^{19}\text{F}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ )  $-92.5$  (t, 2F),  $-117.0$  (t, 2F).

#### EXAMPLE 2

##### Synthesis of $\text{CH}_3\text{SCF}_2\text{CF}_2\text{CH}_2\text{OH}$

The ester  $\text{CH}_3\text{SCF}_2\text{CF}_2\text{CO}_2\text{CH}_3$  (546 g, 2.65 mol) was added dropwise over 3 hr to a solution of 100.2 g (2.65 mol) of sodium borohydride in 920 mL of ethanol which was cooled in an ice water bath. After the addition was complete the mixture was allowed to warm to room temperature over 1 hr. The mixture was cooled in ice water and cautiously hydrolyzed by addition of 1.4 L of 6N hydrochloric acid. The mixture was diluted to 5-L with water and a lower layer was collected. The aqueous solution was extracted with 500 mL of methylene chloride. The organic layers were washed

with 1-L of water and dried over anhydrous magnesium sulfate. The methylene chloride was removed by distillation at atmospheric pressure through an 46 cm Vigreux column. Distillation of the residue through the same column gave 372.5 g (79%) of colorless liquid, bp  $35^\circ\text{C}$ – $38^\circ\text{C}$ . at 20 Pa.  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 2.58 (s, 3H), 2.88 (t, 1H), 4.05 (m, 2H);  $^{19}\text{F}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ )  $-92.7$  (t, 2F),  $-121.7$  (m 2F).

#### EXAMPLE 3

##### Synthesis of $\text{CH}_3\text{SCF}_2\text{CF}_2\text{CH}_2\text{OCF}=\text{CF}_2$

The alcohol  $\text{CH}_3\text{SCF}_2\text{CF}_2\text{CH}_2\text{OH}$  (53.4 g, 0.3 mol) was added dropwise to a suspension of 8.75 g of 95% sodium hydride in 100 mL of anhydrous dioxane which was cooled in an ice water bath. This mixture was stirred overnight at room temperature and transferred to a 400 mL stainless steel pressure vessel using an additional 40 mL of dioxane to rinse. The vessel was closed, cooled in dry ice, evacuated, charged with 50 g of tetrafluoroethylene, warmed to  $50^\circ\text{C}$ . and agitated for 18 hr. The vessel was vented to atmospheric pressure at room temperature and its contents were poured into 1 L of ice water containing 25 mL of concentrated hydrochloric acid. The lower layer was separated and washed with 500 mL of ice water.

The combined product from seven runs was washed again with  $2 \times 500$  mL of ice water and distilled through a 41 cm Vigreux column. A liquid weighing 371 g was collected with a boiling point of  $50^\circ\text{C}$ – $52^\circ\text{C}$ . at 2.7–3.3 kPa. This product in two portions was chromatographed through columns of 1 Kg silica gel, packed in pentane. The columns were eluted with pentane. Early fractions which contained only the desired product by glpc analysis were combined and distilled through the Vigreux column at atmospheric pressure to remove the solvent and then at reduced pressure to give 291.8 g of product, bp  $54^\circ\text{C}$ – $55^\circ\text{C}$ . at 3.5 kPa which was a minimum of 99.5% pure by glpc analysis. An additional 51 g of product which was 95% pure by glpc analysis was obtained from latter chromatography cuts.  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 2.39 (s, 3H), 4.38 (t, 2H);  $^{19}\text{F}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ )  $-92.6$  (s, 2F),  $-120.1$  (m 2F),  $-121.8$  (dd, 1F),  $-127.5$  (dd, 1F),  $-137.0$  (dd, 1F). Another sample prepared in the same fashion was submitted for elemental analysis. Anal. Calcd. for  $\text{C}_6\text{H}_5\text{F}_7\text{OS}$ : C, 27.91; H, 1.95; F, 51.52; S, 12.43. Found: C, 27.89; H, 2.04; F, 52.32; S, 12.34.

#### EXAMPLE 4

##### Polymerization of $\text{CH}_3\text{SCF}_2\text{CF}_2\text{CH}_2\text{OCF}=\text{CF}_2$

A 50 mL round bottom flask was charged with 5.8 g of  $\text{CH}_3\text{SCF}_2\text{CF}_2\text{CH}_2\text{OCF}=\text{CF}_2$  and 10 g of 1,1,2-trichlorotrifluoroethane. This solution was frozen, and the reactor vessel was evacuated and filled with argon several times. A solution (1.0 mL) of about 0.025M  $(\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CO}_2)_2$  in  $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCFHCF}_3$  was added at  $-30^\circ\text{C}$ . The solution was allowed to slowly warm to room temperature and stirred for 72 hr. It was poured into 300 mL of hexane which was cooled in dry ice. The hexane was decanted from the solid polymer which was dried in a vacuum oven at  $125^\circ\text{C}$ . to give 4.3 g of clear glass. DSC analysis showed a  $T_g$  at about  $14^\circ\text{C}$ . on the second heat and no melting peak.

#### EXAMPLE 5

##### Copolymerization of $\text{CH}_3\text{SCF}_2\text{CF}_2\text{CH}_2\text{OCF}=\text{CF}_2$ and Tetrafluoroethylene in a 1:2 Molar Ratio

An 80 mL pressure vessel was cooled in dry ice and charged with 19 g of  $\text{CH}_3\text{SCF}_2\text{CF}_2\text{CH}_2\text{OCF}=\text{CF}_2$ , 44 g of

1,1,2-trichlorotrifluoroethane and 10 mL of a solution of about 0.025M  $(CF_3CF_2CF_2OCF(CF_3)CO_2)_2$  in  $CF_3CF_2CF_2OCFHCFCF_3$ . The tube was closed, evacuated and charged with 15 g of tetrafluoroethylene. The tube was allowed to warm without external heating. Internal pressure reached a maximum of about 1 MPa at 19° C. and fell over the course of several hours to 0.2 MPa at 26° C. The reactor was vented to atmospheric pressure and a thick clear gel in the reactor was dissolved in about 800 mL of 1,1,2-trichlorotrifluoroethane. This solution was filtered, concentrated to about 500 mL and added slowly to 800 mL of hexane which was cooled in dry ice. The solid precipitate was collected, dried under a heat lamp and then in a vacuum oven at 125° C. to give 27.3 g of white polymer which could be pressed at 80° C. to a clear tough film. Inherent viscosity in 1,1,2-trichlorotrifluoroethane was 1 to 1.82. DSC analysis showed a  $T_g$  at 5.4° C. on the second heat and no melting peak. Another polymer sample prepared in similar fashion using perfluoropropionyl peroxide as initiator had an inherent viscosity of 0.197 and about a 1:2 ratio of monomers as calculated from its  $^{19}F$  NMR spectrum. Anal. Calc. for 1:2 copolymer: C, 26.21; H, 1.10; F, 62.20; S, 6.99. Found: C, 25.67; H, 1.15, F, 61.91; S, 6.94.

A third sample of this copolymer was prepared using 29 g of 1,1,2-trichlorotrifluoroethane and 5 mL of the 0.025M  $(CF_3CF_2CF_2OCF(CF_3)CO_2)_2$  in  $CF_3CF_2CF_2OCFHCFCF_3$  initiator solution. This material had an inherent viscosity of 0.30 dL/g.

#### EXAMPLE 6

##### Copolymerization of $CH_3SCF_2CF_2CH_2OCF=CF_2$ and Tetrafluoroethylene in a 1:4 Molar Ratio

Following the procedure of Example 5, a mixture of 14.5 g  $CH_3SCF_2CF_2CH_2OCF=CF_2$ , 5 mL of a solution of about 0.025M  $(CF_3CF_2CF_2OCF(CF_3)CO_2)_2$  in  $CF_3CF_2CF_2OCFHCFCF_3$  and 23 g of tetrafluoroethylene was allowed to react for about 13 hr at a maximum temperature of 28° C. The resulting gel was washed several times with 1,1,2-trichlorotrifluoroethane and dried at 120° C. in a vacuum oven to give 26.5 g of a colorless solid polymer which could be pressed to a clear film at 225° C. DSC analysis showed no thermal events from 0° to 350° C. on the second heating. The polymer was determined to contain 82.3 mole % of tetrafluoroethylene and 17.7 mole % of the sulfur containing comonomer by integration of appropriate resonances in its fluorine NMR spectrum, measured in hexafluorobenzene solution at 80° C.

#### EXAMPLE 7

##### Conversion of the $-CF_2SCH_3$ Side Chain to $-CF_2SCl$

A 2.9 g sample of polymer from Example 5 was dissolved in 50 mL of 1,1,2-trichlorotrifluoroethane in a heavy walled glass tube. The tube contents were frozen and the tube was evacuated, charged with 3.5 mL of liquid chlorine and sealed. The tube was heated in an oven at 120° C. for 14 hr. It was cooled in dry ice and acetone, opened and the clear solution was concentrated under vacuum at 40° C. to a white

opaque solid. A proton NMR spectrum of the solid in 1,1,2-trichlorotrifluoroethane showed the presence of a triplet at 4.46 ppm for the pendant  $OCH_2$  group and the nearly complete absence of the  $SCH_3$  signal at 2.35 ppm.

#### EXAMPLE 8

##### Conversion of the $-CF_2SCl$ Side Chain to $-CF_2SO_2Cl$

The product from Example 7 in 50 mL of 1,1,2-trichlorotrifluoroethane was sealed into a heavy-walled glass tube with 20 mL of water and 4 mL of liquid chlorine. The tube was heated in an oven at 100° C. for 16 hr and at 120° C. for 16 hr. The organic layer was isolated and concentrated under vacuum to 2.87 g of light yellow solid. An infrared spectrum of the solid showed a band at  $1421\text{ cm}^{-1}$  suggesting the presence of the  $CF_2SO_2Cl$  group.

#### EXAMPLE 9

##### Copolymerization of $CH_3SCF_2CF_2CH_2OCF=CF_2$ and Tetrafluoroethylene

An 80-mL Hastelloy® pressure vessel was cooled in dry ice, flushed with argon and charged with 19.3 g of  $CH_3SCF_2CF_2CH_2OCF=CF_2$ , 29 g of 1,1,2-trichlorotrifluoroethane and 1-ml of an approximately 0.025M solution of  $(CF_3CF_2CF_2OCF(CF_3)CO_2)_2$  in  $CF_3CF_2CF_2OCFHCFCF_3$ . The vessel was closed, evacuated and charged with 15 g of tetrafluoroethylene. The vessel was agitated while being allowed to warm to room temperature overnight. The vessel was vented, the contents were diluted with additional 1,1,2-trichlorotrifluoroethane, filtered and concentrated in vacuum to 8.03 g of solid polymer. The polymer was dissolved in 1,1,2-trichlorotrifluoroethane and poured slowly into pentane which was chilled to -40° C. The solid polymer was isolated and dried under vacuum affording 7.36 g of polymer with an inherent viscosity (1,1,2-trichlorotrifluoroethane) of 0.48 dL/g. Its proton and fluorine NMR spectra were as described in Example 5 and the molar ratio of  $CH_3SCF_2CF_2CH_2OCF=CF_2$  to tetrafluoroethylene units in the polymer was calculated as 2:3.

#### EXAMPLE 10

##### Polymerization of $CH_3SCF_2CF_2CH_2OCF=CF_2$

A 50-mL round bottom flask was charged with 10.3 g of the title monomer and evacuated and filled with argon four times. The flask was cooled in a dry ice bath and 1 mL of a solution of about 0.035M  $(CF_3CF_2CF_2OCF(CF_3)CO_2)_2$  in  $CF_3CF_2CF_2OCFHCFCF_3$  was added. This solution was allowed to stir for 48 hr at 0° C., warmed over one day to room temperature, stirred for one day at room temperature and warmed to 50° C. for 3 hr. It was cooled to -5° C. and a second 1-mL portion of the peroxide initiator solution was added. This mixture was allowed to warm to room temperature over 1 day and heated to 50° C. for 3 hr. The product was dissolved in tetrahydrofuran (THF) and precipitated by adding to 500 mL of pentane which had been cooled to -40° C. The finely divided solid was collected, dissolved in THF and evaporated under vacuum giving 6.23 g of polymer. Inherent viscosity in THF was 0.19 dl/g. Analysis by gel permeation chromatography in THF showed  $M_n=34300$  and  $M_w=94300$  versus poly(methyl methacrylate) standards. An  $M_w$  of 94300 g/mol was measured by laser light scattering in toluene solution.  $^1H$  NMR ( $\delta$ , THF- $D_8$ ) 2.4 (3H), 4.5 (2H).  $^{19}F$  NMR ( $\delta$ , THF- $D_8$ ) -92.1 (2F,  $CF_2S$ ), -109 to -119 (2F, backbone  $CF_2$ ), -119.1 (2F,  $CH_2CF_2$ ), -130 to -133.5 (1F).

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## EXAMPLE 11

Emulsion Homopolymerization of  
 $\text{CH}_3\text{SCF}_2\text{CF}_2\text{CH}_2\text{OCF}=\text{CF}_2$ 

A 1-L round bottom flask was swept with argon and charged with 200 mL of deoxygenated water, 1.9 g of ammonium perfluorononanoate, 12.9 g of the title monomer and 2 g of  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ . This mixture was stirred vigorously at room temperature and 0.052 g of sodium bisulfite and 0.057 g of ammonium persulfate were added. This mixture was stirred for 24 hr at room temperature. An additional 0.052 g of sodium bisulfite and 0.057 g of ammonium persulfate were added and this mixture was stirred for 24 hr at room temperature. The emulsion was diluted with 200 mL of distilled water and frozen in dry ice. After thawing, the mixture was filtered and the solid was washed with 2x500 mL of water and dried under vacuum giving 11.8 g of white solid polymer. Inherent viscosity in THF was 0.069 dL/g and the proton and fluorine NMR spectra were as described in Example 10.

## EXAMPLE 12

Conversion of the  $-\text{SCH}_3$  Group to  $-\text{SCl}$  in the  
 $\text{CH}_3\text{SCF}_2\text{CF}_2\text{CH}_2\text{OCF}=\text{CF}_2$  Homopolymer

A 400 mL Hastelloy pressure vessel was charged with 2.0 g of a homopolymer of  $\text{CH}_3\text{SCF}_2\text{CF}_2\text{CH}_2\text{OCF}=\text{CF}_2$  (prepared as described in Example 10 with an inherent viscosity of 0.12) and 150 mL of 1,1,2-trichlorotrifluoroethane. The vessel was closed, cooled with dry ice and charged with 12 g of chlorine. The vessel contents were heated to 90° C. for 2 hr and 125° C. for 18 hr. The vessel was cooled and vented to atmospheric pressure. The light yellow solution was concentrated under vacuum to 1.81 g of solid. Its proton NMR spectrum in 1,1,2-trichlorotrifluoroethane showed absorption at 4.5 ppm for the  $-\text{OCH}_2-$  group and a small peak at 4.85 ppm assigned to an  $-\text{SCH}_2\text{Cl}$  impurity. There was no absorption detected for the  $\text{SCH}_3$  group which is present in the starting polymer.

## EXAMPLE 13

Conversion of the  $-\text{SCH}_3$  Group to  $-\text{SO}_2\text{Cl}$  in the  
 $\text{CH}_3\text{SCF}_2\text{CF}_2\text{CH}_2\text{OCF}=\text{CF}_2$  Homopolymer

A 210 mL Hastelloy® pressure vessel was charged with 5.0 g of the homopolymer of  $\text{CH}_3\text{SCF}_2\text{CF}_2\text{CH}_2\text{OCF}=\text{CF}_2$  (prepared as described in Example 10 with an inherent viscosity of 0.15) and 100 mL of carbon tetrachloride. The vessel was closed, cooled with dry ice and charged with 15 g of chlorine. The vessel contents were heated to 125° C. for 18 hr. The vessel was cooled and vented to atmospheric pressure. The clear light yellow solution from the pressure vessel was bubbled with nitrogen for a few minutes to remove excess chlorine. A proton NMR spectrum of the solution showed a peak at 4.42 ppm ( $-\text{OCH}_2-$ ) and the complete absence of the  $\text{CH}_3$  resonance of the starting polymer.  $^{19}\text{F}$  NMR ( $\delta$ ,  $\text{CCl}_4$ ) -93.7 (2F,  $\text{CF}_2\text{S}$ ), -113.0 (2F, backbone  $\text{CF}_2$ ), -118.0 (2F,  $\text{CH}_2\text{CF}_2$ ), -130 to -133.5 (1F).

About one-half of the above carbon tetrachloride solution was diluted to 100 mL with carbon tetrachloride and transferred to a 500 mL creased flask. Aliquat® 336 surfactant (0.1 g) (Janssen Chimica) was added, followed by 100 mL of an aqueous sodium hypochlorite solution. This mixture was stirred vigorously for 1 hour at room temperature and for 3 hours at 40° C. After standing overnight, the mixture

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was filtered and the solid polymer was dried at 100° C. and 0.05 mm giving 2.61 g of white solid which was insoluble in carbon tetrachloride and 1,1,2-trichlorotrifluoroethane. An infrared spectrum of the solid showed a strong band at 1415  $\text{cm}^{-1}$  confirming presence of the  $\text{SO}_2\text{Cl}$  group.

## EXAMPLE 14

Synthesis of  $(\text{CH}_3)_3\text{CSCF}_2\text{CF}_2\text{CO}_2\text{CH}_3$ 

A 400 mL pressure vessel was charged with 52.8 g of dry sodium tertbutylthiolate and 150 mL of dimethyl sulfoxide. The vessel was closed, cooled, evacuated and charged with 35 g of carbon dioxide and 50 g of tetrafluoroethylene. The mixture was agitated for 1 hr at 25° C. and for 10 hr at 50° C. The vessel was cooled and its contents discharged. The combined product from 7 runs was treated dropwise at 30°-35° C. with 414 g of dimethyl sulfate. This mixture was stirred for 5 hr at 45°-50° C. The volatile products were then collected under full pump vacuum in a dry ice and acetone cooled receiver. The volatile products were added to 4-L of ice water. The organic layer was separated, washed with saturated aqueous sodium bicarbonate solution and dried over magnesium sulfate. Distillation through a glass helix packed column gave 658 g (84%) of product, bp 30°-32° C. at 0.05 mm. H NMR ( $\text{CDCl}_3$ ) 1.55(s, 9H), 3.97 (s, 3H); F NMR ( $\text{CDCl}_3$ ) -86.11 (t, 2F), -117.52 (m, 2F).

## EXAMPLE 15

Synthesis of  $(\text{CH}_3)_3\text{CSCF}_2\text{CF}_2\text{CH}_2\text{OH}$ 

The ester  $(\text{CH}_3)_3\text{CSCF}_2\text{CF}_2\text{CO}_2\text{CH}_3$  (289.5 g, 1.17 mol) was added dropwise to a mixture of 44.6 g (1.18 mol) sodium borohydride in 310 mL of ethanol at 1°-5° C. The resulting mixture was stirred for 1 hr in an ice water bath, then allowed to warm to room temperature for ¼ hr. The mixture was recooled in an ice water bath and 500 mL of 6N hydrochloric acid and 600 mL of water were added dropwise. The solids were removed by filtration and washed with 200 mL of water and 2x200 mL of methylene chloride. The organic layer was separated and the aqueous filtrate was extracted with 3x200 mL of methylene chloride. The combined organic layers were washed with 100 mL of water, dried over magnesium sulfate and concentrated under vacuum. The product was distilled through a short Vigreux column giving 243.7 g (95%), bp 32° C. at 0.25 mm.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 1.54 (s, 9H), 3.07 (t, 1H), 4.02 (dt, 2H);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ) -86.57 (t, 2F), -122.34 (m, 2F).

## EXAMPLE 16

Synthesis of  $(\text{CH}_3)_3\text{CSCF}_2\text{CF}_2\text{CH}_2\text{OCF}=\text{CF}_2$ 

The alcohol  $(\text{CH}_3)_3\text{CSCF}_2\text{CF}_2\text{CH}_2\text{OH}$  (67 g, 0.3 mol) was added dropwise to a suspension of 12.2 g (.51 mol) of sodium hydride in 100 mL of dry dioxane. The mixture was stirred 8 hr, then allowed to stand over a weekend. Its was transferred to a 400 mL Hastelloy® pressure vessel using 50 mL of dioxane for rinsing. The vessel was closed, cooled, evacuated and charged with 45 g (0.45 mole) of tetrafluoroethylene. The vessel was heated at 60° C. for 18 hr. The combined product from 5 runs was poured into ice water and a lower layer was collected. The organic layer was washed with dilute aqueous hydrochloric acid and dried over magnesium sulfate. The product was distilled through a spinning band column giving 267.4 g (64%) of product, bp 48° C. at 3 mm.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 1.53 (s, 9H), 4.35 (t, 2H);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ) -86.4 (s, 2F), -120.8 (s, 2F), -121.8 (dd, 1F),

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-127.5 (dd, 1F), -137.4 (dd, 1F); Anal. Calcd for  $C_6H_{11}F_7SO$ : C, 36.00; H, 3.69; S 10.68; F, 44.30. Found: C, 35.78; H, 3.80; S, 10.80; F, 44.32.

## EXAMPLE 17

Homopolymerization of  $(CH_3)_3CSCF_2CF_2CH_2OCF=CF_2$ 

A dry Carius tube was charged with 6 g of  $(CH_3)_3CSCF_2CF_2CH_2OCF=CF_2$ . The tube was cooled under nitrogen to  $-80^\circ C$ . and charged with 0.8 mL of a 0.13 molar solution of  $(CF_3CF_2CF_2OCF(CF_3)CO_2)_2$  in  $CF_3CF_2CF_2OCFHCF_3$ . After freezing and purging three times, the tube was sealed and placed in a  $10^\circ C$ . bath for 72 hr. It was allowed to warm to room temperature and stand for 4 hr. The tube was opened, the contents dissolved in THF and slowly poured into 500 mL of pentane. The solvent was decanted and the precipitated polymer was dissolved in minimal THF, concentrated under vacuum and dried at  $100^\circ C$ . and 0.05 mm giving 4.1 g.  $^1H$  NMR (THF) 1.52 (s, 9H), 4.45 (t, 2H).  $^{19}F$  NMR (THF) -85.7 (2F), -111.8 (2F), -119.6 (2F), -130 to -135 (1F). GPC (THF)  $M_w=34600$ ,  $M_n=24000$ . Anal. Found: C, 35.95; H, 3.62; F, 43.96; S, 10.47.

## EXAMPLE 18

Copolymerization of  $(CH_3)_3CSCF_2CF_2CH_2OCF=CF_2$  with Tetrafluoroethylene

An 80 mL pressure vessel was charged with 24.2 g of the monomer  $(CH_3)_3CSCF_2CF_2CH_2OCF=CF_2$ , 20 mL of 1,1,2-trichlorotrifluoroethane and 3.8 g of a 7.6 wt % solution of  $(CF_3CF_2CF_2OCF(CF_3)CO_2)_2$  in  $CF_3CF_2CF_2OCFHCF_3$ . The vessel was closed, cooled, evacuated and charged with 10 g of tetrafluoroethylene. The resulting mixture was agitated for 18 hr without external heating. The vessel was vented and the contents were diluted to about 100 mL with 1,1,2-trichlorotrifluoro-ethane. This solution was slowly poured into 600 mL of pentane. The solvents were decanted and the solid was dissolved in 1,1,2-trichlorotrifluoroethane, concentrated and dried under vacuum giving 29.8 g of polymer which could be pressed at  $75^\circ C$ . and 5000 psi to a clear flexible, tough, flexible film. Inherent visc. (CFDC-113) 0.19. Anal. Found: C, 31.69; H, 2.70; F, 54.75; S, 7.38;  $^1H$  NMR 1.50 (s, 9H), 4.40 (t, 2H);  $^{19}F$  NMR -86.7 (int 39) -135 to -138 (int 18) -117 to -123 (int 173). Calcd. composition 58% TFE, 42% comonomer. TGA -18.8% at  $290^\circ$  to  $307^\circ C$ .

## EXAMPLE 19

Conversion of a  $-CF_2SC(CH_3)_3$  Side Chain to  $-CF_2SCI$ 

A 2.0 g sample of the homopolymer of  $(CH_3)_3CSCF_2CF_2CH_2OCF=CF_2$ , prepared as described in Example 17, was mixed with 35 mL of carbon tetrachloride and 3 g of chlorine in a 75 mL Hastelloy pressure vessel. The vessel was heated at  $85^\circ C$ . for 18 hr. The vessel was cooled to room temperature, vented, the contents discharged and diluted to about 100 mL with carbon tetrachloride. The light yellow solution was evaporated to about 50 mL under a stream of nitrogen, diluted to about 100 mL with carbon tetrachloride and concentrated to about 40 mL under nitrogen. An  $^{19}F$  NMR spectrum of the solution indicated complete conversion to SCl:  $^{19}F$  NMR -93.8 (2F), -113.3 (2F), -118.4 (2F), -136.1 (1F).

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## EXAMPLE 20

Conversion of a  $-CF_2SC(CH_3)_3$  Side Chain to  $-CF_2SCI$ 

A 5.08 g sample of the copolymer of Example 18, 125 mL of carbon tetrachloride and 12 g of chlorine were heated in a Hastelloy pressure vessel for 18 hr at  $87^\circ C$ . The vessel was cooled to room temperature, vented and the contents were discharged using 1,1,2-trichlorotrifluoroethane for rinsing. The solution was concentrated under nitrogen to a thick syrup, dissolved in 125 mL of 1,1,2-trichlorotrifluoroethane and filtered into 300 mL of pentane. The solvents were decanted and the solid was dried giving 3.54 g of the SCl copolymer.  $^{19}F$  NMR -93.6 (int 35), -136 to -138 (int 15), -117 to -123 (int 160).

## General Procedure for Working with Fluorine for Examples 21-29

Fluorine is a strong oxidizer and a very corrosive material. An appropriate vacuum line made from copper or monel in a well ventilated area should be constructed for working with this element. The reactions themselves can be carried out in glass vessels. If elementary precautions are taken, work with fluorine is relatively simple.

General Procedure for Producing the  $HOF \cdot CH_3CN$  Oxidizing Reagent

Mixtures of 10%-15%  $F_2$  diluted with nitrogen were used in this work. The gas mixtures were prepared in a secondary container before the reaction was started. This mixture was then passed in a rate of about 400 ml per minute through a cold ( $-10^\circ C$ .) and vigorously stirred mixture of 400 ml  $CH_3CN$  and 40 ml  $H_2O$ . The formation of the oxidizing power was monitored by reacting aliquots with acidic aqueous solution of KI. The liberated iodine was then titrated with thiosulfate. Concentrations of more than 0.5 mol/liter oxidizing reagent were prepared.

## General Oxidation Procedure

An appropriate amount of sulfide was dissolved in about 30-50 ml of  $CH_2Cl_2$  cooled to  $0^\circ C$ . and added in one portion to the reaction vessel in which the oxidizing agent had been prepared. At least a 6 fold excess of  $HOF \cdot CH_3CN$  was used (two mole/eq are needed as two oxygens donors). The cooling bath was removed and the reaction was stopped after 1 to 2 hours by neutralizing it with saturated sodium bicarbonate solution. It should be noted that the reaction could be left much longer but this did not effect the outcome since most of the reagent decomposes in 2 to 3 hours. The reaction mixture was then poured into 500 ml water and if no solids were detected, extracted with  $CH_2Cl_2$  and washed with  $NaHCO_3$  and water until neutral. The organic layer was dried over  $MgSO_4$ , and the solvent distilled. If a solid material was formed during the work-up it was filtered, washed with water and dried under vacuum.

## EXAMPLE 21

Conversion of a  $-CF_2SCI$  Side Chain to  $-CF_2SO_2Cl$  and  $-CF_2SO_2F$ 

A solution of the copolymer prepared in Example 20 (1.3 g) in 300 ml  $CFCl_3$  was added to 300 mmols of the  $HOF \cdot CH_3CN$  oxidizing solution. The 5 reaction was left for an hour at room temperature and worked up as described above. The solid product (1.1 g) proved to be a mixture of



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the corresponding sulfonyl chloride and sulfonyl fluoride in a ratio of 1:2. IR: 1460, 1415  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 3.4 (wide s);  $^{19}\text{F}$  NMR +45.6 ppm (0.7F, s for  $\text{SO}_2\text{F}$ ), -105.5 and -108 (2F,  $\text{CF}_2\text{SO}_2\text{R}$ ), -117 to -122 (13F for the rest of the  $\text{CF}_2$  groups), -134 to -135.5 (1F, CFO). Anal. Calcd. for the above mixture: C, 21.91; H, 0.4. Found: C, 21.66; H, 0.8%.

## EXAMPLE 22

Conversion of a  $-\text{CF}_2\text{SCl}$  Side Chain to  $-\text{CF}_2\text{SO}_2\text{Cl}$  and  $-\text{CF}_2\text{SO}_2\text{F}$

A solution of 2.4 g of the homopolymer, prepared as described in Example 19, dissolved in 300 ml  $\text{CFCl}_3/\text{CCl}_4$  was added to 110 mmols of the oxidizing solution. The reaction was left for an hour at room temperature and worked up as described above. The solid product (2.26 g) proved to be a mixture of the corresponding sulfonyl chloride and sulfonyl fluoride in a ratio of 2:1. IR: 1460, 1415  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 3.4 (wide s);  $^{19}\text{F}$  NMR+45.7 ppm (0.3F, s,  $\text{SO}_2\text{F}$ ), -105 and -108 (2F,  $\text{CF}_2\text{SO}_2\text{R}$ ), -112 (2F,  $\text{CF}_2-\text{CF}$ ) -116, -117.8 (2F,  $\text{CF}_2-\text{CH}_2$ ) and -134 (1F, CFO). Anal. Calcd. for the above mixture: C, 19.72; H, 0.66; S, 10.5; Cl, 7.42. Found: C, 20.12; H, 0.65; S, 9.74, Cl, 7.34%.

## EXAMPLE 23

Conversion of a  $-\text{CF}_2\text{SC}(\text{CH}_3)_3$  Side Chain to  $-\text{CF}_2\text{SO}_2\text{F}$  and  $-\text{CF}_2\text{SO}_2\text{C}(\text{CH}_3)_3$

A solution of 1.8 g of the homopolymer of  $(\text{CH}_3)_3\text{SCF}_2\text{CF}_2\text{CH}_2\text{OCF}=\text{CF}_2$ , prepared as described in Example 17, dissolved in 150 ml  $\text{CHCl}_3/\text{CF}_2\text{ClCFCl}_2$  (1:1) was added to a solution containing 170 mmol of the oxidizing solution. The reaction was left for 2 hours at room temperature and worked up as described above. After concentration of the organic layer a solid (1.5 gr, 81% yield) was precipitated, filtered and dried. It proved to be a mixture of the t-Bu sulfone and the corresponding sulfonyl fluoride in a ratio of 2:1. IR=1460, 1340  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 1.55 ppm (s, t-Bu), 4.7 (b);  $^{19}\text{F}$  NMR=+46 ppm (0.3F,  $\text{SO}_2\text{F}$ ), -108--118 (6F, 3  $\text{CF}_2$  groups), -133.5 (1F CFO). Anal. Calcd. for the above mixture: C, 28.54; H, 2.26; F, 43.87. Found: C, 28.15; H, 35 2.39; F, 43.95.

## EXAMPLE 24

Conversion of a  $-\text{CF}_2\text{SC}(\text{CH}_3)_3$  Side Chain to  $-\text{CF}_2\text{SO}_2\text{C}(\text{CH}_3)_3$

A solution of the copolymer prepared in Example 5 (5.6 g) in 300 ml 1:1  $\text{CHCl}_3:\text{CFCl}_3$ , was added to 400 mmol of the oxidizing solution. The reaction was left for an hour at room temperature and worked up as described above. The solid product (6 g) proved to be the polymeric sulfone derivative. IR: 1340  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 4.9 (2H, b), 1.56 (9H, s);  $^{19}\text{F}$  NMR -108 ppm (2F,  $\text{CF}_2\text{SO}_2\text{R}$ ), -117 to -121 (9F for the rest of the  $\text{CF}_2$  groups), -135 (1F, CFO). Anal. Calcd.: C, 30.26; H, 2.43; S, 7.08. Found: C, 29.72; H, 2.04; S, 7.00.

## EXAMPLE 25

Conversion of a  $-\text{CF}_2\text{SO}_2\text{C}(\text{CH}_3)_3$  Side Chain to  $-\text{CF}_2\text{SO}_2\text{F}$

Warning!  $\text{BrF}_3$  reacts violently with petroleum ether, water, acetone and other oxygenated solvents. Extreme caution should be used when working with this reagent.

The copolymer obtained as in Example 11 (0.5 g) was suspended in 30 mL of FC-75 (a perfluorinated ether con-

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sisting mostly of perfluorobutyltetrahydrofuran). Bromine trifluoride (1 mL) was added and the mixture was heated at 80° C. for 3 hr and then stirred overnight at room temperature. Water was cautiously added to destroy excess  $\text{BrF}_3$  and the mixture was washed with aqueous sodium thiosulfate to remove traces of bromine. A solid product was isolated weighing 0.36 g. TGA analysis showed no weight loss until a temperature of about 300° C. and a 10% weight loss at a temperature of about 340° C. This TGA data indicates complete conversion of the t-butyl sulfone group because the starting polymer showed 13% weight loss at 172° C. IR: 1464  $\text{cm}^{-1}$ ;  $^{19}\text{F}$  NMR+45.6 ppm (s,  $\text{SO}_2\text{F}$ ), -108 ( $\text{CF}_2\text{SO}_2\text{R}$ ), -117 to -122 (the rest of the  $\text{CF}_2$  groups), -135.5 (CFO).

## EXAMPLE 26

Synthesis of  $(\text{CH}_3)_3\text{CSO}_2\text{CF}_2\text{CF}_2\text{CO}_2\text{CH}_3$

The ester  $(\text{CH}_3)_3\text{CSCF}_2\text{CF}_2\text{CO}_2\text{CH}_3$  (13 g) in 100 ml 1:1  $\text{CHCl}_3:\text{CFCl}_3$  was added to a solution containing 460 mmol of the  $\text{HOF}\cdot\text{OCH}_3\text{CN}$  oxidizing agent. The reaction was left for an hour at room temperature and worked up as described in the general procedure. The product was distilled under vacuum (7 Pa) at 70°-80° C. to give the product in 80% yield. IR: 1340  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 3.97 (3H, s), 1.65 (9H, s);  $^{19}\text{F}$  NMR -107 ppm (2F), -117 (2F); MS m/e, 280 (M)<sup>+</sup>; Anal. Calcd. for  $\text{C}_8\text{H}_{12}\text{F}_4\text{O}_4\text{S}$ : C, 34.29; H, 4.32; S, 11.44. Found: C, 33.75; H, 4.32; S, 10.1%.

## EXAMPLE 27

Synthesis of  $(\text{CH}_3)_3\text{CSO}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{OH}$

The ester  $(\text{CH}_3)_3\text{CSO}_2\text{CF}_2\text{CF}_2\text{CO}_2\text{CH}_3$  (52.4 g, 0.19 mol) was added dropwise over 1.5 hr to a solution of 18.2 g of sodium borohydride in 150 mL of ethanol at 5° C. The mixture was stirred for 3/4 hr, warmed briefly to 15° C. and recooled in an ice bath. Hydrochloric acid (20%) was added dropwise until the pH measured about 4 and the mixture was diluted with 500 mL of water. A bottom layer weighing 23.5 g was collected. The aqueous solution was extracted with 3x25 mL of methylene chloride. The combined product and methylene chloride extracts were dried over magnesium sulfate and concentrated. A Kugelrohr distillation at 75° C. and pump vacuum into a dry ice cooled receiver gave 37.9 g (76%) of product.  $^1\text{H}$ NMR ( $\text{CDCl}_3$ ) 1.57 (s, 9H), 2.80 (m, 1H), 4.15 (t, 2H); F NMR ( $\text{CDCl}_3$ ) -108.4 (2F), -119.1 (2F); IR 1334  $\text{cm}^{-1}$

## EXAMPLE 28

Synthesis of  $(\text{CH}_3)_3\text{CSO}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{OCF}=\text{CF}_2$

The alcohol  $(\text{CH}_3)_3\text{CSO}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{OH}$  (37 g, 0.15 mol) was added dropwise to a mixture of 6.0 g (0.25 mol) of sodium hydride in 100 mL of dioxane. After stirring overnight, this mixture was transferred to a 400 mL pressure vessel using 20 mL of dioxane for rinsing. The vessel was closed, cooled, evacuated and charged with 50 g (0.5 mol) of tetrafluoroethylene. The mixture was heated at 60° C. for 18 hr. It was cooled, vented and the contents were poured onto ice water. A lower layer was collected, washed with water and dried over magnesium sulfate. A Kugelrohr distillation at 80°-85° C. and 0.2 mm gave 32.7 g of product which contained trace impurities by NMR. The product was chromatographed on a 5.7x64 cm column of silica gel using pentane, followed by 2% ethyl acetate in pentane to elute. The fractions containing the desired product were combined

and distilled on a Kugelrohr apparatus giving 28.5 g (57%) of product.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 1.57 (s, 9H), 4.55 (t, 2H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ) -109.0 (2F), -118.9 (2F), -121.5 (1F), -127.2 (1F), -137.4 (1F). Anal. Calcd for  $\text{C}_6\text{H}_{11}\text{F}_7\text{SO}_3$ : C, 32.54; H, 3.34; F, 40.03; S, 9.65. Found: C, 32.47; H, 3.25; F, 40.27; S, 9.40.

## EXAMPLE 29

Copolymerization of  $(\text{CH}_3)_3\text{CSO}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{OCF}=\text{CF}_2$  and Tetrafluoroethylene

A 75 mL pressure vessel was charged with 13.5 g of  $(\text{CH}_3)_3\text{CSO}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{OCF}=\text{CF}_2$ , and 26 g of 1,1,2-trichlorotrifluoroethane. The vessel was cooled to  $-40^\circ\text{C}$ . and 2 mL of a 7.6 wt % solution of  $(\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CO}_2)_2$  in  $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCFHCF}_3$  was added. The vessel was closed, evacuate and charge with 6 g of tetrafluoroethylene. This mixture was agitated for 20 hr without external heating. The vessel was vented and the solvent was decanted from a swollen polymer plug. The polymer was recovered and dried under vacuum giving 20.9 g of material which could be pressed to a clear, flexible film at  $90^\circ\text{C}$ .  $^1\text{H}$  NMR (acetone- $d_6$ ) 1.58 (s, 9H), 4.88 (bs, 2H); TGA -13.0% at  $172^\circ\text{C}$ . Anal. Found C, 28.40; H, 1.93; F, 51.21, S, 5.89.

## EXAMPLE 30

Conversion of a  $-\text{CF}_2\text{SC}(\text{CH}_3)_3$  Side Chain to  $-\text{CF}_2\text{SO}_2\text{Cl}$

A 7.5 g sample of the comopolymer of  $(\text{CH}_3)_3\text{CSCF}_2\text{CF}_2\text{CH}_2\text{OCF}=\text{CF}_2$  and tetrafluoroethylene, prepared as described in Example 18 and containing about 22 mole % of the functional comonomer by fluorine NMR analysis, was dissolved in 125 mL of 1,1,2-trichlorotrifluoroethane. This solution was charged to a 500 mL glass pressure vessel and cooled to  $-30^\circ\text{C}$ . Chlorine gas (11 g) was added followed by a mixture of 60 mL trifluoroacetic acid and 30 mL of water. The vessel was sealed and the stirred mixture was heated in an oil bath at  $95^\circ\text{C}$ . for 68

h. The mixture was cooled to room temperature, vented to atmospheric pressure and the 1,1,2-trichlorotrifluoroethane layer was separated. A fluorine NMR analysis showed complete disappearance of the peak at  $-86.7$  ppm for the  $-\text{CF}_2\text{SC}(\text{CH}_3)_3$  group and appearance of a new peak at  $-106.7$  assigned to the  $-\text{CF}_2\text{SO}_2\text{Cl}$  group.

The 1,1,2-trichlorotrifluoroethane solution was diluted to about 250 mL and warmed slightly until all polymer was in solution. This solution was added to 700 mL pentane with stirring and the solvents were decanted from the precipitated polymer. This material was combined with the product from three additional reactions using 7.5 g, 11 g and 11 g of the copolymer and 11 g, 13 g and 13 g of chlorine, respectively. The combined precipitates were slurried in 200 mL pentane, filtered and dried at  $95^\circ\text{C}$ . and 7 Pa to give 33.7 g of product. Anal. Found: C, 22.07; H, 0.31; F, 60.82; Cl, 5.20; S, 4.41.

What is claimed is:

1. A copolymer consisting essentially of the repeat units



and



wherein:

each of  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are independently alkyl containing 1 to 10 carbon atoms;

$n$  is an integer of 1 to 10;

$\text{X}$  is  $-\text{SO}_2\text{F}$  or  $-\text{SO}_2\text{CR}^2\text{R}^3\text{R}^4$ ;

and provided that the molar ratio of (I):(II) is 0:100 to about 99:1.

2. The copolymer as recited in claim 1 wherein each of  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  is methyl.

3. The copolymer as recited in claim 1 wherein  $n$  is 2.

4. The copolymer as recited in claim 1 wherein the molar ratio of (I):(VII) is about 10:1 to about 1:10.

\* \* \* \* \*