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19803 (US). PENG, Sheng [CN/US]; 549 Cabot Drive, Hockessin, Delaware 19707 (US).

(74) Agent: KIRVAN, George, E.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, Delaware 19805 (US).

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(71) Applicant (for all designated States except US): DUPONT PERFORMANCE ELASTOMERS L.L.C. [US/US]; 300 Bellevue Parkway, Wilmington, Delaware 19809 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): HUNG, Ming-Hong [US/US]; 601 Andover Road, Wilmington, Delaware

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(54) Title: FLUOROOLEFIN MONOMERS AND COPOLYMERS THEREOF

(57) Abstract: Disclosed herein are novel fluoroolefins of formula $R_f-O-(CF_2CF_2)_n(CH_2CF_2)_m-CH=CH_2$, wherein n is 1 or 2, m is 0 or 1 and R_f is a C_1 - C_8 fluoroalkyl or fluoroalkoxy group. The fluoroolefins may be oxidized to manufacture fluorinated carboxylic acids. Also disclosed are fluoropolymers comprising copolymerized units of the fluoroolefins of the invention and at least one other fluoromonomer.



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TITLE OF INVENTION

FLUOROOLEFIN MONOMERS AND COPOLYMERS THEREOF

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FIELD OF THE INVENTION

This invention relates to certain fluoroolefin monomers and to copolymers thereof, more particularly to fluoroolefin monomers of the formula $Rf-O-(CF_2CF_2)_n(CH_2CF_2)_m-CH=CH_2$ wherein n is 1 or 2, m is 0 or 1 and Rf is a $C_1 - C_8$ fluoroalkyl or fluoroalkoxy group, to copolymers thereof and to fluorinated carboxylic acids made from such monomers.

BACKGROUND OF THE INVENTION

Elastomeric fluoropolymers (i.e. fluoroelastomers) exhibit excellent resistance to the effects of heat, weather, oil, solvents and chemicals. Such materials are commercially available and are most commonly copolymers of vinylidene fluoride (VF_2) with hexafluoropropylene (HFP) and, optionally, tetrafluoroethylene (TFE). Other known fluoroelastomers include copolymers of TFE with a perfluoro(alkyl vinyl ether) such as perfluoro(methyl vinyl ether) (PMVE), copolymers of TFE with propylene (P) and, optionally VF_2 , and copolymers of ethylene (E) with TFE and PMVE. Often, these fluoroelastomers also contain copolymerized units of a cure site monomer to facilitate vulcanization. While these copolymers have many desirable properties, including low compression set and excellent processability, their low temperature flexibility is not adequate for some end use applications. One particularly desirable improvement would be a reduction in glass transition temperature (T_g) with an accompanying extension of service temperature to lower temperatures. T_g is often used as an indicator of low temperature flexibility because polymers having low glass transition temperatures maintain elastomeric properties at low temperatures.

Semi-crystalline and crystalline thermoplastic fluoropolymers (i.e. fluoroplastics) include homopolymers (e.g. polytetrafluoroethylene or

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polyvinylidene fluoride) or copolymers of TFE or VF₂ containing up to 20 wt.% of a second (different) fluoromonomer, a hydrocarbon olefin or a combination of the latter. Such copolymers include, but are not limited to THV, FEP and PFA. While these polymers have many desirable

5 properties, in some applications, improved green strength would be beneficial.

SUMMARY OF THE INVENTION

It has been surprisingly discovered that the glass transition

10 temperature of fluoroelastomers may be reduced and the green strength of fluoroplastics improved when a fluoroolefin of formula Rf-O-(CF₂CF₂)_n(CH₂CF₂)_m-CH=CH₂ is copolymerized with at least one other fluoromonomer to make the fluoroelastomer or fluoroplastic. In the latter formula n is 1 or 2, m is 0 or 1 and Rf is a C₁ – C₈ fluoroalkyl or

15 fluoroalkoxy group

Accordingly, the present invention is directed to a fluoroolefin having the general formula Rf-O-(CF₂CF₂)_n(CH₂CF₂)_m-CH=CH₂, wherein n is 1 or 2, m is 0 or 1 and Rf is selected from the group consisting of a C₁ – C₈ fluoroalkyl group and a C₁ – C₈ fluoroalkoxy group.

20 Another aspect of the invention is a process for the preparation of a fluoroolefin comprising:

A) reacting a fluorovinyl ether of formula Rf-O-CF=CF₂, wherein Rf is selected from the group consisting of a C₁ – C₈ fluoroalkyl group and a C₁ – C₈ fluoroalkoxy group, with i) iodine monochloride, ii)

25 HF and iii) a Lewis acid catalyst at a temperature of 50°-100°C for 10 to 48 hours to form a fluoroalkyl iodide of formula Rf-O-CF₂CF₂-I wherein Rf is as defined above;

B) reacting said fluoroalkyl iodide with an olefin selected from the group consisting of tetrafluoroethylene and vinylidene fluoride to

30 generate a compound of formula Rf-O-(CF₂CF₂)_n(CH₂CF₂)_m-I wherein n is 1 or 2, m is 0 or 1 and Rf is as defined above;

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C) reacting said compound of formula $\text{Rf-O-(CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-I}$ with ethylene to produce a compound of formula $\text{Rf-O-(CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-CH}_2\text{CH}_2\text{I}$ wherein Rf, n and m are as defined above; and

- 5 D) reacting said compound of formula $\text{Rf-O-(CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-CH}_2\text{CH}_2\text{I}$ with base to produce a fluoroolefin of formula $\text{Rf-O-(CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-CH=CH}_2$, wherein Rf, n and m are as defined above.

Another aspect of the invention is a fluoropolymer comprising

- 10 copolymerized units of:

A) a fluoroolefin having the general formula $\text{Rf-O-(CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-CH=CH}_2$, wherein n is 1 or 2, m is 0 or 1 and Rf is selected from the group consisting of a $\text{C}_1 - \text{C}_8$ fluoroalkyl group and a $\text{C}_1 - \text{C}_8$ fluoroalkoxy group; and

- 15 B) at least one fluoromonomer different from said fluoroolefin.

Another aspect of the invention is a process for the manufacture of a fluorinated carboxylic acid of the formula $\text{Rf-O-(CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-COOH}$, wherein n is 1 or 2, m is 0 or 1 and Rf is selected from the group consisting of a $\text{C}_1 - \text{C}_8$ fluoroalkyl group and a $\text{C}_1 - \text{C}_8$ fluoroalkoxy group,

- 20 said process comprising:

A) reacting a fluorovinyl ether of formula Rf-O-CF=CF_2 , wherein Rf is selected from the group consisting of a $\text{C}_1 - \text{C}_8$ fluoroalkyl group and a $\text{C}_1 - \text{C}_8$ fluoroalkoxy group, with iodine monochloride, HF and a Lewis acid catalyst at a temperature of $50^\circ\text{-}100^\circ\text{C}$ for 10 to 25 48 hours to form a fluoroalkyl iodide of formula $\text{Rf-O-CF}_2\text{CF}_2\text{-I}$ wherein Rf is as defined above;

B) reacting said fluoroalkyl iodide with an olefin selected from the group consisting of tetrafluoroethylene and vinylidene fluoride to generate a compound of formula $\text{Rf-O-(CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-I}$ wherein n is 1 or 2, m is 0 or 1 and Rf is as defined above;

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- C) reacting said compound of formula $\text{Rf-O-(CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-I}$ with ethylene to produce a compound of formula $\text{Rf-O-(CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-CH}_2\text{CH}_2\text{I}$ wherein Rf, n and m are as defined above;
- 5 D) reacting said compound of formula $\text{Rf-O-(CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-CH}_2\text{CH}_2\text{I}$ with base to produce a fluoroolefin of formula $\text{Rf-O-(CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-CH=CH}_2$, wherein Rf, n and m are as defined above and
- 10 E) oxidizing said fluoroolefin to a fluorinated carboxylic acid having the formula $\text{Rf-O-(CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-COOH}$, wherein n is 1 or 2, m is 0 or 1 and Rf is selected from the group consisting of a $\text{C}_1 - \text{C}_8$ fluoroalkyl group and a $\text{C}_1 - \text{C}_8$ fluoroalkoxy group.

DETAILED DESCRIPTION OF THE INVENTION

- 15 The novel fluoroolefins of this invention have the general formula $\text{Rf-O-(CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-CH=CH}_2$, wherein n is 1 or 2, m is 0 or 1 and Rf is selected from the group consisting of a $\text{C}_1 - \text{C}_8$ fluoroalkyl group and a $\text{C}_1 - \text{C}_8$ fluoroalkoxy group. Specific examples of said fluoroolefins include, but are not limited to $\text{CF}_3\text{-O-CF}_2\text{CF}_2\text{-CH=CH}_2$, $\text{C}_2\text{F}_5\text{-O-CF}_2\text{CF}_2\text{-CH=CH}_2$, $\text{C}_3\text{F}_7\text{-O-CF}_2\text{CF}_2\text{-CH=CH}_2$, $\text{C}_3\text{F}_7\text{-O-[CF(CF}_3\text{)CF}_2\text{O]}_p\text{-CF}_2\text{CF}_2\text{-CH=CH}_2$, $\text{CF}_3\text{-O-CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{-CH=CH}_2$, $\text{CF}_3\text{-O-CF}_2\text{CF}_2\text{-CH}_2\text{CF}_2\text{-CH=CH}_2$, $\text{C}_2\text{F}_5\text{-O-CF}_2\text{CF}_2\text{-CH}_2\text{CF}_2\text{-CH=CH}_2$, $\text{C}_3\text{F}_7\text{-O-CF}_2\text{CF}_2\text{-CH}_2\text{CF}_2\text{-CH=CH}_2$, and $\text{C}_3\text{F}_7\text{-O-[CF(CF}_3\text{)CF}_2\text{O]}_p\text{-CF}_2\text{CF}_2\text{-CH}_2\text{CF}_2\text{-CH=CH}_2$ wherein p is an integer 1 to 3.
- 20
- 25 These fluoroolefins are preferably made from fluorovinyl ethers by the following sequence of reactions. First, a fluorovinyl ether of formula Rf-O-CF=CF_2 , wherein Rf is selected from the group consisting of a $\text{C}_1 - \text{C}_8$ fluoroalkyl group and a $\text{C}_1 - \text{C}_8$ fluoroalkoxy group, is reacted with i) iodine monochloride, ii) HF and iii) a Lewis acid catalyst to form a
- 30 fluoroalkyl iodide of formula $\text{Rf-O-CF}_2\text{CF}_2\text{-I}$ wherein Rf is as defined

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above. Examples of Lewis acid catalysts that may be employed in the process include, but are not limited to BF_3 , SbF_3 , TaF_5 , NbF_5 , SbCl_5 and TiCl_4 . The reaction typically takes place at a temperature between 50° and 100°C for 10 to 48 hours. The resulting fluoroalkyl iodide is then

5 reacted with tetrafluoroethylene or vinylidene fluoride to produce a compound of formula $\text{Rf-O-(CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-I}$ wherein n is 1 or 2, m is 0 or 1, and Rf is as defined above.

The compound of formula $\text{Rf-O-(CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-I}$ is then reacted with ethylene to produce a compound of formula Rf-O-

10 $(\text{CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-CH}_2\text{CH}_2\text{I}$ wherein Rf , n and m are as defined above. The reaction with ethylene may be run at a temperature of 190° to 230°C for 6 to 24 hours, or if in the presence of a radical initiator such as benzoyl peroxide or a Vazo® initiator (available from DuPont), at a temperature between 60° to 90°C .

15 The $\text{Rf-O-(CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-CH}_2\text{CH}_2\text{I}$ is then dehydrofluorinated with base to produce a fluoroolefin of the invention having the formula $\text{Rf-O-(CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-CH=CH}_2$, wherein Rf , n and m are as defined above.

This fluoroolefin may be oxidized and cleaved to form a fluorinated

20 carboxylic acid having the formula $\text{Rf-O-(CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-COOH}$, wherein Rf , n and m are as defined above. Oxidizing agents that may be employed in this reaction include, but are not limited to KMnO_4 and CrO_3 with a strong acid such as sulfuric acid. The resulting fluorinated carboxylic acid may be reacted with base (e.g. NH_4HCO_3 , NaOH , KOH ,

25 etc.) to form an anionic fluorosurfactant of formula $\text{Rf-O-(CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-COOM}$, wherein M is a univalent cation such as NH_4^+ , Na^+ , K^+ , etc. These fluorosurfactants may be employed as dispersing agents in the polymerization of fluoropolymers.

The fluoroolefins of the invention may also be employed to

30 manufacture fluoropolymers. Fluoropolymers of the invention, both

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fluoroelastomers and fluoroplastics, comprise copolymerized units of the above described fluoroolefin and at least one other fluoromonomer, different from said fluoroolefin. Preferably the fluoropolymers comprise 0.5 to 10 mol% of the fluoroolefin of the invention.

- 5 Fluoromonomers that may be contained in the fluoropolymers of the invention include, but are not limited to tetrafluoroethylene (TFE), chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), vinylidene fluoride (VF₂), vinyl fluoride (VF), a perfluoro vinyl ether, as well as functional monomers such as CF₂=CFOCF₂CF(CF₃)-O-CF₂CF₂-COOCH₃,
 10 and CF₂=CFOCF₂CF(CF₃)-O-CF₂CF₂-SO₂F.

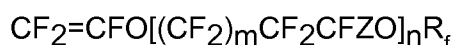
A preferred class of perfluoro vinyl ethers that may be employed in the fluoropolymers of the invention includes ethers of the formula



- where X is F or CF₃, n is 0-5, and R_f is a perfluoroalkyl group of 1-6
 15 carbon atoms.

A most preferred class of perfluoro vinyl ethers includes those ethers wherein n is 0 or 1 and R_f contains 1-3 carbon atoms. Examples of such perfluorinated ethers include perfluoro(methyl vinyl ether) (PMVE) and perfluoro(propyl vinyl ether) (PPVE).

- 20 Other useful perfluoro vinyl ethers include those of the formula



where R_f is a perfluoroalkyl group having 1-6 carbon atoms, m = 0 or 1, n = 0-5, and Z = F or CF₃. Preferred members of this class are those in which R_f is CF₃, m = 1, n = 1, and Z = F; and R_f is C₃F₇, m = 0, and n = 1.

- 25 Additional perfluoro vinyl ethers include compounds of the formula



where m and n independently = 0-10, p = 0-3, and x = 1-5. Preferred members of this class include compounds where n = 0-1, m = 0-1, and x = 1.

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Additional examples of useful perfluoro vinyl ethers include



where $n = 1-5$, $m = 1-3$, and where, preferably, $n = 1$.

In addition to at least one fluoromonomer different from the
 5 fluoroolefin of this invention, the fluoropolymers of this invention may also contain copolymerized units of a hydrocarbon olefin such as ethylene or propylene.

Furthermore fluoropolymers of the invention may contain 0.1 to 7
 mole percent copolymerized units of cure site monomers commonly
 10 employed in the fluoropolymer industry. Such cure site monomers include, but are not limited to bromine- and iodine-containing olefins such as bromotrifluoroethylene, iodotrifluoroethylene, 4-bromo-3,3,4,4-tetrafluorobutene, and 4-iodo-3,3,4,4-tetrafluorobutene. Such cure site monomers are well known in the art (e.g. U.S. Patent Nos. 4,214,060;
 15 5,214,106; and 5,717,036). Other cure site monomers include 2-hydropentafluoropropene, 1-hydropentafluoropropene; 3,3,3-trifluoropropene; and nitrile group-containing fluoroolefins or fluorovinyl ethers such as those disclosed in U.S. Patent No. 6,211,319 B1 (e.g. perfluoro(8-cyano-5-methyl-3,6-dioxo-1-octene)).

20 Fluoropolymers of this invention may be prepared by known emulsion, suspension or solution polymerization processes. A chain transfer agent such as a perfluoroalkyldiiodide (e.g. $\text{I}-(\text{CF}_2)_4\text{-I}$), alcohols, ketones or hydrocarbons may be employed to control the polymerization.

Fluoroelastomers of the present invention are useful in production
 25 of gaskets, tubing, seals, hoses, O-rings and other molded components. Such articles are generally produced by compression molding a compounded formulation of the elastomer, a curing agent and various additives, curing the molded article, and then subjecting it to a post cure cycle. The cured elastomer parts have excellent low temperature flexibility
 30 and processability as well as excellent thermal stability and chemical resistance. They are particularly useful in applications such as seals and

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gaskets requiring a good combination of oil resistance, fuel resistance and low temperature flexibility, for example in fuel injection systems, fuel line connector systems and in other seals for high and low temperature automotive uses.

- 5 Fluoroplastics of the present invention are useful in production of seals, wire and cable jacketing, hoses, etc. They are particularly useful in applications requiring good green strength such as parts for sealing, molding and injection applications.

10 The invention is now illustrated by certain embodiments wherein all parts and percentages are by weight unless otherwise specified.

EXAMPLES

TEST METHODS

Compositions and microstructures were determined by ^{19}F and ^1H NMR. The NMR spectra were recorded on a Bruker AC 400 (400 MHz) instrument, using deuterated acetone as solvent and tetramethylsilane (TMS) (or CFCl_3) as the references for ^1H (or ^{19}F) nuclei. Coupling constants and chemical shifts are given in Hz and ppm, respectively. The experimental conditions for ^1H (or ^{19}F) NMR spectra were the following: flip angle 90° (or 30°), acquisition time 4.5 s (or 0.7 s), pulse delay 2 s (or 5 s), number of scans 16 (or 64), and a pulse width of 5 μs for ^{19}F NMR.

Example 1

In a 1300 mL stainless steel shaker tube was charged perfluoro(propyl vinyl ether) (PPVE, 346 grams, 1.30 moles), iodine
25 monochloride (248.5 grams, 1.53 moles), HF (500 grams, 25 moles), and boron trifluoride (50 grams, 0.737 moles). The tube was sealed and cool-evacuated. By "cool-evacuated" is meant that oxygen was removed from the reactor by cooling reactor contents sufficiently so that all ingredients remained in the reactor while a vacuum was applied to remove oxygen.
30 The tube and contents were then heated at 75°C for 24 hours while being shaken. After cooling, the product mixture was unloaded from the tube,

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and washed with saturated sodium bisulfite solution to remove unreacted residual iodine. After drying, the product ($\text{CF}_3\text{CF}_2\text{CF}_2\text{-O-CF}_2\text{CF}_2\text{-I}$) was distilled to a clear colorless liquid, bp. 85-86 °C, yield: 400 grams (75%).

In a 1300 mL stainless steel shaker tube was charged 1-iodo-3-oxa-perfluorohexane ($\text{CF}_3\text{CF}_2\text{CF}_2\text{-O-CF}_2\text{CF}_2\text{-I}$) (370.8 grams, 0.90 moles) and d-(+)-Limonene (1.0 gram). The tube was sealed and cool-evacuated, and ethylene (42 grams, 1.50 moles) was transferred into the tube. The tube was sealed again and was heated at 220°C for 10 hours. The product ($\text{CF}_3\text{CF}_2\text{CF}_2\text{-O-CF}_2\text{CF}_2\text{-CH}_2\text{CH}_2\text{-I}$) was unloaded from the tube and purified by distillation to give a pale-pink clear liquid, bp. 65-69°C at 50 mm Hg. Yield: 340 grams (86%). $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 3.24 (t, J = 8.7 Hz, 2H), 2.72 (m, 2H); $^{19}\text{F-NMR}$ (CDCl_3 , 376.89 MHz): -81.8 (t, J = 7.5 Hz, 3F), -84.5 (m, 2F), -88.0 (t, J = 13.2 Hz, 2F), -119.3 (t, J = 17 Hz, 2F), -130.4 (s, 2F).

In a reaction flask was charged TLF-2370C phase transfer catalyst ($[\text{C}_{12}\text{H}_{25}][\text{PhCH}_2][\text{CH}_2\text{CH}(\text{OH})\text{CH}_3]_2$ available from DuPont) (60% aqueous solution) (29.6 grams, 0.042 moles), 10 M KOH solution (280 mL, 2.80 moles), along with 1-iodo-1,1,2,2-tetrahydro-5-oxa-perfluorooctane ($\text{CF}_3\text{CF}_2\text{CF}_2\text{-O-CF}_2\text{CF}_2\text{-CH}_2\text{CH}_2\text{-I}$) (176 grams, 0.40 moles). The reaction mixture was allowed to stir for 14 hours at ambient temperature. The product mixture was transferred into a separatory funnel and the bottom organic layer was separated, washed with water twice, dried over magnesium sulfate, then distilled to give $\text{CF}_3\text{CF}_2\text{CF}_2\text{-O-CF}_2\text{CF}_2\text{-CH=CH}_2$ product as a clear, colorless liquid, bp. 75-76°C, Yield: 172 grams (72%). $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 5.90 (m, 1H), 5.92 (m, 2H); $^{19}\text{F-NMR}$ (CDCl_3 , 376.89 MHz): -81.9 (t, J = 7.5 Hz, 3F), -85.1 (m, 2F), -85.3 (t, J = 13.2 Hz, 2F), -118.3 (d, J = 11.3 Hz, 2F), -130.5 (s, 2F).

Example 2

In a 400 mL stainless steel shaker tube was charged de-ionized water (280 mL), ammonium perfluorooctanoate surfactant (1.5 grams),

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disodium phosphate heptahydrate (1.0 gram), ammonium persulfate (0.1 gram) and 1,1,2-trihydro-5-oxa-perfluoro-1-octene monomer ($\text{CF}_3\text{CF}_2\text{CF}_2\text{-O-CF}_2\text{CF}_2\text{-CH=CH}_2$) (4 grams). The tube was sealed and cool-evacuated. Tetrafluoroethylene (TFE, 45 grams, 0.45 moles) and perfluoro(methyl vinyl ether) (PMVE, 38 grams, 0.229 moles) were transferred into the tube. The tube was sealed again and was then heated at 75°C for 8 hours. After cooling, the latex was unloaded from the tube and coagulated with saturated magnesium sulfate solution. The precipitated polymer was collected, and washed thoroughly with warm water. After drying, a white polymer (69 grams) was obtained. This polymer had a Tg of -6.14°C as measured by DSC, and had a composition of TFE/PMVE/ $\text{CF}_3\text{CF}_2\text{CF}_2\text{-O-CF}_2\text{CF}_2\text{-CH=CH}_2$ = 60.0/37.9/2.1 (mole%) as determined by NMR spectroscopy.

15 Example 3

In a semi-batch reactor was charged de-ionized water (2,000 mL), ammonium perfluorooctanoate surfactant (3.9 grams), disodium phosphate heptahydrate (20 gram), and 1,1,2-trihydro-5-oxa-perfluoro-1-octene monomer ($\text{CF}_3\text{CF}_2\text{CF}_2\text{-O-CF}_2\text{CF}_2\text{-CH=CH}_2$) (20 grams). The reactor was cool-evacuated, and was then charged with a gas mixture of vinylidene fluoride (VF_2) (320 grams), TFE (10 grams), and PMVE (670 grams) until the pressure reached 1.38 MPa at 80°C. Ammonium persulfate (20 mL of a 2 wt% aqueous solution) was fed initially, followed by feeding the 2 wt.% solution at a rate of 10 mL/min. When a pressure drop of 13.8 kPa was observed, a gas mixture of VF_2 (212 grams/hr), TFE (37 grams/hr), and PMVE (140 grams/hr) was fed at a rate sufficient to maintain the reactor pressure at 1.24 MPa. The polymerization was stopped when about a total amount of 720 grams of gas had been fed. The polymer latex was unloaded from the reactor and was coagulated and isolated as described in the above example. The white polymer obtained (760 grams) was analyzed to have a composition of

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VF₂/TFE/PMVE/CF₃CF₂CF₂-O-CF₂CF₂-CH=CH₂ of 75.0/6.4/18.6/0.05 (mole%) as determined by NMR spectroscopy. The T_g of this polymer was -30.1°C as determined by DSC.

5 Example 4

KMnO₄ (50 g, 0.315 mol) was dissolved in deionized water, followed by addition of H₂SO₄ (53 g, 0.541 moles). C₃F₇OCF₂CF₂CH=CH₂ (prepared as in the examples above) (20 g, 0.094 moles) was added dropwise at 60°C to the permanganate solution, and the oxidation reaction was run at 70°C for 3 hours. Then, the resulting solution was cooled to room temperature and thrice extracted with 100 mL ether. The extract was dried over MgSO₄ and then filtered. The fluorinated carboxylic acid product (C₃F₇OCF₂CF₂COOH) was distilled via vacuum distillation (9 g, 29% yield), b.p. 62-63°C at 30 mm Hg.

¹⁹F NMR (376 MHz, CDCl₃): -84.52 (3F, t, J=8 Hz), -84.7~-85.0 (2F, m), -86.17~86.23 (2F, m), -125.20~-125.21 (2H, t, J=2.1 Hz), -134.49 (2F, s).

Ammonium bicarbonate solution (1.48 g, 0.0187 mol, in 10 mL water) was added to the fluorinated carboxylic acid C₃F₇OCF₂CF₂COOH (6 g, 0.0182 mol) produced above. The reaction was stirred at room temperature for an hour. Water was removed in a rotovap resulting in the product (C₃F₇OCF₂CF₂COONH₄) as a white solid (4 g, 79% yield), b.p. 121-123°C.

¹⁹F NMR (376 MHz, CDCl₃): -81.61 (3F, t, J=8 Hz), -84.7~-85.0 (2F, m), -86.17~86.23 (2F, m), -121.17~121.19 (2H, t, J=2.1 Hz), -130.27 (2F, s).

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WHAT IS CLAIMED IS:

1. A fluoroolefin having the general formula Rf-O-
 5 (CF₂CF₂)_n(CH₂CF₂)_m-CH=CH₂, wherein n is 1 or 2, m is 0 or 1 and Rf is selected from the group consisting of a C₁ – C₈ fluoroalkyl group and a C₁ – C₈ fluoroalkoxy group.
2. A fluoroolefin of claim 1 wherein said fluoroolefin is selected from the group consisting of CF₃-O-CF₂CF₂-CH=CH₂, C₂F₅-O-CF₂CF₂-
 10 CH=CH₂, C₃F₇-O-CF₂CF₂-CH=CH₂, C₃F₇O-[CF(CF₃)CF₂O]_p-CF₂CF₂-CH=CH₂, CF₃-O-CF₂CF₂CF₂CF₂-CH=CH₂, CF₃-O-CF₂CF₂-CH₂CF₂-CH=CH₂, C₂F₅-O-CF₂CF₂-CH₂CF₂-CH=CH₂, C₃F₇-O-CF₂CF₂-CH₂CF₂-CH=CH₂, and C₃F₇O-[CF(CF₃)CF₂O]_p-CF₂CF₂-CH₂CF₂-CH=CH₂ wherein p is an integer 1 to 3.
- 15 3. A process for the preparation of a fluoroolefin comprising:
 A) reacting i) a fluorovinyl ether of formula Rf-O-CF=CF₂, wherein Rf is selected from the group consisting of a C₁ – C₈ fluoroalkyl group and a C₁ – C₈ fluoroalkoxy group, with ii) iodine monochloride, iii) HF and iv) a Lewis acid catalyst at a temperature
 20 of 50°-100°C for 10 to 48 hours to form a fluoroalkyl iodide of formula Rf-O-CF₂CF₂-I wherein Rf is as defined above;
 B) reacting said fluoroalkyl iodide with an olefin selected from the group consisting of tetrafluoroethylene and vinylidene fluoride to generate a compound of formula Rf-O-(CF₂CF₂)_n(CH₂CF₂)_m-I
 25 wherein n is 1 or 2, m is 0 or 1 and Rf is as defined above;
 C) reacting said compound of formula Rf-O-(CF₂CF₂)_n(CH₂CF₂)_m-I with ethylene to produce a compound of formula Rf-O-(CF₂CF₂)_n(CH₂CF₂)_m-CH₂CH₂-I wherein Rf, n and m are as defined above; and
 30 D) reacting said compound of formula Rf-O-(CF₂CF₂)_n(CH₂CF₂)_m-CH₂CH₂-I with base to produce a fluoroolefin of formula Rf-O-

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$(\text{CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-CH=CH}_2$, wherein Rf, n and m are as defined above.

4. A process for the preparation of a fluoroolefin of claim 3 wherein said Lewis acid catalyst is selected from the group consisting of BF_3 , SbF_3 ,

5 TaF_5 , NbF_5 , SbCl_5 and TiCl_4 .

5. A process for the preparation of a fluoroolefin of claim 3 wherein step C) is run at 190° to 230°C for 6 to 24 hours in the absence of a radical initiator.

6. A process for the preparation of a fluoroolefin of claim 3 wherein
10 step C) is run at 60° to 90°C in the presence of radical initiator.

7. A fluoropolymer comprising copolymerized units of:

A) a fluoroolefin having the general formula Rf-O-

$(\text{CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-CH=CH}_2$, wherein n is 1 or 2, m is 0 or 1 and

15 Rf is selected from the group consisting of a $\text{C}_1 - \text{C}_8$ fluoroalkyl group and a $\text{C}_1 - \text{C}_8$ fluoroalkoxy group; and

B) at least one fluoromonomer different from said fluoroolefin.

8. A fluoropolymer of claim 7 wherein fluoroolefin is selected from the group consisting of $\text{CF}_3\text{-O-CF}_2\text{CF}_2\text{-CH=CH}_2$, $\text{C}_2\text{F}_5\text{-O-CF}_2\text{CF}_2\text{-CH=CH}_2$, $\text{C}_3\text{F}_7\text{-O-CF}_2\text{CF}_2\text{-CH=CH}_2$, $\text{C}_3\text{F}_7\text{O-[CF(CF}_3\text{)CF}_2\text{O]}_p\text{-CF}_2\text{CF}_2\text{-CH=CH}_2$, $\text{CF}_3\text{-}$
20 $\text{O-CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{-CH=CH}_2$, $\text{CF}_3\text{-O-CF}_2\text{CF}_2\text{-CH}_2\text{CF}_2\text{-CH=CH}_2$, $\text{C}_2\text{F}_5\text{-O-}$
 $\text{CF}_2\text{CF}_2\text{-CH}_2\text{CF}_2\text{-CH=CH}_2$, $\text{C}_3\text{F}_7\text{-O-CF}_2\text{CF}_2\text{-CH}_2\text{CF}_2\text{-CH=CH}_2$, and $\text{C}_3\text{F}_7\text{O-}$
 $\text{[CF(CF}_3\text{)CF}_2\text{O]}_p\text{-CF}_2\text{CF}_2\text{-CH}_2\text{CF}_2\text{-CH=CH}_2$ wherein p is an integer 1 to 3.

9. A fluoropolymer of claim 7 wherein fluoromonomer is selected from the group consisting of tetrafluoroethylene, chlorotrifluoroethylene,
25 hexafluoropropylene, vinylidene fluoride, vinyl fluoride and a perfluoro vinyl ether.

10. A fluoropolymer of claim 7 further comprising 0.1 to 7 mole percent copolymerized units of cure site monomer.

11. A process for the manufacture of a fluorinated carboxylic acid
30 of the formula $\text{Rf-O-(CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-COOH}$, wherein n is 1 or 2, m is

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0 or 1 and Rf is selected from the group consisting of a C₁ – C₈ fluoroalkyl group and a C₁ – C₈ fluoroalkoxy group, said process comprising:

- 5 A) reacting i) a fluorovinyl ether of formula Rf-O-CF=CF₂, wherein Rf is selected from the group consisting of a C₁ – C₈ fluoroalkyl group and a C₁ – C₈ fluoroalkoxy group, with ii) iodine monochloride, iii) HF and iv) a Lewis acid catalyst at a temperature of 50°-100°C for 10 to 48 hours to form a fluoroalkyl iodide of formula Rf-O-CF₂CF₂-I wherein Rf is as defined above;
 - 10 B) reacting said fluoroalkyl iodide with an olefin selected from the group consisting of tetrafluoroethylene and vinylidene fluoride to generate a compound of formula Rf-O-(CF₂CF₂)_n(CH₂CF₂)_m-I wherein n is 1 or 2, m is 0 or 1 and Rf is as defined above;
 - 15 C) reacting said compound of formula Rf-O-(CF₂CF₂)_n(CH₂CF₂)_m-I with ethylene to produce a compound of formula Rf-O-(CF₂CF₂)_n(CH₂CF₂)_m-CH₂CH₂I wherein Rf, n and m are as defined above;
 - 20 D) reacting said compound of formula Rf-O-(CF₂CF₂)_n(CH₂CF₂)_m-CH₂CH₂I with base to produce a fluoroolefin of formula Rf-O-(CF₂CF₂)_n(CH₂CF₂)_m-CH=CH₂, wherein Rf, n and m are as defined above and
 - E) oxidizing said fluoroolefin to a fluorinated carboxylic acid having the formula Rf-O-(CF₂CF₂)_n(CH₂CF₂)_m-COOH, wherein n is 1 or 2, m is 0 or 1 and Rf is selected from the group consisting of a C₁ – C₈ fluoroalkyl group and a C₁ – C₈ fluoroalkoxy group.
- 25 12. A process for the manufacture of a fluorinated carboxylic acid of claim 11 wherein said Lewis acid catalyst is selected from the group consisting of BF₃, SbF₃, TaF₅, NbF₅, SbCl₅ and TiCl₄.
- 30 13. A process for the manufacture of a fluorinated carboxylic acid of claim 11 wherein step C) is run at 190° to 230°C for 6 to 24 hours in the absence of a radical initiator.

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14. A process for the manufacture of a fluorinated carboxylic acid of claim 11 wherein step C) is run at 60° to 90°C in the presence of radical initiator.

5 15. A process for the manufacture of a fluorinated carboxylic acid of claim 11 wherein an oxidizing agent selected from the group consisting of KMnO_4 and CrO_3 is employed in step E).

16. A process for the manufacture of a fluorinated carboxylic acid of claim 11 further comprising F) neutralizing said fluorinated carboxylic acid with base to form an anionic fluorosurfactant of formula Rf-O-
10 $(\text{CF}_2\text{CF}_2)_n(\text{CH}_2\text{CF}_2)_m\text{-COOM}$, wherein M is a univalent cation.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2008/082748

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C43/17 C07C51/285 C07C59/135 C08F214/18 C07C41/22
C07C41/24 C07C41/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, BEILSTEIN Data, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 224 773 A (ALLIED CHEM [US]) 10 March 1971 (1971-03-10)	1,2
Y	page 7; examples 1,2	3-6, 11-16
X	JP 06 016586 A (ASAHI GLASS CO LTD) 25 January 1994 (1994-01-25)	1,2
Y	paragraphs [0008], [0015], [0016]	3-6, 11-16
X	EP 0 571 793 A (SHINETSU CHEMICAL CO [JP]) 1 December 1993 (1993-12-01)	1,2
Y	page 4; example 1 page 3, line 47 - line 52	7-10
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☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

van Bergen, Marc

INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	----- WO 98/30631 A (DYNEON LLC [US]) 16 July 1998 (1998-07-16) page 17; table 1	7-10
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