



(43) International Publication Date  
30 June 2016 (30.06.2016)

(10) International Publication Number  
**WO 2016/105907 A1**

(51) International Patent Classification:

C07C 41/22 (2006.01) C07C 43/12 (2006.01)  
C07C 41/18 (2006.01)

(21) International Application Number:

PCT/US2015/063947

(22) International Filing Date:

4 December 2015 (04.12.2015)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/095,300 22 December 2014 (22.12.2014) US

(71) Applicant: **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(72) Inventors: **HINTZER, Klaus**; Carl-Schurz-Strasse 1, 41453 Neuss (DE). **HIRSCHBERG, Markus E.**; Carl-Schurz-Strasse 1, 41453 Neuss (DE). **LOCHHAAS, Kai Helmut**; Carl-Schurz-Strasse 1, 41453 Neuss (DE). **SHY-SHKOV, Oleg**; Wendelsteinstrasse 25, 84508 Burgkirchen (DE).

(74) Agents: **LAPOS-KUCHAR, Julie A.** et al.; 3M Center, Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

**Declarations under Rule 4.17:**

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

**Published:**

- with international search report (Art. 21(3))

(54) Title: METHODS OF MAKING HALOGENATED PARTIALLY FLUORINATED COMPOUNDS

(57) Abstract: Described herein is method of making a halogenated partially fluorinated compound, comprising: (a) providing a compound having the following structure of formula (I):  $R_f-CF=CXY$  wherein X and Y are independently selected from F and Cl; wherein  $R_f$  is a fluorinated monovalent group comprising 1 to 10 carbon atoms; (b) contacting the compound with at least one of (i) an iodine or bromine containing salt in the presence of an acid; and (ii) aqueous solution of HZ wherein Z is selected from I and Br to form the halogenated partially fluorinated compound of the formula (II):  $R'_f-CFH-CXYZ$  wherein X and Y are independently selected from F and Cl; Z is selected from I and Br; and  $R'_f$  is a fluorinated monovalent group comprising 1 to 10 carbon atoms.



WO 2016/105907 A1

## **METHODS OF MAKING HALOGENATED PARTIALLY FLUORINATED COMPOUNDS**

### **TECHNICAL FIELD**

[0001] Methods of making halogenated partially fluorinated compounds from a perhalogenated terminal olefin are disclosed.

### **BACKGROUND**

[0002] Bromine/iodine containing compounds are key materials for producing peroxide curable elastomers. They are used as chain transfer agents (CTA) and/or as cure site monomers (CSM) in polymer synthesis. For example, diiodoperfluorobutane  $[\text{I}(\text{CF}_2)_4\text{I}]$  is a popular chain transfer agent.

[0003] Typically,  $\alpha,\omega$ -diiodo (per)fluoroalkanes are prepared by radical reaction of iodine with a fluoroolefin, reaction of  $\text{ICF}_2\text{I}$  with a (fluoro)olefin, telomerization of a (fluoro)olefin with shorter-chained  $\alpha,\omega$ -diiodo fluoroalkanes, and coupling reactions of diiodofluoroalkanes.

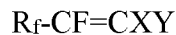
[0004] Partially fluorinated  $\alpha,\omega$ -diiodo fluoroalkanes, such as  $\text{I-CF}_2\text{-CFH-CF}_2\text{-I}$  have been prepared by reaction of pentafluorocyclopropane (*c*- $\text{C}_3\text{F}_5\text{H}$ ) with iodine, as described in *J. Am. Chem. Soc.* **1995**, *117*, 5397-5398; or by the reaction of  $\text{CF}_2\text{I}_2$  with trifluoroethylene ( $\text{CF}_2=\text{CHF}$ ), as described in *J. Org. Chem.* **2004**, *69*, 2394-2403.

### **SUMMARY**

[0005] There is a desire for alternative methods of making partially fluorinated compounds, which may be simpler, use more readily available starting materials, and/or are more cost effective than current manufacturing processes.

[0006] In one aspect, a method of making a partially fluorinated halogenated compound is described comprising:

- (a) providing a compound having the following structure of formula (I):



wherein X and Y are independently selected from F and Cl; wherein  $R_f$  is a fluorinated monovalent group comprising 1 to 10 carbon atoms;

(b) contacting the compound with at least one of

- (i) an iodine or bromine containing salt in the presence of an acid; and
- (ii) aqueous solution of HZ wherein Z is selected from I and Br

to form the halogenated partially fluorinated compound of the formula (II):



wherein X and Y are independently selected from F and Cl; Z is selected from I and Br; and  $R'_f$  is a fluorinated monovalent group comprising 1 to 10 carbon atoms.

[0007] In another aspect, novel halogenated partially fluorinated compounds are described.

[0008] The above summary is not intended to describe each embodiment. The details of one or more embodiments of the invention are also set forth in the description below.

Other features, objects, and advantages will be apparent from the description and from the claims.

## DETAILED DESCRIPTION

[0009] As used herein, the term

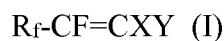
“a”, “an”, and “the” are used interchangeably and mean one or more; and

“and/or” is used to indicate one or both stated cases may occur, for example A and/or B includes, (A and B) and (A or B).

[0010] Also herein, recitation of ranges by endpoints includes all numbers subsumed within that range (e.g., 1 to 10 includes 1.4, 1.9, 2.33, 5.75, 9.98, etc.).

[0011] Also herein, recitation of “at least one” includes all numbers of one and greater (e.g., at least 2, at least 4, at least 6, at least 8, at least 10, at least 25, at least 50, at least 100, etc.).

[0012] The present disclosure is directed toward the addition reaction of an iodine or bromine containing compound to a terminal double bond containing compound of the formula (I)



wherein X and Y are independently selected from F and Cl; wherein R<sub>f</sub> is a fluorinated monovalent group comprising 1 to 10 carbon atoms.

[0013] R<sub>f</sub> may be partially fluorinated (comprising at least one carbon-hydrogen bond and at least one carbon-fluorine bond) or perfluorinated (comprising at least one carbon-fluorine bond and no carbon-hydrogen bonds). R<sub>f</sub> may be linear, branched, or cyclic. R<sub>f</sub> may be saturated or unsaturated, optionally comprising at least one catenated O, S, and/or N (e.g., an ether linkage). In some embodiments, R<sub>f</sub> comprises at least one halogen selected from Cl, Br, and I.

[0014] In one embodiment, R<sub>f</sub> comprises a functional group selected from a sulfate, a carboxylate, a nitrile, and a sulfonate.

[0015] In one embodiment, R<sub>f</sub> is selected from -CF<sub>2</sub>-O-SO<sub>2</sub>F; -CF<sub>2</sub>-I; -CF<sub>2</sub>-Br; -O-(CF<sub>2</sub>)<sub>a</sub>-F; -O-(CF<sub>2</sub>)<sub>a</sub>-I; -O-(CF<sub>2</sub>)<sub>a</sub>-Br; -O-(CF<sub>2</sub>)<sub>b</sub>-O-CF=CXY wherein X and Y are independently selected from F and Cl; a is an integer from 1-10; and b is an integer from 2-4.

[0016] Exemplary, compounds of formula (I) have the structure:

X'-CF<sub>2</sub>-CF=CF<sub>2</sub>, CF<sub>3</sub>-O-CF=CF<sub>2</sub>, C<sub>3</sub>F<sub>7</sub>-O-CF=CF<sub>2</sub>, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>-O-CF(CF<sub>3</sub>)-CF<sub>2</sub>-O-CF=CF<sub>2</sub>, X'-(CF<sub>2</sub>)<sub>1-4</sub>-CF=CF<sub>2</sub>, CF<sub>3</sub>-O-(CF<sub>2</sub>)<sub>3</sub>-O-CF=CF<sub>2</sub>, CF<sub>2</sub>=CF-O-(CF<sub>2</sub>)<sub>2-4</sub>-O-CF=CF<sub>2</sub>, X'-CF<sub>2</sub>-CF<sub>2</sub>-O-(CF<sub>2</sub>)<sub>2-4</sub>-O-CF=CF<sub>2</sub>, CF<sub>2</sub>=CF-O-(CF<sub>2</sub>)<sub>2-4</sub>-O-CF<sub>2</sub>-CF=CF<sub>2</sub>, CF<sub>2</sub>=CF-CF<sub>2</sub>-O-(CF<sub>2</sub>)<sub>2-4</sub>-O-CF<sub>2</sub>-CF=CF<sub>2</sub>, X'-CF<sub>2</sub>-CF<sub>2</sub>-O-(CF<sub>2</sub>)<sub>2-4</sub>-O-CF<sub>2</sub>CF=CF<sub>2</sub>, X'-CF<sub>2</sub>-CF<sub>2</sub>-O-CF=CF<sub>2</sub>, X'-CF<sub>2</sub>-CF<sub>2</sub>-O-CF<sub>2</sub>-CF=CF<sub>2</sub>, X'-CF(CF<sub>3</sub>)-CF<sub>2</sub>-O-CF=CF<sub>2</sub>, X'-CF(CF<sub>3</sub>)-CF<sub>2</sub>-O-CF<sub>2</sub>-CF=CF<sub>2</sub>, X'-CF<sub>2</sub>-CF<sub>2</sub>-(O-CF(CF<sub>3</sub>)-CF<sub>2</sub>)<sub>1-2</sub>-O-CF=CF<sub>2</sub>, X'-CF<sub>2</sub>-CF<sub>2</sub>-(O-CF(CF<sub>3</sub>)-CF<sub>2</sub>)<sub>1-2</sub>-O-CF<sub>2</sub>-CF=CF<sub>2</sub>, X'-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-O-CF=CF<sub>2</sub>, X'-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-O-CF<sub>2</sub>-CF=CF<sub>2</sub>, X'-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-(O-CF(CF<sub>3</sub>)-CF<sub>2</sub>)<sub>1-2</sub>-O-CF=CF<sub>2</sub>, X'-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-(O-CF(CF<sub>3</sub>)-CF<sub>2</sub>)<sub>1-2</sub>-O-CF<sub>2</sub>-CF=CF<sub>2</sub>, X'-CF<sub>2</sub>-CF<sub>2</sub>-O-(CF<sub>2</sub>)<sub>2</sub>-(O-CF(CF<sub>3</sub>)-CF<sub>2</sub>)<sub>1-2</sub>-O-CF<sub>2</sub>=CF<sub>2</sub> wherein X' is selected from Br, I, C(O)X'', and SO<sub>2</sub>X'' wherein X'' is selected from F, Cl, OH, and salts thereof. Exemplary salts of C(O)OH include for example, ammonium salts, alkali and alkaline earth metal salts, such as C(O)ONa.

[0017] It has been discovered that by reacting the compound of formula (I) with either (i) an iodine or bromine containing salt in the presence of an acid or (ii) an aqueous solution of HZ wherein Z is selected from I and Br, the compound of formula (I) undergoes an addition reaction forming a halogenated partially fluorinated compound of formula II



wherein X and Y are the same as above, Z is selected from I and Br, and R'<sub>f</sub> is a monovalent fluorinated group.

[0018] In one embodiment, R'<sub>f</sub> is the same as R<sub>f</sub> in the starting material. In another embodiment R'<sub>f</sub> is different from R<sub>f</sub>.

[0019] Exemplary, compounds of formula (II) have the structure:

X'-CF<sub>2</sub>-CFH-CF<sub>2</sub>-Z, CF<sub>3</sub>-O-CFH-CF<sub>2</sub>-Z, C<sub>3</sub>F<sub>7</sub>-O-CFH-CF<sub>2</sub>-Z, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>-O-CF(CF<sub>3</sub>)-CF<sub>2</sub>-O-CFH-CF<sub>2</sub>-Z, X'-(CF<sub>2</sub>)<sub>1-4</sub>-CFH-CF<sub>2</sub>-Z, CF<sub>3</sub>-O-(CF<sub>2</sub>)<sub>3</sub>-O-CFH-CF<sub>2</sub>-Z, Z-CF<sub>2</sub>-CFH-O-(CF<sub>2</sub>)<sub>2-4</sub>-O-CF=CF<sub>2</sub>, Z-CF<sub>2</sub>-CFH-O-(CF<sub>2</sub>)<sub>2-4</sub>-O-CFH-CF<sub>2</sub>-Z, Z-CF<sub>2</sub>-CFH-O-(CF<sub>2</sub>)<sub>2-4</sub>-O-CF<sub>2</sub>-CF=CF<sub>2</sub>, Z-CF<sub>2</sub>-CFH-O-(CF<sub>2</sub>)<sub>2-4</sub>-O-CF<sub>2</sub>-CFH-CF<sub>2</sub>-Z, CF<sub>2</sub>=CF-O-(CF<sub>2</sub>)<sub>2-4</sub>-O-CF<sub>2</sub>-CFH-CF<sub>2</sub>-Z, Z-CF<sub>2</sub>-CFH-CF<sub>2</sub>-O-(CF<sub>2</sub>)<sub>2-4</sub>-O-CF<sub>2</sub>-CF=CF<sub>2</sub>, Z-CF<sub>2</sub>-CFH-CF<sub>2</sub>-O-(CF<sub>2</sub>)<sub>2-4</sub>-O-CF<sub>2</sub>-CFH-CF<sub>2</sub>-Z, X'-CF<sub>2</sub>-CF<sub>2</sub>-O-(CF<sub>2</sub>)<sub>2-4</sub>-O-CF<sub>2</sub>CFH-CF<sub>2</sub>-Z, X'-CF<sub>2</sub>-CF<sub>2</sub>-O-CFH-CF<sub>2</sub>-Z, X'-CF<sub>2</sub>-CF<sub>2</sub>-O-CF<sub>2</sub>-CFH-CF<sub>2</sub>-Z, X'-CF(CF<sub>3</sub>)-CF<sub>2</sub>-O-CFH-CF<sub>2</sub>-Z, X'-CF(CF<sub>3</sub>)-CF<sub>2</sub>-O-CF<sub>2</sub>-CFH-CF<sub>2</sub>-Z, X'-CF<sub>2</sub>-CF<sub>2</sub>-(O-CF(CF<sub>3</sub>)-CF<sub>2</sub>)<sub>1-2</sub>-O-CFH-CF<sub>2</sub>-Z, X'-CF<sub>2</sub>-CF<sub>2</sub>-(O-CF(CF<sub>3</sub>)-CF<sub>2</sub>)<sub>1-2</sub>-O-CF<sub>2</sub>-CFH-CF<sub>2</sub>-Z, X'-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-O-CFH-CF<sub>2</sub>-Z, X'-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-O-CF<sub>2</sub>-CFH-CF<sub>2</sub>-Z, X'-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-(O-CF(CF<sub>3</sub>)-CF<sub>2</sub>)<sub>1-2</sub>-O-CFH-CF<sub>2</sub>-Z, X'-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-(O-CF(CF<sub>3</sub>)-CF<sub>2</sub>)<sub>1-2</sub>-O-CF<sub>2</sub>-CFH-CF<sub>2</sub>-Z, X'-CF<sub>2</sub>-CF<sub>2</sub>-O-(CF<sub>2</sub>)<sub>2</sub>-(O-CF(CF<sub>3</sub>)-CF<sub>2</sub>)<sub>1-2</sub>-O-CFH-CF<sub>2</sub>-Z wherein Z is Br and I; X' is selected from Br, I, C(O)X'', and SO<sub>2</sub>X'' wherein X'' is selected from F, Cl, OH, and salts thereof. Exemplary salts of the C(O)OH include for example, ammonium salts, alkali and alkaline earth metal salts, such as C(O)ONa.

[0020] In one embodiment, the compound of formula (I) is reacted with an iodine or bromine containing salt in the presence of an acid.

[0021] The iodine or bromine containing salt is of the formula Z<sub>i</sub>M<sup>+</sup><sup>i</sup>, where Z is selected from I and Br, and M is a counter ion with a valency of i in the range of 1 to 4, preferably i is 1 to 2. In one embodiment, the counter ion is organic, such as an alkylammonium (e.g., tetramethylammonium, terabutylammonium, etc.). In another embodiment, the counter ion is inorganic, such as an ammonium, or a metal, such as alkali metal (e.g., Na, K, Li, etc.) or alkaline earth metal (e.g., Mg, Ca, etc.).

[0022] Typically the molar ratio of the salt to formula (I) is 0.5:1 to 10:1, preferably 1:1 to 5:1.

[0023] An acid is used to favor the addition reaction of the halogenide to the terminal olefin. Generally the lower the pK<sub>a</sub> (the stronger the acid) the better the yield for the

addition reaction. In one embodiment the acid has a pKa of no more than 4.8 at 25 °C, or even no more than 2. Exemplary acids include sulfonic acids (e.g. trifluoromethanesulfonic acid) and carboxylic acids (e.g. acetic acid and trifluoroacetic acid), or mixtures thereof. The acids may be diluted with water to any concentration, preferably the acids or mixtures thereof are used in the absence of water.

[0024] The reaction of the iodine or bromine containing salt with the compound of formula (I) may occur in an aqueous solution or a non-aqueous solution.

[0025] Exemplary solvents that are preferably used are non-reactive organic solvents, such as those which have a boiling point up to 275 °C (e.g. triglyme and tetraglyme), preferably those having a boiling point up to 170 °C (e.g. CH<sub>3</sub>CN, tetrahydrofuran, propionitrile, monoglyme, diglyme) or mixtures thereof. Exemplary solvents include: acetonitrile, diglyme, monoglyme, propionitrile, triglyme, tetraglyme, tetrahydrofuran, water, and mixtures thereof.

[0026] In one embodiment, the reaction of the iodine or bromine containing salt with the compound of formula (I) may occur at pressures from at least ambient (1 bar), 3 bar, or even 5 bar to pressures no higher than 10 bar, 15 bar, or even 20 bar. In one embodiment, the reaction of the iodine or bromine containing salt with the compound of formula (I) may occur at temperatures of at least -10 °C, 0 °C, 20 °C, 25 °C, 30 °C, 40 °C, or even 50 °C; and at most 275 °C, 250 °C, 220 °C, 200 °C, 180 °C, 150 °C, 120 °C, 110 °C, or even 100 °C.

[0027] In another embodiment, the compound of formula (I) is reacted with an aqueous solution comprising HZ wherein Z is selected from I and Br.

[0028] In one embodiment, the molar ratio of HZ to formula (I) is 0.5:1 to 10:1, preferably 1:1 to 5:1.

[0029] In one embodiment, the reaction of HZ with the compound of formula (I) may occur at pressures from at least ambient (1 bar), 3 bar, or even 5 bar to pressures no higher than 10 bar, 15 bar, or even 20 bar. In one embodiment, the reaction of HZ with compound of formula (I) may occur at temperatures of at least -10 °C, 0 °C, 20 °C, 25 °C, 30 °C, 40 °C, or even 50 °C; and at most 275 °C, 250 °C, 220 °C, 200 °C, 180 °C, 150 °C, 120 °C, 110 °C, or even 100 °C.

[0030] In one embodiment, the reaction of HZ with the compound of formula (I) can be conducted in the presence of cosolvents. Exemplary cosolvents that are preferably used

are non-reactive organic solvents, as those which have a boiling point up to 275 °C (e.g. triglyme and tetraglyme), preferably those having a boiling point up to 170 °C (e.g. CH<sub>3</sub>CN, tetrahydrofuran, propionitrile, monoglyme, diglyme) or mixtures thereof. Exemplary solvents include: acetonitrile, diglyme, monoglyme, propionitrile, triglyme, tetraglyme, tetrahydrofuran, water, and mixtures thereof.

[0031] The reactions described above involve the addition of the HBr and HI group across the double bond of formula (I), thus, the R<sub>f</sub> group should remain unchanged in the product (i.e., R'<sub>f</sub> in formula (II)). However, as mentioned above, in one embodiment, R'<sub>f</sub> is different from R<sub>f</sub>. Such differences may be due to the reaction of the iodine or bromine containing compounds (i.e., the iodine or bromine salts in the presence of an acid or HZ with Z = I, Br) with reactive groups located in the R<sub>f</sub> group (e.g. carboxylate, nitrile, or unsaturated groups).

[0032] When the compound of formula (I) comprises two terminal double bonds (such as divinyl ethers of the formula CF<sub>2</sub>=CF-O-(CF<sub>2</sub>)<sub>2-4</sub>-O-CF=CF<sub>2</sub> or CF<sub>2</sub>=CF-O-CF=CF<sub>2</sub>), the amount of compound according to formula (I) to the amount of the iodine or bromine containing compounds (i.e., the iodine or bromine salts in the presence of an acid or HZ with Z = I, Br) can be adjusted to favor the reaction of one or both terminal double bonds.

[0033] As will be shown in the examples, the preparation of I-CF<sub>2</sub>-CFH-CF<sub>2</sub>-I using the methods disclosed herein can occur in either a two-step or a one-step synthesis. For example, perfluoroallyl fluorosulfate (CF<sub>2</sub>=CF-CF<sub>2</sub>-O-SO<sub>2</sub>F) can be reacted in a first step with an iodine containing salt *via* nucleophilic substitution reaction, followed by a second step, wherein the CF<sub>2</sub>=CF-CF<sub>2</sub>-I is reacted with an iodine containing salt in the presence of an acid. Alternatively, the perfluoroallyl fluorosulfate can directly be reacted with an iodine containing salt in the presence of an acid.

[0034] Further, in another embodiment, the halogenated partially fluorinated compound of formula (II) can be reacted with a hydrocarbon olefin such as ethylene to elongate the halogenated partially fluorinated compound, adding, for example, a -CH<sub>2</sub>-CH<sub>2</sub>- group. This group on the elongated halogenated partially fluorinated compound can then be reduced to form a partially fluorinated compound according to formula (III):



wherein R'' is selected from X'-CF<sub>2</sub>-, CH<sub>2</sub>=CH-CF<sub>2</sub>-, CF<sub>3</sub>O-, CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>-O-, or CF<sub>3</sub>-O-(CF<sub>2</sub>)<sub>3</sub>-O-, wherein X' is selected from Br, I, C(O)X'', and SO<sub>2</sub>X'' wherein X'' is selected from F, Cl, OH, and salts thereof

[0035] Such insertions of the hydrocarbon olefin into the halogenated partially fluorinated compounds of formula (II) could be conducted by known methods in the absence or in the presence of a radical initiator (e.g. di-tert-butyl peroxide, azobisisobutyronitrile), in the absence or in the presence of a catalyst (e.g. Ni, Cu, Fe, CuCl/CH<sub>3</sub>CN, P(OEt)<sub>3</sub>, Ru/C, Pt/C, Ag/Al<sub>2</sub>O<sub>3</sub>, Ni(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, W(CO)<sub>5</sub>P(OEt)<sub>3</sub>, Mo(CO)<sub>5</sub>(PPh<sub>3</sub>), where Et is ethyl and Ph is phenyl). Exemplary reaction times are from at least 2, 3, 6, or even 10 hrs up to 12, 15, or even 24 hrs or more. Exemplary reaction temperatures are from at least 30, 50, 75, 100, or even 150 °C up to 175, 200, 225, or even 250 °C. Typically the reaction is conducted in a steel or hastelloy autoclave.

[0036] Subsequently, the corresponding ethylene elongated compound can be reduced to a double bond by known methods (e.g. *via* KOH/phase transfer catalysts, KOH/EtOH, trialkylamines, Zn/DMF at temperatures ranging from at least 0, 25, 50, 75 or even 100 °C up to 175, 200, 225, or even 250 °C).

[0037] The compounds according to formulas (II) and (III) can be used, for example, as starting materials or building blocks in chemical synthesis, and/or as a chain transfer agents and/or cure site monomers in a fluoropolymer polymerization.

[0038] The reactions disclosed herein involve contacting the compound of formula (I) with an iodide or bromide ion in the presence of an acid. Advantageously, the reactions can be conducted at mild pressures and temperatures (for example, ambient pressure at 100 °C). Advantageously, in one embodiment, the resulting products can be isolated from the reaction by phase separation. For example, the reaction product is washed with an aqueous solution which separates the compound of formula (II) from the starting materials and by-products. In one embodiment the desired product is isolated *via* distillation.

[0039] Exemplary embodiments of the present disclosure are listed below:

[0040] Embodiment 1: A method of making a halogenated partially fluorinated compound, the method comprising:

- (a) providing a compound having the following structure of formula (I):  
R<sub>f</sub>-CF=CXY

wherein X and Y are independently selected from F and Cl; wherein  $R_f$  is a fluorinated monovalent group comprising 1 to 10 carbon atoms;

(b) contacting the compound with at least one of

- (i) an iodine or bromine containing salt in the presence of an acid; and
- (ii) aqueous solution of HZ wherein Z is selected from I and Br

to form the halogenated partially fluorinated compound of the formula (II):



wherein X and Y are independently selected from F and Cl; Z is selected from I and Br; and  $R'_f$  is a fluorinated monovalent group comprising 1 to 10 carbon atoms.

[0041] Embodiment 2: The method of embodiment 1, wherein  $R_f$  comprises at least one catenated oxygen or sulfur atom.

[0042] Embodiment 3: The method of any one of the previous embodiments, wherein  $R_f$  comprises at least one halogen selected from at least one Cl, Br, and I.

[0043] Embodiment 4: The method of any one of the previous embodiments, wherein  $R_f$  is a linear, branched or cyclic group.

[0044] Embodiment 5: The method of any one of the previous embodiments, wherein  $R_f$  is selected from  $-\text{CF}_2\text{-O-SO}_2\text{F}$ ;  $-\text{CF}_2\text{I}$ ;  $-\text{CF}_2\text{Br}$ ;  $-\text{O}-(\text{CF}_2)_a\text{-F}$ ;  $-\text{O}-(\text{CF}_2)_a\text{-I}$ ;  $-\text{O}-(\text{CF}_2)_a\text{-Br}$ ;  $-\text{O}-(\text{CF}_2)_b\text{-O-CF=XY}$  wherein X and Y are independently selected from F and Cl and a is an integer from 1-10 and b is an integer from 2-4.

[0045] Embodiment 6: The method of any one of the previous embodiments, wherein the compound of formula (I) is selected from:

$X'\text{-CF}_2\text{-CF=CF}_2$ ,  $\text{CF}_3\text{-O-CF=CF}_2$ ,  $\text{C}_3\text{F}_7\text{-O-CF=CF}_2$ ,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{-O-CF(CF}_3\text{)-CF}_2\text{-O-CF=CF}_2$ ,  $X'\text{-(CF}_2\text{)}_m\text{-CF=CF}_2$ ,  $\text{CF}_3\text{-O-(CF}_2\text{)}_3\text{-O-CF=CF}_2$ ,  $\text{CF}_2\text{=CF-O-(CF}_2\text{)}_n\text{-O-CF=CF}_2$ ,  $X'\text{-CF}_2\text{-CF}_2\text{-O-(CF}_2\text{)}_n\text{-O-CF=CF}_2$ ,  $\text{CF}_2\text{=CF-O-(CF}_2\text{)}_n\text{-O-CF}_2\text{-CF=CF}_2$ ,  $\text{CF}_2\text{=CF-CF}_2\text{-O-(CF}_2\text{)}_n\text{-O-CF}_2\text{-CF=CF}_2$ ,  $X'\text{-CF}_2\text{-CF}_2\text{-O-(CF}_2\text{)}_n\text{-O-CF}_2\text{CF=CF}_2$ ,  $X'\text{-CF}_2\text{-CF}_2\text{-O-CF=CF}_2$ ,  $X'\text{-CF}_2\text{-CF}_2\text{-O-CF}_2\text{-CF=CF}_2$ ,  $X'\text{-CF(CF}_3\text{)-CF}_2\text{-O-CF=CF}_2$ ,  $X'\text{-CF(CF}_3\text{)-CF}_2\text{-O-CF}_2\text{-CF=CF}_2$ ,  $X'\text{-CF}_2\text{-CF}_2\text{-(O-CF(CF}_3\text{)-CF}_2\text{)}_p\text{-O-CF=CF}_2$ ,  $X'\text{-CF}_2\text{-CF}_2\text{-(O-CF(CF}_3\text{)-CF}_2\text{)}_p\text{-O-CF}_2\text{-CF=CF}_2$ ,  $X'\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-O-CF=CF}_2$ ,  $X'\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-O-CF}_2\text{-CF=CF}_2$ ,  $X'\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-(O-CF(CF}_3\text{)-CF}_2\text{)}_p\text{-O-CF=CF}_2$ ,  $X'\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-(O-CF(CF}_3\text{)-CF}_2\text{)}_p\text{-O-CF}_2\text{-CF=CF}_2$ , and  $X'\text{-CF}_2\text{-CF}_2\text{-O-(CF}_2\text{)}_2\text{-(O-CF(CF}_3\text{)CF}_2\text{)}_p\text{-O-CF}_2\text{=CF}_2$  wherein  $X'$  is selected from Br, I,  $\text{C(O)X''}$ , and  $\text{SO}_2\text{X''}$  wherein  $X''$  is

selected from F, Cl, OH, and salts thereof; m is an integer from 1-4; n is an integer from 2-4; and p is an integer from 1-2 .

[0046] Embodiment 7: The method of any one of the previous embodiments, wherein  $R'_f$  is the same as  $R_f$ .

[0047] Embodiment 8: The method of any one of the previous embodiments, wherein the iodine or bromine containing salt is selected from alkaline halogenides, alkaline earth halogenides, and tetraalkylammonium halogenides.

[0048] Embodiment 9: The method of any one of the previous embodiments, wherein the pKa of the acid is at most 4.8.

[0049] Embodiment 10: The method of any one of the previous embodiments, wherein the contacting of the compound of formula (I) with the iodine or bromine containing salt occurs in the presence of a solvent.

[0050] Embodiment 11: The method of embodiment 10, wherein the solvent is selected from acetonitrile, diglyme, monoglyme, propionitrile, tetraglyme, triglyme, tetrahydrofuran, and water.

[0051] Embodiment 12: The method of any one of the previous embodiments, wherein the contacting of the compound with the iodine or bromine containing salt or the aqueous solution of HZ is conducted at a pressure of 1 to 20 bar and a temperature of 20 to 200 °C.

[0052] Embodiment 13: The method of any one of the previous embodiments, further comprising, (c) reacting the halogenated partially fluorinated compound of formula (II) with a (terminal) hydrocarbon olefin to elongate the halogenated partially fluorinated compound.

[0053] Embodiment 14: The method of embodiment 13, further comprising:

reducing the elongated halogenated partially fluorinated compound of embodiment 13 to form a compound of formula (III):



wherein  $R''$  is selected from  $X'-CF_2-$ ,  $CH_2=CH-CF_2-$ ,  $CF_3O-$ ,  $CF_3CF_2CF_2O-$ , and  $CF_3O-(CF_2)_3O-$ , wherein  $X'$  is selected from Br, I,  $C(O)X''$ , and  $SO_2X''$  wherein  $X''$  is selected from F, Cl, OH, and salts thereof.

[0054] Embodiment 15: A compound having the following structure:

Br-CF<sub>2</sub>-CFH-CF<sub>2</sub>-I, CF<sub>3</sub>-O-CFH-CF<sub>2</sub>-I, C<sub>3</sub>F<sub>7</sub>-O-CFH-CF<sub>2</sub>-Z, CF<sub>3</sub>-CF<sub>2</sub>-CF<sub>2</sub>-O-CF(CF<sub>3</sub>)-CF<sub>2</sub>-O-CFH-CF<sub>2</sub>-Z, I-(CF<sub>2</sub>)<sub>n</sub>-CFH-CF<sub>2</sub>-I, I-(CF<sub>2</sub>)<sub>m</sub>-CFH-CF<sub>2</sub>-Br, Br-(CF<sub>2</sub>)<sub>m</sub>-CFH-CF<sub>2</sub>-I, Br-(CF<sub>2</sub>)<sub>q</sub>-CFH-CF<sub>2</sub>-Br, CF<sub>3</sub>-O-(CF<sub>2</sub>)<sub>3</sub>-O-CFH-CF<sub>2</sub>-Z, Z-CF<sub>2</sub>-CFH-O-(CF<sub>2</sub>)<sub>n</sub>-O-CF=CF<sub>2</sub>, Z-CF<sub>2</sub>-CFH-O-(CF<sub>2</sub>)<sub>n</sub>-O-CFH-CF<sub>2</sub>-Z, Z-CF<sub>2</sub>-CFH-O-(CF<sub>2</sub>)<sub>n</sub>-O-CF<sub>2</sub>-CF=CF<sub>2</sub>, Z-CF<sub>2</sub>-CFH-O-(CF<sub>2</sub>)<sub>n</sub>-O-CF<sub>2</sub>-CFH-CF<sub>2</sub>-Z, CF<sub>2</sub>=CF-O-(CF<sub>2</sub>)<sub>n</sub>-O-CF<sub>2</sub>-CFH-CF<sub>2</sub>-Z, Z-CF<sub>2</sub>-CFH-CF<sub>2</sub>-O-(CF<sub>2</sub>)<sub>n</sub>-O-CF<sub>2</sub>-CF=CF<sub>2</sub>, Z-CF<sub>2</sub>-CFH-CF<sub>2</sub>-O-(CF<sub>2</sub>)<sub>n</sub>-O-CF<sub>2</sub>-CFH-CF<sub>2</sub>-Z, X'-CF<sub>2</sub>-CF<sub>2</sub>-O-(CF<sub>2</sub>)<sub>n</sub>-O-CF<sub>2</sub>-CFH-CF<sub>2</sub>-Z, X'-CF<sub>2</sub>-CF<sub>2</sub>-O-CFH-CF<sub>2</sub>-Z, X'-CF<sub>2</sub>-CF<sub>2</sub>-O-CF<sub>2</sub>-CFH-CF<sub>2</sub>-Z, X'-CF(CF<sub>3</sub>)-CF<sub>2</sub>-O-CFH-CF<sub>2</sub>-Z, X'-CF(CF<sub>3</sub>)-CF<sub>2</sub>-O-CF<sub>2</sub>-CFH-CF<sub>2</sub>-Z, X'-CF<sub>2</sub>-CF<sub>2</sub>-(O-CF(CF<sub>3</sub>)-CF<sub>2</sub>)<sub>p</sub>-O-CFH-CF<sub>2</sub>-Z, X'-CF<sub>2</sub>-CF<sub>2</sub>-(O-CF(CF<sub>3</sub>)-CF<sub>2</sub>)<sub>p</sub>-O-CF<sub>2</sub>-CFH-CF<sub>2</sub>-Z, X'-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-O-CFH-CF<sub>2</sub>-Z, X'-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-O-CF<sub>2</sub>-CFH-CF<sub>2</sub>-Z, X'-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-(O-CF(CF<sub>3</sub>)-CF<sub>2</sub>)<sub>p</sub>-O-CFH-CF<sub>2</sub>-Z, X'-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-(O-CF(CF<sub>3</sub>)-CF<sub>2</sub>)<sub>p</sub>-O-CF<sub>2</sub>-CFH-CF<sub>2</sub>-Z, X'-CF<sub>2</sub>-CF<sub>2</sub>-O-(CF<sub>2</sub>)<sub>2</sub>-(O-CF(CF<sub>3</sub>)-CF<sub>2</sub>)<sub>p</sub>-O-CFH-CF<sub>2</sub>-Z, wherein Z is Br, I; X' is selected from Br, I, C(O)X'', and SO<sub>2</sub>X'' wherein X'' is selected from F, Cl, OH, and salts thereof; m is an integer from 1-4; n is an integer from 2-4; and p is 1 or 2; and q is 3 or 4.

## EXAMPLES

[0055] Advantages and embodiments of this disclosure are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. In these examples, all percentages, proportions and ratios are by weight unless otherwise indicated.

[0056] All materials are commercially available, for example from Sigma-Aldrich Chemical Company; Milwaukee, WI, or known to those skilled in the art unless otherwise stated or apparent.

[0057] These abbreviations are used in the following examples: b.p. = boiling point, g = gram, h and hr = hour, min = minutes, mol = mole, mbar = millibar, and L = liter.

[0058] Example 1

[0059] Synthesis of CF<sub>2</sub>=CF-CF<sub>2</sub>-I

[0060] Perfluoroallylfluorosulfate (CF<sub>2</sub>=CF-CF<sub>2</sub>-O-SO<sub>2</sub>F; 1270 g, 5.5 mol) was added over the course of 9 hrs to a slurry of NaI (531 g, 3.5 mol) and KI (433 g, 2.6 mol) in monoglyme (1910 g) maintained at a temperature between 5 and 20 °C. Afterwards, the

reaction mixture was poured into H<sub>2</sub>O (4 L), creating a biphasic material. The organic phase was separated and washed with water, followed by a washing with a 5 % solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The organic phase was then distilled, collecting CF<sub>2</sub>=CF-CF<sub>2</sub>-I (1246 g, 4.8 mol; b.p. 57 °C at 967 mbar) in an isolated yield of 87 %.

[0061] Synthesis of I-CF<sub>2</sub>-CFH-CF<sub>2</sub>-I:

[0062] A mixture of acetonitrile (1010 g), trifluoroacetic acid (220 g, 1.9 mol), LiI (511 g, 3.8 mol) and CF<sub>2</sub>=CF-CF<sub>2</sub>-I (328 g, 1.3 mol, from above) was heated to 60 °C for 110 hr. Then the reaction mixture was poured into H<sub>2</sub>O (4 L), creating a biphasic material. The organic phase was separated and washed with water, followed by a washing with a 5 % solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The organic phase was then distilled, collecting I-CF<sub>2</sub>-CFH-CF<sub>2</sub>-I (402 g, 1.1 mol; b.p. 79 °C at 133 mbar) in an isolated yield of 85 %.

[0063] Example 2

[0064] Synthesis of I-CF<sub>2</sub>-CFH-CF<sub>2</sub>-I:

[0065] In a steel autoclave, a mixture of CF<sub>2</sub>=CF-CF<sub>2</sub>-I (7.7 g, 29.9 mmol), [NBu<sub>4</sub>]I (0.6 g, 1.6 mmol), HI<sub>aq</sub> (57%; 9.1 mL, 15.5 g, 69.0 mmol) and CH<sub>3</sub>CN (38.9 g) was heated at 96 °C for 14 hr. Afterwards, the reaction mixture was cooled to 25 °C poured into H<sub>2</sub>O (50 mL) creating a biphasic material. The organic phase was separated and washed with water, followed by a washing with a 5 % solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. I-CF<sub>2</sub>-CFH-CF<sub>2</sub>-I (2.8 g, 7.8 mmol) was obtained in an isolated yield of 26 %.

[0066] Example 3

[0067] Synthesis I-CF<sub>2</sub>-CFH-CF<sub>2</sub>-I

[0068] CF<sub>2</sub>=CF-CF<sub>2</sub>-OSO<sub>2</sub>F (300 g, 1.3 mol) was added to a mixture of LiI (455 g, 3.4 mol) and acetonitrile (1010 g) at 10 °C. After 6 hr, trifluoroacetic acid (222 g, 1.9 mol) was added at 10 °C and the reaction mixture was intensively stirred and heated up to 60 °C for 106 hr. Subsequently, the reaction mixture was poured into H<sub>2</sub>O (4 L) creating a biphasic material. The organic phase was separated and washed with water, followed by a washing with a 5 % solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The organic phase was then distilled, collecting I-CF<sub>2</sub>-CFH-CF<sub>2</sub>-I (77 g, 0.2 mol) in an isolated yield of 15 %.

[0069] Example 4

[0070] Synthesis of CF<sub>3</sub>-O-(CF<sub>2</sub>)<sub>3</sub>-O-CFH-CF<sub>2</sub>-I *via* HI<sub>(aq)</sub> in a steel autoclave

[0071] In a steel autoclave a mixture of CF<sub>3</sub>-O-(CF<sub>2</sub>)<sub>3</sub>-O-CF=CF<sub>2</sub> (10 g, 31.3 mmol), LiI (1.9 g, 14.2 mmol), HI<sub>aq</sub> (57%; 9.5 mL, 16 g, 72.2 mmol) and CH<sub>3</sub>CN (35 g) was heated at

142 °C for 14 h. Afterwards, the reaction mixture was cooled to 25 °C poured into H<sub>2</sub>O (50 mL) creating a biphasic material. The organic phase was separated and washed with water, followed by a washing with a 5 % solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. CF<sub>3</sub>-O-(CF<sub>2</sub>)<sub>3</sub>-O-CFH-CF<sub>2</sub>-I (6.2 g, 13.5 mmol) was obtained in an isolated yield of 43 %.

[0072] Example 5:

[0073] Synthesis of I-CF<sub>2</sub>-CFH-CF<sub>2</sub>-I

[0074] A reaction mixture of acetonitrile (1016 g), acetic acid (114 g, 1.9 mol), LiI (513 g, 3.8 mol) and CF<sub>2</sub>=CF-CF<sub>2</sub>-I (330 g, 1.3 mol) was heated up to 60 °C for 112 h.

Subsequently, the reaction mixture was poured into H<sub>2</sub>O (4 L) creating a biphasic material. The organic phase was separated and washed with water, followed by a washing with a 5 % solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The organic phase was then distilled, collecting I-CF<sub>2</sub>-CFH-CF<sub>2</sub>-I (251 g, 0.7 mol) in an isolated yield of 54 %.

[0075] Foreseeable modifications and alterations of this invention will be apparent to those skilled in the art without departing from the scope and spirit of this invention. This invention should not be restricted to the embodiments that are set forth in this application for illustrative purposes.

**What is claimed is:**

1. A method of making a halogenated partially fluorinated compound, the method comprising:
  - (a) providing a compound having the following structure of formula (I):
 
$$R_f-CF=CXY$$
 wherein X and Y are independently selected from F and Cl; wherein  $R_f$  is a fluorinated monovalent group comprising 1 to 10 carbon atoms;
    - (c) contacting the compound with at least one of
      - (iii) an iodine or bromine containing salt in the presence of an acid; and
      - (iv) aqueous solution of HZ wherein Z is selected from I and Br
 to form the halogenated partially fluorinated compound of the formula (II):
 
$$R'_f-CFH-CXYZ$$
 wherein X and Y are independently selected from F and Cl; Z is selected from I and Br; and  $R'_f$  is a fluorinated monovalent group comprising 1 to 10 carbon atoms.
2. The method of claim 1, wherein  $R_f$  comprises at least one catenated oxygen or sulfur atom.
3. The method of claim 1, wherein  $R_f$  is selected from  $-CF_2-O-SO_2F$ ;  $-CF_2I$ ;  $-CF_2Br$ ;  $-O-(CF_2)_a-F$ ;  $-O-(CF_2)_a-I$ ;  $-O-(CF_2)_a-Br$ ;  $-O-(CF_2)_b-O-CF=XY$  wherein X and Y are independently selected from F and Cl and a is an integer from 1-10 and b is an integer from 2-4.
4. The method of claim 1, wherein the compound of formula (I) is selected from:
 
$$X'-CF_2-CF=CF_2, CF_3-O-CF=CF_2, C_3F_7-O-CF=CF_2, CF_3CF_2CF_2-O-CF(CF_3)-CF_2-O-CF=CF_2, X'-(CF_2)_m-CF=CF_2, CF_3-O-(CF_2)_3-O-CF=CF_2, CF_2=CF-O-(CF_2)_n-O-CF=CF_2, X'-CF_2-CF_2-O-(CF_2)_n-O-CF=CF_2, CF_2=CF-O-(CF_2)_n-O-CF_2-CF=CF_2, CF_2=CF-CF_2-O-(CF_2)_n-O-CF_2-CF=CF_2, X'-CF_2-CF_2-O-(CF_2)_n-O-CF_2CF=CF_2, X'-CF_2-CF_2-O-CF=CF_2, X'-CF(CF_3)-CF_2-O-CF=CF_2, X'-$$

CF(CF<sub>3</sub>)-CF<sub>2</sub>-O-CF<sub>2</sub>-CF=CF<sub>2</sub>, X'-CF<sub>2</sub>-CF<sub>2</sub>-(O-CF(CF<sub>3</sub>)-CF<sub>2</sub>)<sub>p</sub>-O-CF=CF<sub>2</sub>, X'-CF<sub>2</sub>-CF<sub>2</sub>-(O-CF(CF<sub>3</sub>)-CF<sub>2</sub>)<sub>p</sub>-O-CF<sub>2</sub>-CF=CF<sub>2</sub>, X'-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-O-CF=CF<sub>2</sub>, X'-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-O-CF<sub>2</sub>-CF=CF<sub>2</sub>, X'-CF<sub>2</sub>-CF<sub>2</sub>-(O-CF(CF<sub>3</sub>)-CF<sub>2</sub>)<sub>p</sub>-O-CF=CF<sub>2</sub>, X'-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-(O-CF(CF<sub>3</sub>)-CF<sub>2</sub>)<sub>p</sub>-O-CF<sub>2</sub>-CF=CF<sub>2</sub>, and X'-CF<sub>2</sub>-CF<sub>2</sub>-O-(CF<sub>2</sub>)<sub>2</sub>-(O-CF(CF<sub>3</sub>)-CF<sub>2</sub>)<sub>p</sub>-O-CF<sub>2</sub>-CF=CF<sub>2</sub> wherein X' is selected from Br, I, C(O)X'', and SO<sub>2</sub>X'' wherein X'' is selected from F, Cl, OH, and salts thereof; m is an integer from 1-4; n is an integer from 2-4; and p is an integer from 1-2.

5. The method of claim 1, wherein the iodine or bromine containing salt is selected from alkaline halogenides, alkaline earth halogenides, and tetraalkylammonium halogenides.
6. The method of claim 1, wherein the pKa of the acid is at most 4.8.
7. The method of claim 1, wherein the contacting of the compound of formula (I) with the iodine or bromine containing salt occurs in the presence of a solvent, wherein the solvent is optionally selected from acetonitrile, diglyme, monoglyme, propionitrile, tetraglyme, triglyme, tetrahydrofuran, and water.
8. The method of claim 1, wherein the contacting of the compound with the iodine or bromine containing salt or the aqueous solution of HZ is conducted at a pressure of 1 to 20 bar and a temperature of 20 to 200 °C.
9. The method of claim 1, further comprising, (c) reacting the halogenated partially fluorinated compound of formula (II) with a (terminal) hydrocarbon olefin to elongate the halogenated partially fluorinated compound.
10. A compound having the following structure:  
 Br-CF<sub>2</sub>-CFH-CF<sub>2</sub>-I, CF<sub>3</sub>-O-CFH-CF<sub>2</sub>-I, C<sub>3</sub>F<sub>7</sub>-O-CFH-CF<sub>2</sub>-Z, CF<sub>3</sub>-CF<sub>2</sub>-CF<sub>2</sub>-O-CF(CF<sub>3</sub>)-CF<sub>2</sub>-O-CFH-CF<sub>2</sub>-Z, I-(CF<sub>2</sub>)<sub>n</sub>-CFH-CF<sub>2</sub>-I, I-(CF<sub>2</sub>)<sub>m</sub>-CFH-CF<sub>2</sub>-Br, Br-(CF<sub>2</sub>)<sub>m</sub>-CFH-CF<sub>2</sub>-I, Br-(CF<sub>2</sub>)<sub>q</sub>-CFH-CF<sub>2</sub>-Br, CF<sub>3</sub>-O-(CF<sub>2</sub>)<sub>3</sub>-O-CFH-CF<sub>2</sub>-Z, Z-CF<sub>2</sub>-CFH-O-(CF<sub>2</sub>)<sub>n</sub>-O-CF=CF<sub>2</sub>,

$Z-CF_2-CFH-O-(CF_2)_n-O-CFH-CF_2-Z$ ,  $Z-CF_2-CFH-O-(CF_2)_n-O-CF_2-CF=CF_2$ ,  $Z-CF_2-CFH-O-(CF_2)_n-O-CF_2-CFH-CF_2-Z$ ,  $CF_2=CF-O-(CF_2)_n-O-CF_2-CFH-CF_2-Z$ ,  $Z-CF_2-CFH-CF_2-O-(CF_2)_n-O-CF_2-CF=CF_2$ ,  $Z-CF_2-CFH-CF_2-O-(CF_2)_n-O-CF_2-CFH-CF_2-Z$ ,  $X'-CF_2-CF_2-O-(CF_2)_n-O-CF_2-CFH-CF_2-Z$ ,  $X'-CF_2-CF_2-O-CFH-CF_2-Z$ ,  $X'-CF_2-CF_2-O-CF_2-CFH-CF_2-Z$ ,  $X'-CF(CF_3)-CF_2-O-CFH-CF_2-Z$ ,  $X'-CF(CF_3)-CF_2-O-CF_2-CFH-CF_2-Z$ ,  $X'-CF_2-CF_2-(O-CF(CF_3)-CF_2)_p-O-CFH-CF_2-Z$ ,  $X'-CF_2-CF_2-(O-CF(CF_3)-CF_2)_p-O-CF_2-CFH-CF_2-Z$ ,  $X'-CF_2-CF_2-CF_2-O-CFH-CF_2-Z$ ,  $X'-CF_2-CF_2-CF_2-O-CF_2-CFH-CF_2-Z$ ,  $X'-CF_2-CF_2-CF_2-(O-CF(CF_3)-CF_2)_p-O-CFH-CF_2-Z$ ,  $X'-CF_2-CF_2-CF_2-(O-CF(CF_3)-CF_2)_p-O-CF_2-CFH-CF_2-Z$ ,  $X'-CF_2-CF_2-O-(CF_2)_2-(O-CF(CF_3)-CF_2)_p-O-CFH-CF_2-Z$ , wherein Z is Br, I; X' is selected from Br, I, C(O)X'', and SO<sub>2</sub>X'' wherein X'' is selected from F, Cl, OH, and salts thereof; m is an integer from 1-4; n is an integer from 2-4; and p is 1 or 2; and q is 3 or 4.

## INTERNATIONAL SEARCH REPORT

International application No.  
**PCT/US2015/063947****A. CLASSIFICATION OF SUBJECT MATTER****C07C 41/22(2006.01)i, C07C 41/18(2006.01)i, C07C 43/12(2006.01)i**

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 41/22; C08G 61/12; C07C 247/04; C07C 53/38; C07C 51/08; C07C 255/00; C07C 41/18; C07C 43/12

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) &amp; Keywords: halogenated, fluorinated, perhalogenated terminal olefin, chain transfer agents, cure site monomer

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                      | Relevant to claim No. |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| A         | I. L. KNUNYANTS et al., `Addition of hydrogen halides to fluoro olefins`, 1960, Bulletin of the Academy Sciences of the USSR, Vol.9, pp.1568-1569<br>See whole article. | 1-10                  |
| A         | J. D. PARK et al., `The addition of hydrogen bromide to fluorinated olefins`, 1949, J. Am. Chem. Soc., Vol.71, pp.2339-2340<br>See whole article.                       | 1-10                  |
| A         | F. W. STACEY et al., `The radical addition of hydrogen bromide to hexafluoropropene`, 1962, J. Org. Chem., Vol.27, pp.4089-4096<br>See whole article.                   | 1-10                  |
| A         | GB 1,012,797 A (FARBWERKE HOECHST AKTIENGESELLSCHAFT) 08 December 1965<br>See examples; and claims.                                                                     | 1-10                  |
| A         | US 2011-0245520 A1 (ZIPPLIES TILMAN et al.) 06 October 2011<br>See abstract; examples; and claims.                                                                      | 1-10                  |
| A         | US 2010-0261869 A1 (HORIUTI MASAYOSI et al.) 14 October 2010<br>See abstract; examples; and claims.                                                                     | 1-10                  |

☒ 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 application or patent 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

"&amp;" document member of the same patent family

Date of the actual completion of the international search

16 February 2016 (16.02.2016)

Date of mailing of the international search report

**16 February 2016 (16.02.2016)**

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea

Facsimile No. +82-42-472-7140

Authorized officer

LEE YOUNJOO

Telephone No. +82-42-481-3477



## INTERNATIONAL SEARCH REPORT

International application No.

**PCT/US2015/063947**

| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                    |                       |
|-------------------------------------------------------|------------------------------------------------------------------------------------|-----------------------|
| Category*                                             | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A                                                     | US 05504248 A (PAUL J. KRUSIC et al.) 02 April 1996                                | 1-9                   |
| X                                                     | See abstract; examples; and claims.                                                | 10                    |

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/US2015/063947**

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s)                                                                                                                                                                              | Publication<br>date                                                                                                                                    |
|-------------------------------------------|---------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------|
| GB 1012797 A                              | 08/12/1965          | CH 442260 A<br>DE 1150665 B                                                                                                                                                                             | 31/08/1967<br>27/06/1963                                                                                                                               |
| US 2011-0245520 A1                        | 06/10/2011          | CN 102272087 A<br>CN 102272087 B<br>EP 2373608 A1<br>EP 2373608 B1<br>GB 0823120 D0<br>JP 05536097 B2<br>JP 2012-512870 A<br>US 2013-0231494 A1<br>US 8440858 B2<br>US 8633328 B2<br>WO 2010-071730 A1  | 07/12/2011<br>18/06/2014<br>12/10/2011<br>03/04/2013<br>28/01/2009<br>02/07/2014<br>07/06/2012<br>05/09/2013<br>14/05/2013<br>21/01/2014<br>24/06/2010 |
| US 2010-0261869 A1                        | 14/10/2010          | CA 2698522 A1<br>CA 2698522 C<br>CN 101801895 A<br>CN 101801895 B<br>EP 2192100 A1<br>EP 2192100 A4<br>JP 05146455 B2<br>KR 10-1170321 B1<br>KR 10-2010-0075868 A<br>US 8357772 B2<br>WO 2009-034859 A1 | 19/03/2009<br>20/11/2012<br>11/08/2010<br>30/10/2013<br>02/06/2010<br>28/01/2015<br>20/02/2013<br>02/08/2012<br>05/07/2010<br>22/01/2013<br>19/03/2009 |
| US 05504248 A                             | 02/04/1996          | EP 0772575 A1<br>EP 0772575 B1<br>JP 03836508 B2<br>JP 10-503206 A<br>WO 96-03358 A1                                                                                                                    | 21/01/1998<br>30/09/1998<br>25/10/2006<br>24/03/1998<br>08/02/1996                                                                                     |