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(54) Title: PERFLUOROPOLYETHER POLYMERS

(57) Abstract: The present invention relates to a copolymer comprising (per)fluoropolyether chains and functional groups that confer discharging properties to the copolymer itself.



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## Description

### Perfluoropolyether polymers

#### Cross reference to related patent applications

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- [0001] This application claims priority filed on 12 January 2023 in Europe with Nr. 23151335.9, the whole content of this application being incorporated herein by reference for all purposes.

#### Technical field

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- [0002] The present invention relates to a copolymer comprising (per)fluoropolyether chains and functional groups that confer discharging properties to the copolymer itself.

#### Background Art

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- [0003] (Per)fluoropolyether polymers (in the following referred to as "PFPE polymers") have been long known as base oils or as additives in several lubricant applications.
- [0004] Several syntheses of PFPE polymers have been disclosed in the art. The first synthesis of unspecified perfluorinated polyether mixtures was reported in 1953, when an oily product was obtained in the course of photoligomerization of hexafluoropropene. Since then, a number of different perfluorinated polyethers have been synthesised and described in literature.
- [0005] **US 4500739 (in the name of Montedison)** discloses the reaction of a peroxidic PFPE with - among the others - perfluoro butadiene (Group II of fluoroolefins). Example 4 discloses the reaction with perfluoro butadiene, with a large excess of perfluorinated bis-olefin, resulting in pendant unsaturated groups along the macromolecular chain such that the reaction can further proceed in the presence of hexamethylenediamine.
- [0006] **US 8,258,090 (in the name of Solvay Solexis S.p.A.)** discloses fluorinated lubricants of formula:  
 (I)  $T-O-[A-B]_z-[A'-B']_{z'}-A-T$   
 wherein  
 T and T' are C<sub>1-3</sub> perfluoroalkyl or C<sub>1-6</sub> alkyl,  
 A and A' are a perfluoropolyether chain,  
 B derives from two different olefins, of which at least one homopolymerizable by radical route, of formula:  
 (Ia)  $-[(CR_1R_2-CR_3R_4)_j-(CR_5R_6-CR_7R_8)_j]-$   
 wherein  
 j is from 1 to 5, j' is from 0 to 4 and the sum of j+j' is between 2 and 5;  
 R<sub>1</sub> to R<sub>8</sub> are halogen, H, C<sub>1-6</sub> (per)haloalkyl, C<sub>1-6</sub> alkyl, C<sub>1-6</sub> oxy(per)fluoroalkyl;  
 z is higher than or equal to 2, z' is an integer and the sum of z and z' is such that the number average molecular weight of the polymer of formula

- (I) is in the range 500-500000;  
B' is (Ia) but at least one of R1 to R8 has a meaning different from that in B.
- [0007] This patent discloses block copolymers characterised by a linear backbone, without any branching. Indeed, no branching is obtained within B, notably comprising (per)fluoropolyether chains.
- [0008] PFPE polymers comprising functional groups along the backbone have been disclosed in the art, being useful as reactive intermediate compounds and as additives.
- [0009] Perfluoropolyether polymers obtained from the reaction of polyperoxidic perfluoropolyether and fluorinated olefin in the presence of U.V. radiations have been disclosed in **US 4,500,739** (Montedison S.p.A.).
- [0010] Polyfunctional (per)fluoropolyether polymers have been further disclosed in **US 5,719,259** (E.I. DuPont de Nemours and Company), **US 4,853,097** (Ausimont S.r.l.), **US 5,104,911** (Ausimont S.r.l.).
- [0011] **US 2011/0230631** (Solvay Solexis S.p.A.) discloses (per)fluoropolyethers comprising at least one (per)fluoropolyoxyalkylene chain comprising at least one recurring unit of formula  $-\text{CF}_2-\text{CF}(\text{CF}_2\text{O}-\text{SO}_2\text{F})-\text{O}-$ , wherein fluorosulfate group in brackets is a pendant group, which is subsequently reacted with a nucleophilic agent to provide functional groups, such as notably carboxylic acid, acyl fluoride, amide and esters.
- [0012] **WO 2019/048394** (Solvay Specialty Polymers Italy S.p.A.) discloses polyfunctional perfluoropolyether derivatives including a block (with sub "n2") comprising a plurality of ionisable groups selected from the group consisting of  $-\text{SO}_3\text{Xa}$ ,  $-\text{PO}_3\text{Xa}$  and  $-\text{COOXa}$ , wherein Xa is H, ammonium group or a monovalent metal; and a block (with sub "n1") comprising PFPE chain(s). Such polyfunctional PFPE is then used as a dispersant in the synthesis of TFE-based elastomers. This document however neither discloses nor suggests copolymers comprising PFPE chains, a plurality of ionisable groups and at least one further block derived from at least one olefin or a bis-perfluorinated-olefin.

### Summary of invention

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- [0013] The Applicant is aware that lubricants based on PFPE-polymers are currently used to lubricate electric and electronic components, including for example electrical connectors. However, the Applicant is also aware that such lubricants are provided in the form of greases and often comprise solid particles as thickeners. When thickeners in the form of solid particles are used, issues in the stability can arise and for example separation of the solid particles can be observed.
- [0014] Starting from this issue, the Applicant faced the problem of developing lubricants that can be used to lubricate electric and electronic components, without the need of adding solid particles to the formulation.
- [0015] Further to the above, the Applicant also faced the problem of developing lubricants that can be used to lubricate electric and electronic components with the aim of decreasing the static discharge that can be generated in electric and electronic equipment.

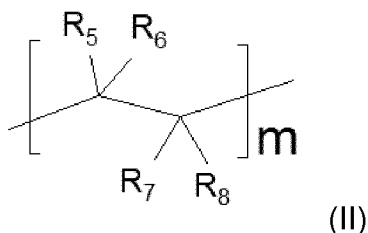
- [0016] Surprisingly, the Applicant developed copolymers that can be used as oils for such applications, such oils showing inherent reduced electrical resistivity without the need of adding conductive additives.
- [0017] Also, such copolymers can be used as oils without the need of adding thickeners in the form of solid particles, thus simplifying the manufacturing process and the storage of the same. Also, no compatibility issues arose with the additive and no phase separation occurred.
- [0018] Advantageously, the copolymer according to the present invention also showed low-to-zero weight loss when used at high temperatures

### Detailed description of the invention

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- [0019] For the purpose of the present description and of the following claims:
- the use of parentheses around symbols or numbers identifying the formulae, for example in expressions like "polymer (P)", etc., has the mere purpose of better distinguishing the symbol or number from the rest of the text and, hence, said parenthesis can also be omitted;
  - the acronym "PFPE" stands for "perfluoropolyether" and, when used as substantive, is intended to mean either the singular or the plural form, depending on the context;
  - the term "functionality (F)" is intended to indicate the amount of functional groups in the copolymer according to the present invention as measured via NMR or titration.
- [0020] In a first aspect, the present invention relates to a block copolymer [copolymer (P)] comprising a first and a second perfluoropolyether chain [PFPE chain] each having two chain ends, wherein:
- the first chain end of each one of said first and second PFPE chain is a chain end of copolymer (P) and each one comprises a group selected from a perfluorinated linear or branched alkyl chain comprising from 1 to 6 carbon atoms or  $-C(=O)O^- M^+$  wherein  $M^+$  is at least one inorganic metal salt or at least one organic group preferably selected from ammonium or phosphonium; and
- the second chain ends of said first and second PFPE chain are bonded to each other via:
- at least one first block [block (1)] complying with formula (I):
- $$-[CR_{100}R_{101}-CR_{102}R_{103}]_{L^{\wedge}}(D)_L- \quad (I)$$
- wherein
- $L^{\wedge}$  is 0 or an integer from 1 to 250;
  - $R_{100}$ ,  $R_{101}$ ,  $R_{102}$  and  $R_{103}$  are each independently selected from hydrogen atom, halogen atom, more preferably fluorine or chlorine atom; linear or branched alkyl chain comprising from 1 to 6 carbon atoms;  $-OR_{200}$  wherein  $R_{200}$  is a linear or branched perfluorinated chain comprising from 1 to 6 carbon atoms or a group of formula  $-CF_2OR_{201}$  in which  $R_{201}$  is a perfluorinated alkyl chain comprising from 1 to 6 carbon atoms, optionally interrupted by one or more oxygen ether atoms; or
  - one of  $R_{100}$  and  $R_{101}$  and one of  $R_{102}$  and  $R_{103}$  are a fluorine atom and the other of  $R_{100}$  and  $R_{101}$  and the other of  $R_{102}$  and  $R_{103}$  together form a perhalogenated cyclic ring having from 4 to 6 members, optionally comprising heteroatoms, such as oxygen atoms;

L is 0 or an integer from 1 to 250, and  
 D is a group of formula  $-(CR_{100}^*R_{101}^*-CR_{102}^*R_{103}^*)-$  wherein at least one of  $R_{100}^*$ ,  $R_{101}^*$ ,  $R_{102}^*$  and  $R_{103}^*$  is different from  $R_{100}$ ,  $R_{101}$ ,  $R_{102}$ , and  $R_{103}$ , such that (D) is different from  $-[CR_{100}R_{101}-CR_{102}R_{103}]L^{\wedge}-$ ;  
 with the proviso that, when  $L^{\wedge}$  and L are both different from 0, the recurring units are statistically distributed;  
 – at least one second block [block (2)] complying with formula (II):



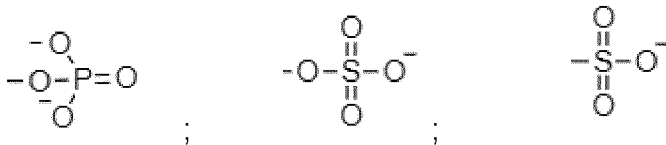
wherein  
 m is an integer from 1 to 5;  
 $R_5$  to  $R_8$ , each independently, is selected in the group comprising, preferably consisting of, -F, perfluorinated linear or branched alkyl chain having from 1 to 6 carbon atoms, and group of formula (III):

(III)  $-R_{20}-(X)_y$

wherein

$R_{20}$  is a sigma bond, or linear or branched perfluoroalkyl chain comprising from 1 to 12 carbon atoms, preferably comprising and/or interrupted by at least one oxygen atom,

X is an anionic functional group selected from:

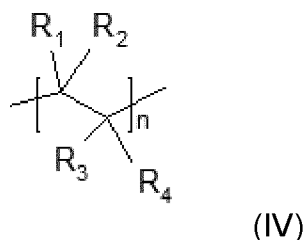


each being salified with at least one inorganic metal salt or with at least one organic group preferably selected from ammonium or phosphonium, and

y is an integer equal to 1 or 2;

with the proviso that in formula (II), at least one, preferably one, of  $R_5$  to  $R_8$  is group of formula (III);

– at least one third block [block (3)] complying with formula (IV):



wherein

n is 0 or an integer from 1 to 3;

$R_1$  to  $R_4$ , each independently, is selected in the group comprising, preferably consisting of, fluorine atom, perfluorinated linear or branched alkyl group having from 1 to 6 carbon atoms, group of formula (V):

(V)  $-(R_{10})_t[C(R_{11})(R_{12})-C(R_{13})(R_{14})(R_{15})]_z$

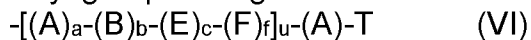
wherein

R<sub>10</sub> is an oxygen atom, or a bi-/tri-/tetravalent perfluorinated alkyl chain comprising from 1 to 24 carbon atoms and being optionally interrupted by at least one oxygen atom,

t is zero or 1,

z is an integer from 1 to 3,

R<sub>11</sub> to R<sub>15</sub>, each independently, is selected in the group comprising, preferably consisting of: fluorine atom, perfluorinated linear or branched alkyl group having from 1 to 6 carbon atoms and group of formula (VI):



wherein

u is zero or an integer from 1 to 50;

T is a group selected from a perfluorinated linear or branched alkyl chain comprising from 1 to 6 carbon atoms or -C(=O)O<sup>-</sup> M<sup>+</sup> wherein M<sup>+</sup> is at least one inorganic metal salt or at least one organic group preferably selected from ammonium or phosphonium;

a is zero or 1,

each A is independently a PFPE chain;

b is zero or an integer from 1 to 3,

B is a block of formula (IV\*)

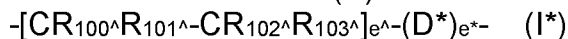


wherein

R<sub>1<sup>^</sup></sub> to R<sub>4<sup>^</sup></sub> each independently has the meaning defined above for each of R<sub>1</sub> to R<sub>4</sub>, respectively;

c is 0 or an integer from 1 to 50,

E is a block of formula (I\*)



wherein

e<sup>^</sup> has the same meaning provided above for L<sup>^</sup>,

each of R<sub>100<sup>^</sup></sub>, R<sub>101<sup>^</sup></sub>, R<sub>102<sup>^</sup></sub> and R<sub>103<sup>^</sup></sub> has the same meaning provided above for R<sub>100</sub>, R<sub>101</sub>, R<sub>102</sub> and R<sub>103</sub>, respectively,

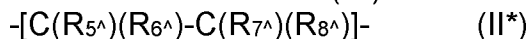
e\* has the same meaning provided above for L, and

D\* has the same meaning provided above for D,

with the proviso that, when e<sup>^</sup> and e\* are both different from 0, the recurring units are statistically distributed;

f is 0 or an integer from 1 to 5, preferably from 1 to 2;

F is a block of formula (II\*)



wherein

R<sub>5<sup>^</sup></sub> to R<sub>8<sup>^</sup></sub>, each independently, has the meaning provided above for each of R<sub>5</sub> to R<sub>8</sub>, respectively;

with the proviso that :

- in said formula (IV), at least one of R<sub>1</sub> to R<sub>4</sub> is a group of formula (V),
- in said formula (IV\*), at least one of R<sub>1<sup>^</sup></sub> to R<sub>4<sup>^</sup></sub> is a group of formula (V)
- in said formula (V), one of R<sub>11</sub> or R<sub>12</sub> and one of R<sub>13</sub> to R<sub>15</sub>, is a group of formula (VI),
- in said formula (VI), when a, b, c and f are all different from 0, the recurring units (A), (B), (E) and (F) are statistically distributed;

and

– optionally, at least one fourth block [block (4)] comprising a PFPE chain; with the proviso that, in copolymer (P):

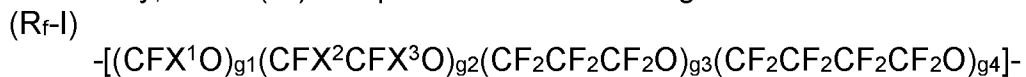
- at least one of L, L<sup>^</sup> or n is different from 0;
- the sum of (m+f) is at least 1, preferably from 1 to 100; and
- said at least one block (1), said at least one block (2), said at least one block (3) and, when present, said at least one block (4) are statistically distributed.

[0021] It will be understood by those skilled in the art that said first chain end of said first and second PFPE chain correspond to the two chain ends of copolymer (P).

[0022] Preferably, in copolymer (P), each of said PFPE chain is a fully fluorinated chain [chain (R<sub>f</sub>)] comprising, preferably consists of, repeating units R<sup>o</sup>, said repeating units being independently selected from the group consisting of:

- (i) -CFXO-, wherein X is -F or -CF<sub>3</sub>;
- (ii) -CFXCFXO-, wherein X, equal or different at each occurrence, is -F or -CF<sub>3</sub>, with the proviso that at least one of X is -F;
- (iii) -CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>O-;
- (iv) -CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>O-;
- (v) -(CF<sub>2</sub>)<sub>j</sub>-CFZ-O- wherein j is an integer from 0 to 3 and Z is a group of general formula -O-R<sub>(f-a)</sub>-T, wherein R<sub>(f-a)</sub> is a fluoropolyoxyalkene chain comprising a number of repeating units from 0 to 10, said recurring units being chosen among the following : -CFXO-, -CF<sub>2</sub>CFXO-, -CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>O-, -CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>O-, with each of X being independently -F or -CF<sub>3</sub> and T being a C<sub>1</sub>-C<sub>3</sub> perfluoroalkyl alkyl chain.

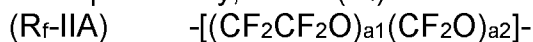
[0023] Preferably, chain (R<sub>f</sub>) complies with the following formula:



wherein

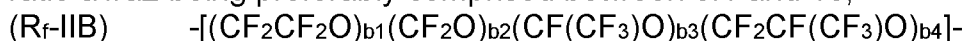
- X<sup>1</sup> is independently selected from -F and -CF<sub>3</sub>,
- X<sup>2</sup>, X<sup>3</sup>, equal or different from each other and at each occurrence, are independently -F, -CF<sub>3</sub>, with the proviso that at least one of X is -F;
- g<sub>1</sub>, g<sub>2</sub>, g<sub>3</sub>, and g<sub>4</sub>, equal or different from each other, are independently integers ≥ 0, such that g<sub>1</sub>+g<sub>2</sub>+g<sub>3</sub>+g<sub>4</sub> is in the range from 2 to 300, preferably from 2 to 100; should at least two of g<sub>1</sub>, g<sub>2</sub>, g<sub>3</sub> and g<sub>4</sub> be different from zero, the different recurring units are generally statistically distributed along the chain.

[0024] More preferably, chain (R<sub>f</sub>) is selected from chains of formula:



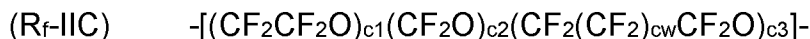
wherein:

- a<sub>1</sub> and a<sub>2</sub> are independently integers ≥ 0 such that the number average molecular weight is between 400 and 100,000, preferably between 400 and 50,000; both a<sub>1</sub> and a<sub>2</sub> are preferably different from zero, with the ratio a<sub>1</sub>/a<sub>2</sub> being preferably comprised between 0.1 and 10;



wherein:

- b<sub>1</sub>, b<sub>2</sub>, b<sub>3</sub>, b<sub>4</sub>, are independently integers ≥ 0 such that the number average molecular weight is between 400 and 100,000, preferably between 400 and 50,000; preferably each of b<sub>1</sub>, b<sub>2</sub>, b<sub>3</sub>, b<sub>4</sub> are > 0;

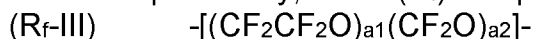


wherein:

$cw = 1$  or  $2$ ;

$c1$ ,  $c2$ , and  $c3$  are independently integers  $\geq 0$  chosen so that the number average molecular weight is between 400 and 100,000, preferably between 400 and 50,000; preferably  $c1$ ,  $c2$  and  $c3$  are all  $> 0$ , with the ratio  $c3/(c1+c2)$  being generally lower than 0.2.

[0025] Still more preferably, chain ( $R_f$ ) complies with formula ( $R_f\text{-III}$ ) here below:



wherein:

-  $a1$ , and  $a2$  are integers  $> 0$  such that the number average molecular weight is between 400 and 100,000, preferably between 400 and 50,000, with the ratio  $a1/a2$  being generally between 0.1 and 10, more preferably between 0.2 and 5.

[0026] According to an embodiment, in block (1), at least one of  $L^{\wedge}$  and  $L$ , preferably both  $L^{\wedge}$  and  $L$ , is different from 0.

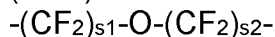
[0027] Preferably,  $R_{100}$ ,  $R_{101}$ ,  $R_{102}$  and  $R_{103}$ , each independently, is a halogen atom, such as fluorine atom or chlorine atom.

[0028] Preferably, in block (2),  $m$  is an integer from 1 to 2.

[0029] Preferably, in block (2), one of  $R_5$  to  $R_8$  is a group of formula (V).

[0030] Preferably, in block (2),  $R_{20}$  is a sigma bond or a group selected from those of formula ( $R_{20\text{-i}}$ ) to ( $R_{20\text{-iv}}$ ) as defined hereinafter:

( $R_{20\text{-i}}$ )



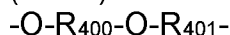
wherein each of  $s1$  and  $s2$  is independently an integer from 1 to 6, preferably from 1 to 3;

( $R_{20\text{-ii}}$ )



wherein  $s3$  is an integer from 1 to 6, preferably from 1 to 5;

( $R_{20\text{-iii}}$ )

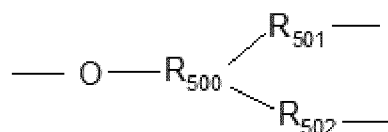


wherein

$R_{400}$  is a linear or branched perfluorinated alkyl chain comprising from 1 to 6, preferably from 1 to 3, carbon atoms, and more preferably complying with formula  $\text{-CF}_2\text{-}$ ,  $\text{-CF}_2\text{CF}_2\text{-}$ ,  $\text{-CF}_2\text{CF}_2\text{CF}_2\text{-}$ ,  $\text{-CF}_2\text{CF}(\text{CF}_3)\text{-}$ ; and

$R_{401}$  is a linear or branched perfluorinated alkyl chain comprising from 1 to 3 carbon atoms, more preferably complying with formula  $\text{-CF}_2\text{-}$ ,  $\text{-CF}_2\text{CF}_2\text{-}$ ,  $\text{-CF}(\text{CF}_3)\text{-}$ ;

( $R_{20\text{-iv}}$ )



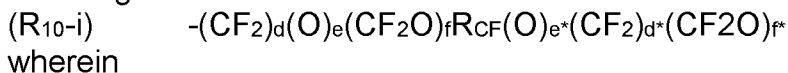
wherein

$R_{500}$  is a linear perfluorinated alkyl chain comprising from 1 to 6 carbon atoms, preferably from 1 to 3 carbon atoms and optionally interrupted by at least one oxygen atom;

$R_{501}$  is a chain of formula  $\text{-OR}_{503}$  wherein  $R_{503}$  is a linear perfluorinated alkyl chain comprising from 1 to 3 carbon atoms;

R<sub>502</sub> is a linear perfluorinated alkyl chain comprising from 1 to 4 carbon atoms and optionally interrupted by at least one oxygen atom;  
each of R<sub>501</sub> and R<sub>502</sub> bonding a group X as defined above.

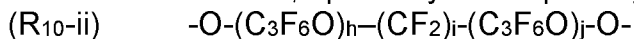
[0031] Preferably, in block (3) and formula (V), R<sub>10</sub> complies with one of the following formulae:



wherein

each of d, d\*, e, e\*, f and f\* is independently zero or 1 and

R<sub>CF</sub> is either a perfluoroalkyl chain comprising from 1 to 12, preferably from 1 to 8 carbon atoms, optionally interrupted by one or more oxygen atoms



wherein h = j and h + j is from 2 to 6, and i is from 2 to 6.

[0032] In a further aspect, the present invention relates to a process [process (P)] for the manufacture of copolymer (P) as defined above.

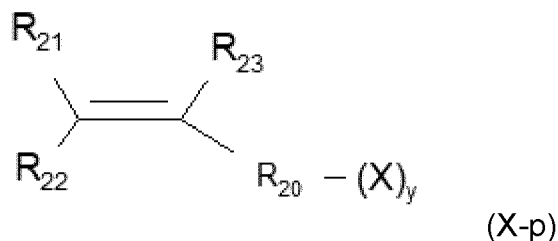
[0033] The process according to the present invention can be easily scaled up from laboratory scale to pilot and industrial scale.

[0034] Advantageously, copolymer (P) of the present invention is prepared via process (P) comprising at least the following steps :

(a) contacting:

- at least one perfluoropolyether polymer comprising at least one peroxidic group [PFPE peroxy];

- at least one perfluorinated compound of formula (X-p):



wherein

each of R<sub>21</sub> to R<sub>23</sub> is independently -F or perfluorinated linear or branched alkyl chain having from 1 to 6 carbon atoms,

R<sub>20</sub> and y are as defined above for formula (III) and

X is selected from :

(X-a) a group of formula: -OP(=O)(OH)<sub>2</sub>, -OS(=O)<sub>2</sub>OH, -S(=O)<sub>2</sub>OH

(X-b) a group of formula: -S(=O)<sub>2</sub>F;

and at least one of:

- at least one compound [compound (O)] selected in the group comprising, preferably consisting of:

(i) hydrogenated olefin comprising from 2 to 15 carbon atoms, partially or fully halogenated olefin comprising from 2 to 15 carbon atoms;

(ii) CF<sub>2</sub>=CFOR<sub>f</sub>,

wherein

R<sub>f</sub> is a C<sub>1</sub>-C<sub>6</sub> (per)fluoroalkyl group, preferably -CF<sub>3</sub>, -C<sub>2</sub>F<sub>5</sub>, -C<sub>3</sub>F<sub>7</sub>; a group C<sub>1</sub>-C<sub>12</sub> [(per)fluoro]-oxyalkyl comprising catenary oxygen atoms, preferably perfluoro-2-propoxypropyl group;

(iii) CF<sub>2</sub>=CFOCF<sub>2</sub>OR<sub>f2</sub>

wherein

R<sub>f2</sub> is selected from the group consisting of C<sub>1</sub>-C<sub>6</sub> perfluoro-alkyls; C<sub>5</sub>-C<sub>6</sub> cyclic perfluoro-alkyls, and C<sub>2</sub>-C<sub>6</sub> perfluoro-oxy-alkyls, comprising at least

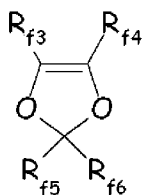
one catenary oxygen atom, preferably  $R_{f2}$  is  $-CF_2CF_3$ ,  $-CF_2CF_2OCF_3$ , or  $-CF_3$ ;

(iv)  $CF_2=CFCF_2OR_{f7}$

wherein

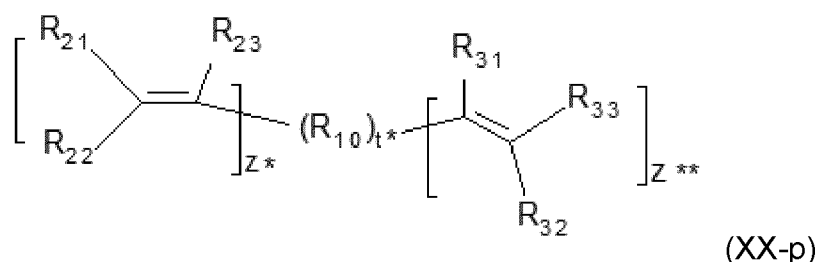
$R_{f7}$  is selected from the group consisting of  $C_1$ - $C_6$  perfluoro-alkyls,  $C_5$ - $C_6$  cyclic perfluoro-alkyls, and  $C_2$ - $C_6$  perfluoro-oxy-alkyls, comprising at least one catenary oxygen atom;

(v) perfluorodioxoles having formula :



wherein each of  $R_{f3}$ ,  $R_{f4}$ ,  $R_{f5}$ ,  $R_{f6}$ , equal to or different from each other, is independently selected from the group consisting of fluorine atom and  $C_1$ - $C_6$  perfluoroalkyl groups, optionally comprising one or more than one oxygen atom, such as notably  $-CF_3$ ,  $-C_2F_5$ ,  $-C_3F_7$ ,  $-OCF_3$ ,  $-OCF_2CF_2OCF_3$ ; and/or

- at least one perfluorinated compound of formula (XX-p):



wherein

each of  $R_{21}$  to  $R_{23}$  are as defined above in formula (X-p),

each of  $R_{31}$  to  $R_{33}$  is independently  $-F$  or perfluorinated alkyl group having from 1 to 6 carbon atoms,

$R_{10}$  is an oxygen atom, a perfluorinated alkyl chain comprising from 1 to 24 carbon atoms, optionally interrupted by at least one oxygen atom,

$t$  is zero or 1;

each of  $z^*$  and  $z^{**}$  is independently 1 or 2; and

(b) reacting said PFPE peroxy, said at least one compound of formula (X-p), optionally said at least one compound of formula (XX-p) and optionally at least one compound (O), in the presence of UV radiation or under heating; and

\* when in formula (X-p) above, X is (X-a) a group of formula: -

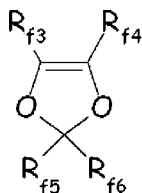
$OP(=O)(OH)_2$ ,  $-OS(=O)_2OH$ ,  $-S(=O)_2OH$ , a step (c1) of salifying such group with at least one compound containing an inorganic metal, an ammonium or a phosphonium group;

\* when in formula (X-p) above, X is (X-b) a group  $-S(=O)_2F$ , a step (c2) of hydrolysis to provide group  $-S(=O)_2O^-$ .

[0035] In step (a), the order in which the reactants are added is not limited.

Accordingly, the PFPE peroxy, the compound of formula (X-p), and when

- used both or either or the compound of formula (XX-p) and at least one compound (O), can be supplied to the reaction environment in any order.
- [0036] Before step (a), the PFPE peroxy can be subjected to partial reduction of the peroxide bonds, for example by chemical reduction or UV treatment or thermal treatment.
- [0037] Preferably, said PFPE peroxy is a peroxidic perfluoropolyether polymer having two chain ends, each comprising a group selected from a linear or branched perfluorinated alkyl chain comprising from 1 to 6 carbon atoms or  $-C(=O)F$ , said two chain ends being bonded to opposite sides of a perfluoropolyether chain [chain ( $R_f$ )] comprising, preferably consisting of, repeating units ( $R^\circ$ ) being independently selected from the group consisting of formulae (i) to (v) as above defined and having a peroxidic content (PO), defined as grams of active oxygen ( $M_w = 16$ ) in 100 g of PFPE peroxy between 0.1 and 4, preferably between 0.1 and 3.5.
- [0038] Preferably, in said PFPE peroxy, chain ( $R_f$ ) complies with formulae (Rf-I), or (Rf-IIA), (Rf-IIB), (Rf-IIC) or (Rf-IIII) as defined above.
- [0039] According to a preferred embodiment, step (a) of the process of the present invention is performed with at least one compound (O).
- [0040] Preferably, said at least one compound (O) is selected in the group comprising, preferably consisting of:
- (i) fully halogenated olefin comprising from 2 to 10 carbon atoms, preferably from 2 to 8 carbon atoms. More preferably, it is selected in the group comprising: tetrafluoroethylene (TFE), hexafluoropropylene (HFP), chlorotrifluoroethylene (CTFE). TFE and HFP being particularly preferred.
- [0041] When two or more compounds (O) are used, preferably, the first compound (O) is selected from those defined in (i) above and a second compound (O) is selected in the group comprising, more preferably consisting of:
- (ii)  $CF_2=CFOR_f$ ,  
wherein  
 $R_f$  is a  $C_1$ - $C_6$  (per)fluoroalkyl group, preferably  $-CF_3$ ,  $-C_2F_5$ ,  $-C_3F_7$ ; a group  $C_1$ - $C_{12}$  [(per)fluoro]-oxyalkyl comprising catenary oxygen atoms, preferably perfluoro-2-propoxypropyl group;
- (iii)  $CF_2=CFOCF_2OR_{f2}$   
wherein  
 $R_{f2}$  is selected from the group consisting of  $C_1$ - $C_6$  perfluoro-alkyls;  $C_5$ - $C_6$  cyclic perfluoro-alkyls, and  $C_2$ - $C_6$  perfluoro-oxy-alkyls, comprising at least one catenary oxygen atom, preferably  $R_{f2}$  is  $-CF_2CF_3$ ,  $-CF_2CF_2OCF_3$ , or  $-CF_3$ ;
- (iv)  $CF_2=CFCF_2OR_{f7}$   
wherein  
 $R_{f7}$  is selected from the group consisting of  $C_1$ - $C_6$  perfluoro-alkyls,  $C_5$ - $C_6$  cyclic perfluoro-alkyls, and  $C_2$ - $C_6$  perfluoro-oxy-alkyls, comprising at least one catenary oxygen atom;
- (v) perfluorodioxoles having formula :

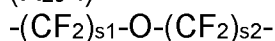


wherein each of  $R_{f3}$ ,  $R_{f4}$ ,  $R_{f5}$ ,  $R_{f6}$ , equal to or different from each other, is independently selected from the group consisting of fluorine atom and C<sub>1</sub>-C<sub>6</sub> perfluoroalkyl groups, optionally comprising one or more than one oxygen atom, such as notably -CF<sub>3</sub>, -C<sub>2</sub>F<sub>5</sub>, -C<sub>3</sub>F<sub>7</sub>, -OCF<sub>3</sub>, -OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>3</sub>.

[0042] Preferably, in said at least one compound of formula (X-p), each of  $R_{21}$ ,  $R_{22}$  and  $R_{23}$  is -F.

[0043] Preferably, in said compound (X-p),  $R_{20}$  is a sigma bond or a group selected from those of formula (R<sub>20</sub>-i) to (R<sub>20</sub>-iv) as defined hereinafter:

(R<sub>20</sub>-i)



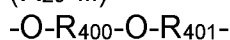
wherein each of  $s_1$  and  $s_2$  is independently an integer from 1 to 6, preferably from 1 to 3;

(R<sub>20</sub>-ii)



wherein  $s_3$  is an integer from 1 to 6, preferably from 1 to 5;

(R<sub>20</sub>-iii)

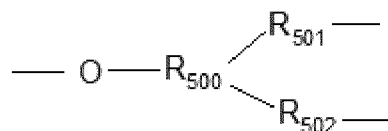


wherein

$R_{400}$  is a linear or branched perfluorinated alkyl chain comprising from 1 to 6, preferably from 1 to 3, carbon atoms, and more preferably complying with formula -CF<sub>2</sub>-, -CF<sub>2</sub>CF<sub>2</sub>-, -CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>-, -CF<sub>2</sub>CF(CF<sub>3</sub>)-, and

$R_{401}$  is a linear or branched perfluorinated alkyl chain comprising from 1 to 3 carbon atoms, more preferably complying with formula -CF<sub>2</sub>-, -CF<sub>2</sub>CF<sub>2</sub>-, -CF(CF<sub>2</sub>)-,

(R<sub>20</sub>-iv)



wherein

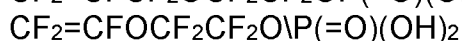
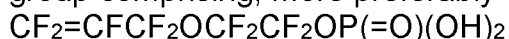
$R_{500}$  is a linear perfluorinated alkyl chain comprising from 1 to 6 carbon atoms, preferably from 1 to 3 carbon atoms and optionally interrupted by at least one oxygen atom;

$R_{501}$  is a chain of formula -OR<sub>503</sub> wherein  $R_{503}$  is a linear perfluorinated alkyl chain comprising from 1 to 3 carbon atoms;

$R_{502}$  is a linear perfluorinated alkyl chain comprising from 1 to 4 carbon atoms and optionally interrupted by at least one oxygen atom;

each of  $R_{501}$  and  $R_{502}$  bonding a group X as defined above.

[0044] Preferably, said at least one compound of formula (X-p) is selected in the group comprising, more preferably consisting of :



$\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{SO}_3\text{H}$   
 $\text{CF}_2=\text{CFSO}_3\text{H}$   
 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{SO}_2\text{F}$   
 $\text{CF}_2=\text{CFSO}_2\text{F}$   
 $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{SO}_2\text{F})_2$   
 $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})$   
 $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_2\text{CF}_2\text{SO}_2\text{F})(\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})$   
 $\text{CF}_2=\text{CFOCF}_2\text{OCF}_2\text{CF}(\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F})(\text{SO}_2\text{F})$ .

- [0045] Some exemplary compounds of formula (X-p) and the preparation thereof are provided in **WO 03/106515** (Daikin Ind.), **JP 2017-025242** (ASAHI GLASS CO., LTD.) and in **US 2008/138685** (AGC Inc.).
- [0046] Preferably, in said compound of formula (XX-p), when t is 1, the one, two, three or four unsaturated moieties are bonded to the same or different atoms, preferably carbon atoms, belonging to R<sub>10</sub>.
- [0047] Preferably, said at least one compound of formula (XX-p) complies with the following formula:  
 $\text{CF}_2=\text{CF}(\text{R}_{10})_t\text{CF}=\text{CF}_2$   
 wherein t is zero or 1, and  
 R<sub>10</sub> complies with one of the following formulae:  
 $(\text{R}_{10-i})-(\text{CF}_2)_d(\text{O})_e(\text{CF}_2\text{O})_f\text{R}_{\text{CF}}(\text{O})_{e^*}(\text{CF}_2)_{d^*}(\text{CF}_2\text{O})_{f^*}$   
 wherein  
 each of d, d\*, e, e\*, f and f\* is independently zero or 1 and  
 R<sub>CF</sub> is either a perfluoroalkyl chain comprising from 1 to 12, preferably from 1 to 8 carbon atoms, optionally interrupted by one or more oxygen atoms  
 $(\text{R}_{10-ii})-\text{O}-(\text{C}_3\text{F}_6\text{O})_h-(\text{CF}_2)_i-(\text{C}_3\text{F}_6\text{O})_j-\text{O}-$   
 wherein h = j and h + j is from 2 to 6, and i is from 2 to 6.
- [0048] According to a particularly preferred embodiment, said at least one compound of formula (XX-p) complies with the following formula:  
 $\text{CF}_2=\text{CF}(\text{R}_{10})_t\text{CF}=\text{CF}_2$   
 wherein t is 1 and  
 R<sub>10</sub> complies with formula:  
 $(\text{R}_{10-i})-(\text{CF}_2)_d(\text{O})_e(\text{CF}_2\text{O})_f\text{R}_{\text{CF}}(\text{O})_{e^*}(\text{CF}_2)_{d^*}(\text{CF}_2\text{O})_{f^*}$   
 wherein  
 d, f, d\* and f\* are zero,  
 e and e\* are 1, and  
 R<sub>CF</sub> is a linear perfluoroalkyl chain comprising from 1 to 10, preferably from 1 to 8 carbon atoms.
- [0049] Preferably, said compound of formula (XX-p) is selected from the group comprising, more preferably consisting of:  
 $\text{CF}_2=\text{CFCF}=\text{CF}_2$   
 $\text{CF}_2=\text{CFOCF}=\text{CF}_2$   
 $\text{CF}_2=\text{CFCF}_2\text{OCF}_2\text{CF}=\text{CF}_2$   
 $\text{CF}_2=\text{CFO}-(\text{CF}_2)_3\text{CF}=\text{CF}_2$   
 $\text{CF}_2=\text{CFCF}_2\text{O}(\text{CF}_2)_3\text{OCF}_2-\text{CF}=\text{CF}_2$   
 $\text{CF}_2=\text{CFCF}_2\text{CF}=\text{CF}_2$   
 $\text{CF}_2=\text{CF}(\text{CF}_2)_2\text{CF}=\text{CF}_2$   
 $\text{CF}_2=\text{CF}(\text{CF}_2)_3\text{CF}=\text{CF}_2$   
 $\text{CF}_2=\text{CF}(\text{CF}_2)_4\text{CF}=\text{CF}_2$   
 $\text{CF}_2=\text{CFOCF}_2\text{OCF}=\text{CF}_2$   
 $\text{CF}_2=\text{CFO}(\text{CF}_2)_2\text{OCF}=\text{CF}_2$

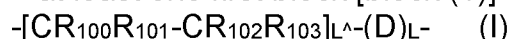
$CF_2=CFO(CF_2)_3OCF=CF_2$   
 $CF_2=CFO(CF_2)_4OCF=CF_2$   
 $CF_2=CF(CF_2)_2OCF=CF_2$   
 $CF_2=CF(CF_2)_3OCF=CF_2$   
 $CF_2=CF(CF_2)_4OCF=CF_2$   
 $CF_2=CFCF_2O(CF_2)_2OCF_2O-CF=CF_2$   
 $CF_2=CFCF_2O(CF_2)_3OCF_2O-CF=CF_2$   
 $CF_2=CFCF_2O(CF_2)_4OCF_2OCF=CF_2$   
 $CF_2=CFCF_2O(CF_2)_6OCF_2CF=CF_2$   
 $CF_2=CFO-CF_2O-(CF_2)_2O-CF_2O-CF=CF_2$   
 $CF_2=CFO-CF_2O-(CF_2)_3O-CF_2O-CF=CF_2$   
 $CF_2=CFO-CF_2O-(CF_2)_4O-CF_2O-CF=CF_2$   
 $CF_2=CFO-(CF_2O)_6-CF=CF_2$   
 $CF_2=CFO-(CF_2CF_2O)_2-CF=CF_2$   
 $CF_2=CFO-(CF_2CF_2O)_2-CF_2OCF=CF_2$   
 $CF_2=CFO(C_3F_6O)_h-(CF_2)_i-(C_3F_6O)_j-OCF=CF_2$   
 wherein h and j are the same and  
 their sum is from 2 to 6 and i is from 2 to 6.

- [0050] The amount of each of said at least one compound (X-p), and when used compound (XX-p) and/or at least one compound (O) is not limited. As explained above, the amount of each of the above mentioned compounds can advantageously be selected based on both the amount of the PFPE peroxy, as well as its peroxidic content, and the properties desired in the final copolymer (P).
- [0051] For example, the equivalents of double bonds of said compound (X-p) to the equivalents of peroxidic groups preferably range from 1:100 to 5000:100. Also, the equivalents of double bonds of said compound (XX-p) to the equivalents of peroxidic groups preferably range from 1:100 to 100:100.
- [0052] Step (a) of process (P) can be advantageously performed by contacting said PFPE peroxy with one compound of formula (X-p).
- [0053] Alternatively, said step (a) can be performed by contacting said PFPE peroxy with two or more compounds of formula (X-p).
- [0054] Step (a) and step (b) can be performed in the presence of a fluorinated solvent.
- [0055] Preferably said fluorinated solvent is selected in the group comprising: perfluorocarbons, hydrofluorocarbons, perfluoropolyethers, hydrofluoropolyethers.
- [0056] Preferably, step (b) is performed in the presence of UV radiation for a time from 2 to 150 hours, more preferably from 5 to 100 hours.
- [0057] Preferably, step (b) is performed in the presence of UV radiation at a temperature from -60°C to +150°C, more preferably from -20°C to +100°C and even more preferably from 0°C to 60°C.
- [0058] As an alternative, step (b) can be performed under thermal treatment, preferably by heating at a temperature from 150 °C to 250 °C.
- [0059] Preferably, said step (b) is performed in an inert atmosphere.
- [0060] Optionally, after step (b) and before step (c1) or (c2), a fluorination step can be performed. Such fluorination step allows neutralising the end groups -COF at the chain end(s) of the PFPE peroxy.

- [0061] Preferably, said step (c1) of salifying is performed with at least one inorganic metal salt, which is preferably an alkaline metal.
- [0062] More preferably, said alkaline metal is selected in the group comprising: sodium, potassium, cesium, lithium, magnesium and calcium.
- [0063] Preferably, said step (c2) of hydrolysis is performed in the presence of an alkaline compound.
- [0064] Such step (c2) of hydrolysis allows obtaining a group  $-S(=O)_2O^-$  salified with at least one inorganic metal salt.
- [0065] For example, such step can be performed using metal hydroxide, such as a solution of sodium or potassium hydroxide in water.
- [0066] Preferably, such step (c2) is performed at 20-100°C.
- [0067] Preferably, such step (c2) is performed for a time from 1 hour to 10 hours.
- [0068] The copolymer (P) as obtained at the end of step (c2) can be further reacted in order to obtain the organic salt with a compound containing the ammonium group or the phosphonium group.
- [0069] Preferably, the compound comprising the ammonium group complies with formula:  
 $N^+H(R_{21})(R_{22})(R_{23})$   
wherein each of  $R_{21}$ ,  $R_{22}$ ,  $R_{23}$  is selected from: linear or branched  $C_1$ - $C_{20}$  aliphatic chain, optionally containing at least one heteroatom, preferably -O-; or two of  $R_{21}$ ,  $R_{22}$ ,  $R_{23}$  together form a 5- or 6- membered aliphatic or aromatic ring, said ring optionally containing at least one heteroatom and/or being optionally substituted by at least one linear or branched alkyl chain comprising from 1 to 10 carbon atoms and optionally containing at least one heteroatom, preferably selected from -O- and -N-, and the third of  $R_{21}$ ,  $R_{22}$ ,  $R_{23}$  is as defined above.
- [0070] More preferably, said compound comprising the ammonium group is selected from triethanol ammonium, triethyl ammonium, pyridinium, trimethyl ammonium, tributyl ammonium, 1-methyl imidazolium, di(ethyl)cyclohexyl-ammonium, benzimidazolium, 1-benzyl imidazolium.
- [0071] Preferably, the compound comprising the phosphonium group complies with formula:  
 $P^+H(R_{211})(R_{221})(R_{231})$   
wherein each of  $R_{211}$ ,  $R_{221}$ ,  $R_{231}$  is selected from: linear or branched  $C_1$ - $C_{20}$  aliphatic chain, optionally containing at least one heteroatom, preferably -O-; or two of  $R_{211}$ ,  $R_{221}$ ,  $R_{231}$  together form a 5- or 6- membered aliphatic or aromatic ring, said ring optionally containing at least one heteroatom and/or being optionally substituted by at least one linear or branched alkyl chain comprising from 1 to 10 carbon atoms and optionally containing at least one heteroatom, preferably selected from O and N, and the third of  $R_{211}$ ,  $R_{221}$ ,  $R_{231}$  is as defined above.
- [0072] More preferably, said compound comprising the organic phosphonium salt is selected from triethyl phosphine, tri propyl phosphine, tributylphosphine, triethylphosphine, trioctylphosphine.
- [0073] In a third aspect, the present invention relates to copolymer (P) obtained via process (P) as described above.
- [0074] In a second aspect, the present invention relates to a method for lubricating at least one element in an electric, electronic or mechanical device, said method comprising a step of applying to such element at least one copolymer (P) as defined above and/or at least one block copolymer

[copolymer (P°)], said copolymer (P°) comprising a first and a second perfluoropolyether chain [PFPE chain] each having two chain ends, wherein  
 the first chain end of each one of said first and second PFPE chain is a chain end of copolymer (P°) and each one comprises a group selected from a perfluorinated linear or branched alkyl chain comprising from 1 to 6 carbon atoms, or  $-C(=O)O^- M^+$  wherein  $M^+$  is at least one inorganic metal salt or at least one organic group preferably selected from ammonium or phosphonium, and  
 the second chain ends of said first and second PFPE chain are bonded to each other via:

– at least one first block [block (1)] complying with formula (I):



wherein

$L^{\wedge}$  is 0 or an integer from 1 to 250;

$R_{100}$ ,  $R_{101}$ ,  $R_{102}$  and  $R_{103}$  are each independently selected from hydrogen atom, halogen atom, more preferably fluorine or chlorine atom; linear or branched alkyl chain comprising from 1 to 6 carbon atoms;  $-OR_{200}$  wherein  $R_{200}$  is a linear or branched perfluorinated chain comprising from 1 to 6 carbon atoms or a group of formula  $-CF_2OR_{201}$  in which  $R_{201}$  is a perfluorinated alkyl chain comprising from 1 to 6 carbon atoms, optionally interrupted by one or more oxygen ether atoms; or

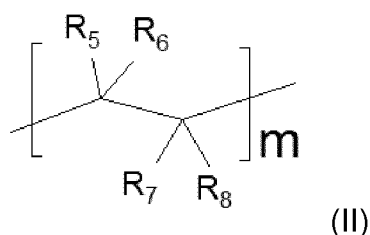
one of  $R_{100}$  and  $R_{101}$  and one of  $R_{102}$  and  $R_{103}$  are a fluorine atom and the other of  $R_{100}$  and  $R_{101}$  and the other of  $R_{102}$  and  $R_{103}$  together form a perhalogenated cyclic ring having from 4 to 6 members, optionally comprising heteroatoms, such as oxygen atoms;

$L$  is 0 or an integer from 1 to 250, and

$D$  is a group of formula  $-(CR_{100}^*R_{101}^*-CR_{102}^*R_{103}^*)-$  wherein at least one of  $R_{100}^*$ ,  $R_{101}^*$ ,  $R_{102}^*$  and  $R_{103}^*$  is different from  $R_{100}$ ,  $R_{101}$ ,  $R_{102}$ , and  $R_{103}$ , such that  $(D)$  is different from  $-[CR_{100}R_{101}-CR_{102}R_{103}]_{L^{\wedge}}$ ;

with the proviso that, when  $L^{\wedge}$  and  $L$  are both different from 0, the recurring units are statistically distributed;

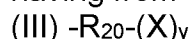
– at least one second block [block (2)] complying with formula (II):



wherein

$m$  is an integer from 1 to 5;

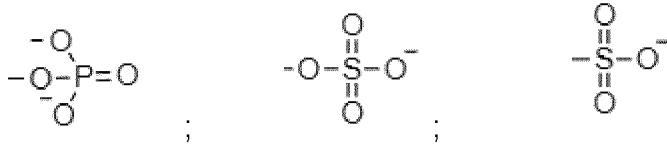
$R_5$  to  $R_8$ , each independently, is selected in the group comprising, preferably consisting of,  $-F$ , perfluorinated linear or branched alkyl chain having from 1 to 6 carbon atoms, and group of formula (III):



wherein

$R_{20}$  is a sigma bond, or linear or branched perfluoroalkyl chain comprising from 1 to 12 carbon atoms, preferably comprising and/or interrupted by at least one oxygen atom,

X is an anionic functional group selected from:  
 $-C(=O)O^-$

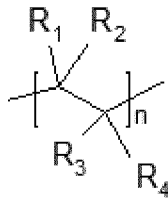


each being salified with at least one inorganic metal salt or with at least one organic group preferably selected from ammonium or phosphonium, and

y is an integer equal to 1 or 2;

with the proviso that in formula (II), at least one, preferably one, of R<sub>5</sub> to R<sub>8</sub> is group of formula (III);

– at least one third block [block (3)] complying with formula (IV):

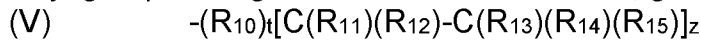


(IV)

wherein

n is 0 or an integer from 1 to 3;

R<sub>1</sub> to R<sub>4</sub>, each independently, is selected in the group comprising, preferably consisting of, fluorine atom, perfluorinated linear or branched alkyl group having from 1 to 6 carbon atoms, group of formula (V):



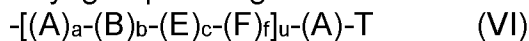
wherein

R<sub>10</sub> is an oxygen atom, or a bi-/tri-/tetravalent perfluorinated alkyl chain comprising from 1 to 24 carbon atoms and being optionally interrupted by at least one oxygen atom,

t is zero or 1,

z is an integer from 1 to 3,

R<sub>11</sub> to R<sub>15</sub>, each independently, is selected in the group comprising, preferably consisting of: fluorine atom, perfluorinated linear or branched alkyl group having from 1 to 6 carbon atoms and group of formula (VI):



wherein

u is zero or an integer from 1 to 50;

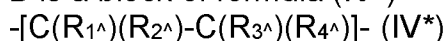
T is a group selected from a perfluorinated linear or branched alkyl chain comprising from 1 to 6 carbon atoms or  $-C(=O)O^- M^+$  wherein M<sup>+</sup> is at least one inorganic metal salt or at least one organic group preferably selected from ammonium or phosphonium

a is zero or 1,

each A is independently a PFPE chain;

b is zero or an integer from 1 to 3,

B is a block of formula (IV\*)



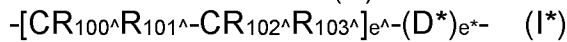
wherein

R<sub>1<sup>A</sup></sub> to R<sub>4<sup>A</sup></sub> each independently has the meaning defined above for each of

R<sub>1</sub> to R<sub>4</sub>, respectively;

c is 0 or an integer from 1 to 50,

E is a block of formula (I\*)



wherein

e<sup>∧</sup> has the same meaning provided above for L<sup>∧</sup>,

each of R<sub>100</sub><sup>∧</sup>, R<sub>101</sub><sup>∧</sup>, R<sub>102</sub><sup>∧</sup> and R<sub>103</sub><sup>∧</sup> has the same meaning provided above for R<sub>100</sub>, R<sub>101</sub>, R<sub>102</sub> and R<sub>103</sub>, respectively,

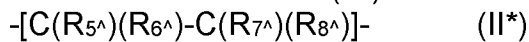
e\* has the same meaning provided above for L, and

D\* has the same meaning provided above for D,

with the proviso that, when e<sup>∧</sup> and e\* are both different from 0, the recurring units are statistically distributed;

f is 0 or an integer from 1 to 5, preferably from 1 to 2;

F is a block of formula (II\*)



wherein

R<sub>5</sub><sup>∧</sup> to R<sub>8</sub><sup>∧</sup>, each independently, has the meaning provided above for each of R<sub>5</sub> to R<sub>8</sub>, respectively;

with the proviso that :

- in said formula (IV), at least one of R<sub>1</sub> to R<sub>4</sub> is a group of formula (V),
- in said formula (IV\*), at least one of R<sub>1</sub><sup>∧</sup> to R<sub>4</sub><sup>∧</sup> is a group of formula (V)
- in said formula (V), one of R<sub>11</sub> or R<sub>12</sub> and one of R<sub>13</sub> to R<sub>15</sub>, is a group of formula (VI),
- in said formula (VI), when a, b, c and f are all different from 0, the recurring units (A), (B), (E) and (F) are statistically distributed;

and

– optionally, at least one fourth block [block (4)] comprising a PFPE chain; with the proviso that, in copolymer (P):

- the sum of (m+f) is at least 1, preferably from 1 to 100; and
- when present, said at least one block (1), said at least one block (2), said at least one block (3) and said at least one block (4) are statistically distributed.

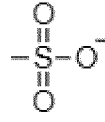
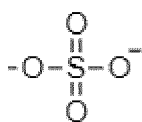
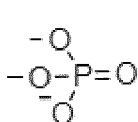
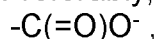
[0075] Preferably, the PFPE chain of copolymer (P°) is as defined above for copolymer (P).

[0076] Preferably, block (1) of copolymer (P°) is as defined above for copolymer (P).

[0077] Preferably, block (3) of copolymer (P°) is as defined above for copolymer (P).

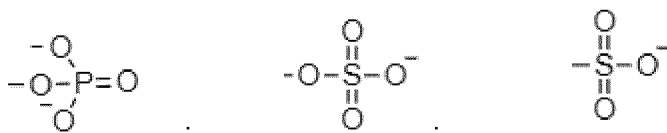
[0078] Preferably, each of m, R<sub>5</sub> to R<sub>8</sub> and R<sub>20</sub> in block (2) of copolymer (P°) have the same meanings defined above for copolymer (P).

[0079] Preferably, X in block (2) of copolymer (P°) is selected from :



each being salified with at least one inorganic metal salt or with at least one organic group preferably selected from ammonium or phosphonium, as defined above for copolymer (P).

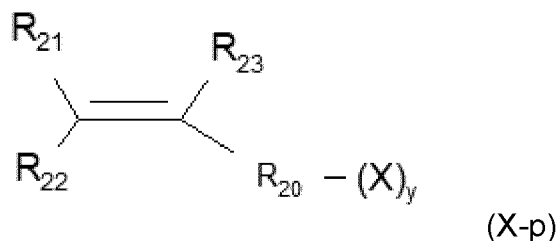
[0080] Advantageously, when X is an anionic group of formula



copolymer (P°) is prepared via a process [process (P°)], said process (P°) comprising the same steps (a), (b) and (c1) or (c2) as defined for process (P).

[0081] Advantageously, when X is an anionic group of formula -C(=O)O<sup>-</sup>, copolymer (P°°) is prepared via process (P°°) comprising in step (a) contacting:

- at least one perfluoropolyether polymer comprising at least one peroxidic group [PFPE peroxy];
- at least one perfluorinated compound of formula (X-p):



wherein

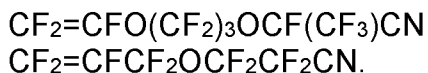
each of R<sub>21</sub> to R<sub>23</sub> is independently -F or perfluorinated linear or branched alkyl chain having from 1 to 6 carbon atoms, R<sub>20</sub> and y are as defined above for formula (III) and X is selected from :

(X-c) a group of formula: -COF, -C(=O)OH or -CN.

[0082] According to this embodiment, process (P°) of the present invention comprises after step (b), at least one of the following steps:  
 (c°-3) of hydrolysis of group -COF to provide group -COOH, followed by a step of salifying said group -COOH to provide group -COO<sup>-</sup> as defined above;  
 (c°-4) of salifying said group -COOH to provide group -COO<sup>-</sup> as defined above; or  
 (c°-5) of hydrolysis of group -CN to provide group -COO<sup>-</sup> as defined above.

[0083] Preferably, according to this embodiment, said at least one compound (X-p) is selected in the group comprising, more preferably consisting of:

- CF<sub>2</sub>=CFCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>COOH
- CF<sub>2</sub>=CFOCF<sub>2</sub>COOH
- CF<sub>2</sub>=CFO(CF<sub>2</sub>)<sub>5</sub>COOH
- CF<sub>2</sub>=CFOCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>COOH
- CF<sub>2</sub>=CF CF<sub>2</sub> CF<sub>2</sub> COOH
- CF<sub>2</sub>=CFCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>COF
- CF<sub>2</sub>=CFOCF<sub>2</sub>COF
- CF<sub>2</sub>=CFO(CF<sub>2</sub>)<sub>3</sub>OCF(CF<sub>3</sub>)COF
- CF<sub>2</sub>=CFO(CF<sub>2</sub>)<sub>5</sub>COF
- CF<sub>2</sub>=CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>CN
- CF<sub>2</sub>=CFOCF<sub>2</sub>CN
- CF<sub>2</sub>=CFO(CF<sub>2</sub>)<sub>5</sub>CN



- [0084] Each of copolymer (P) and copolymer (P°) according to the present invention is advantageously used to lubricate electric and electronic components, in particular with the aim of decreasing the static discharge that can be generated in electric and electronic equipment.
- [0085] For this application, the element in the electric, electronic or mechanical device to be lubricated with copolymer (P) or copolymer (P°) according to the present invention is preferably selected from electrical connectors, sensors, switchgears, circuit breakers, battery terminals, or ball bearings.
- [0086] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence
- [0087] The invention will be hereinafter illustrated in greater detail by means of the Examples contained in the following Experimental Section; the Examples are merely illustrative and are by no means to be interpreted as limiting the scope of the invention.

## Experimental section

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- [0088] **Materials**
- [0089] Peroxidic perfluoropolyether oil was obtained by Solvay Specialty Polymers Italy S.p.A., complying with formula  $\text{XO}-(\text{CF}_2\text{CF}_2\text{O})_{a1}(\text{CF}_2\text{O})_{a2}(\text{O})_h\text{-X}'$  wherein X and X' were  $-\text{CF}_3$ ,  $-\text{CF}_2\text{COF}$ ,  $-\text{COF}$  and having the following properties: Mn = 31 990 g/mol; P.O. = 1.61%; a1/a2 = 1.0
- [0090] Perfluorinated solvents Galden(R) HT200, Galden SV70, as well as Fomblin(R) HV25 (highly viscous neutral PFPE) and the perfluorinated sulfonyl vinyl ether (VEFS)  $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{SO}_2\text{F}$  were obtained by Solvay Specialty Polymers Italy S.p.A..
- [0091] Sodium hydroxide (powder, 97%), hydrochloric acid 37% (aq.), triethylamine ( $\geq 99.5\%$ ), 1-butyylimidazole (98%) were supplied by Sigma Aldrich as used as received.
- [0092] **Methods:**
- [0093]  $^{19}\text{F}$ -NMR-Varian Mercury 300 MHz spectrometer working for the  $^{19}\text{F}$  nucleus was used to obtain the structure, molecular weight, chain end composition of the perfluoropolyether oils. The  $^{19}\text{F}$ -NMR spectrum was obtained on pure samples using  $\text{CFCl}_3$  as internal reference.
- [0094] The peroxidic content (PO) was expressed as grams of peroxidic oxygen per 100 g of polymer. The analysis of the peroxide content was carried out by iodometric titration using a Mettler DL40 device equipped with platinum electrode. The sensitivity limit for the PO determination was 0.0002%.
- [0095] GPC analyses were performed on a Waters GPC equipped with an RI detector and operating at 35°C. All average molecular weight results are reported compared to perfluoropolyethers linear neutral internal standards.
- [0096] **Preparation 1 - PFPE copolymer with VEFS**

- [0097] 320.7 g of the peroxidic perfluoropolyether oil described above were charged in a 1500mL stirred cylindrical photochemical reactor equipped with a high-pressure mercury lamp model HANAU TQ150, a thermocouple, a condenser and a mechanical stirrer. The oil was diluted with 1805.3 g of Galden(R) HT200. Next, 3.52 g of VEFS were added to the reactor and the mixture was purged with nitrogen. The UV lamp was then switched on and the reaction was conducted at 20°C for 55h. After this reaction time, the UV lamp was switched off, the olefins flow was interrupted and the reaction mixture was flushed with nitrogen.
- [0098] The mixture was transferred into a second glass photochemical reactor and treated with UV light and 1 NL/h of fluorine gas at 60°C for 8 hours. The UV lamp was switched off and the mixture was thoroughly flushed with nitrogen. The reactor content then was transferred in a round bottom flask equipped with a magnetic stirrer and treated at 240°C for 6h to remove solvent and residual P.O. The distillation was conducted first at atmospheric pressure, then under reduced pressure (0.1 mbar) until complete removal of the solvent. Iodometric titration confirmed the complete removal of the peroxide units.
- [0099] 256g of the oil obtained from the previous step and 180g of Galden(R) SV70 were added to a 1L round bottom flask equipped with a magnetic stirrer and a condenser. Next, 35.4g of a 6.6wt% of NaOH (aq.) were charged into the flask under stirring. The resulting mixture was heated to 65°C and kept under stirring for 4 hours. At the end of this time, the mixture was cooled down to room temperature and 130g of HCl 10wt% (aq.) were added to the flask. The mixture was thoroughly stirred at room temperature and then added to a separating flask. The bottom phase was recovered and the solvents were stripped at 80°C under vacuum.
- [00100] <sup>19</sup>F-NMR analysis of the product confirmed the structure:  
 $\text{XO}-(\text{CF}_2\text{CF}_2\text{O})_m(\text{CF}_2\text{O})_n(\text{CF}_2\text{CFO}(\text{CF}_2\text{CF}_2\text{SO}_3\text{H}))_a-\text{X}'$   
where  $m/n = 1.0$ ,  $a = 1.1$  on average and X and X' = -CF<sub>3</sub>.
- [00101] The number average molecular weight (M<sub>n</sub>) was 24 530 g/mol.
- [00102] **Example 1 – Copolymer (P) salified with triethyl amine**
- [00103] 100g of the oil from Preparation 1 were charged to a 250ml round bottom flask equipped with a magnetic stirrer.
- [00104] Next, 50 g of Galden(R) SV70 and 0.5 g of triethyl amine were added to the flask. The mixture was left to stir at room temperature for 2 hours and then heated at 50°C for 4 hours. At the end of this time, the mixture was stripped under reduced vacuum at 50°C.
- [00105] **Example 2 - Copolymer (P) salified with 1-butylimidazole**
- [00106] The procedure disclosed for Example 1 was followed, with the difference that 0.6 g of 1-butyl Imidazole were used.
- [00107] The liquid volume resistivity and the kinematic viscosity of the copolymers (P) according to the present invention prepared according to Example 1 and Example 2 were evaluated and are reported in Table 1 below. The copolymer prepared in Preparation 1 was also evaluated as comparison.

Table 1

	Liquid volume resistivity $\rho V (\Omega\text{cm})^{-1}$		Kinematic viscosity (@0.1 rad/s) cSt	
	25°C	80°C	25°C	80°C
<b>Preparation 1(*)</b>	$2 \times 10^{14}$	$9 \times 10^{13}$	n/p	n/p
<b>Example 1</b>	$7 \times 10^{13}$	$2 \times 10^{13}$	32900	2480
<b>Example 2</b>	$6 \times 10^{13}$	$8 \times 10^{12}$	59770	4070
<b>Fomblin<sup>(R)</sup> HV25</b>	$2 \times 10^{15}$	$4 \times 10^{15}$	25000	n/p

(\*) comparative

n/p = not performed

[00108] The results reported above showed that the copolymers of Examples 1 and 2 according to the present invention were characterised by a lower liquid volume resistivity when compared to both the non-salified copolymer of Preparation 1(\*) and the highly viscous neutral PFPE Fomblin<sup>(R)</sup> HV25.

## Claims

Claim 1. A block copolymer [copolymer (P)] comprising a first and a second perfluoropolyether chain [PFPE chain] each having two chain ends, wherein: the first chain end of each one of said first and second PFPE chain is a chain end of copolymer (P) and each one comprises a group selected from a perfluorinated linear or branched alkyl chain comprising from 1 to 6 carbon atoms or  $-C(=O)O^- M^+$  wherein  $M^+$  is at least one inorganic metal salt or at least one organic group preferably selected from ammonium or phosphonium; and the second chain ends of said first and second PFPE chain are bonded to each other via:

– at least one first block [block (1)] complying with formula (I):



wherein

$L^{\wedge}$  is 0 or an integer from 1 to 250;

$R_{100}$ ,  $R_{101}$ ,  $R_{102}$  and  $R_{103}$  are each independently selected from hydrogen atom, halogen atom, more preferably fluorine or chlorine atom; linear or branched alkyl chain comprising from 1 to 6 carbon atoms;  $-OR_{200}$  wherein  $R_{200}$  is a linear or branched perfluorinated chain comprising from 1 to 6 carbon atoms or a group of formula  $-CF_2OR_{201}$  in which  $R_{201}$  is a perfluorinated alkyl chain comprising from 1 to 6 carbon atoms, optionally interrupted by one or more oxygen ether atoms; or

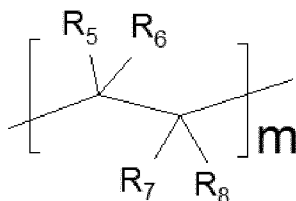
one of  $R_{100}$  and  $R_{101}$  and one of  $R_{102}$  and  $R_{103}$  are a fluorine atom and the other of  $R_{100}$  and  $R_{101}$  and the other of  $R_{102}$  and  $R_{103}$  together form a perhalogenated cyclic ring having from 4 to 6 members, optionally comprising heteroatoms, such as oxygen atoms;

$L$  is 0 or an integer from 1 to 250, and

$D$  is a group of formula  $-(CR_{100}^*R_{101}^*-CR_{102}^*R_{103}^*)-$  wherein at least one of  $R_{100}^*$ ,  $R_{101}^*$ ,  $R_{102}^*$  and  $R_{103}^*$  is different from  $R_{100}$ ,  $R_{101}$ ,  $R_{102}$ , and  $R_{103}$ , such that  $(D)$  is different from  $-[CR_{100}R_{101}-CR_{102}R_{103}]_{L^{\wedge}}-$ ;

with the proviso that, when  $L^{\wedge}$  and  $L$  are both different from 0, the recurring units are statistically distributed;

– at least one second block [block (2)] complying with formula (II):

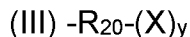


(II)

wherein

$m$  is an integer from 1 to 5;

$R_5$  to  $R_8$ , each independently, is selected in the group comprising, preferably consisting of,  $-F$ , perfluorinated linear or branched alkyl chain having from 1 to 6 carbon atoms, and group of formula (III):



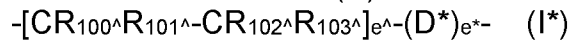
wherein

$R_{20}$  is a sigma bond, or linear or branched perfluoroalkyl chain comprising from 1 to 12 carbon atoms, preferably comprising and/or interrupted by at least one



c is 0 or an integer from 1 to 50,

E is a block of formula (I\*)



wherein

$\text{e}^{\wedge}$  has the same meaning provided above for  $\text{L}^{\wedge}$ ,

each of  $\text{R}_{100}^{\wedge}$ ,  $\text{R}_{101}^{\wedge}$ ,  $\text{R}_{102}^{\wedge}$  and  $\text{R}_{103}^{\wedge}$  has the same meaning provided above for  $\text{R}_{100}$ ,  $\text{R}_{101}$ ,  $\text{R}_{102}$  and  $\text{R}_{103}$ , respectively,

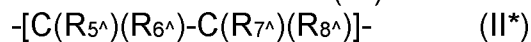
$\text{e}^{*-}$  has the same meaning provided above for L, and

$\text{D}^*$  has the same meaning provided above for D,

with the proviso that, when  $\text{e}^{\wedge}$  and  $\text{e}^{*-}$  are both different from 0, the recurring units are statistically distributed;

f is 0 or an integer from 1 to 5, preferably from 1 to 2;

F is a block of formula (II\*)



wherein

$\text{R}_5^{\wedge}$  to  $\text{R}_8^{\wedge}$ , each independently, has the meaning provided above for each of  $\text{R}_5$  to  $\text{R}_8$ , respectively;

with the proviso that :

- in said formula (IV), at least one of  $\text{R}_1$  to  $\text{R}_4$  is a group of formula (V),
- in said formula (IV\*), at least one of  $\text{R}_{1}^{\wedge}$  to  $\text{R}_{4}^{\wedge}$  is a group of formula (V)
- in said formula (V), one of  $\text{R}_{11}$  or  $\text{R}_{12}$  and one of  $\text{R}_{13}$  to  $\text{R}_{15}$ , is a group of formula (VI),
- in said formula (VI), when a, b, c and f are all different from 0, the recurring units (A), (B), (E) and (F) are statistically distributed;

and

– optionally, at least one fourth block [block (4)] comprising a PFPE chain;

with the proviso that, in copolymer (P):

- at least one of L,  $\text{L}^{\wedge}$  or n is different from 0;
- the sum of (m+f) is at least 1, preferably from 1 to 100; and
- said at least one block (1), said at least one block (2), said at least one block (3) and, when present, said at least one block (4) are statistically distributed.

Claim 2. The copolymer (P) according to Claim 1, wherein each of said PFPE chain is a fully fluorinated chain [chain ( $\text{R}_f$ )] comprising, preferably consists of, repeating units  $\text{R}^{\circ}$ , said repeating units being independently selected from the group consisting of:

(i)  $-\text{CFXO}-$ , wherein X is  $-\text{F}$  or  $-\text{CF}_3$ ;

(ii)  $-\text{CFXCFXO}-$ , wherein X, equal or different at each occurrence, is  $-\text{F}$  or  $-\text{CF}_3$ , with the proviso that at least one of X is  $-\text{F}$ ;

(iii)  $-\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$ ;

(iv)  $-\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$ ;

(v)  $-(\text{CF}_2)_j-\text{CFZ}-\text{O}-$  wherein j is an integer from 0 to 3 and Z is a group of general formula  $-\text{O}-\text{R}_{(f-a)}-\text{T}$ , wherein  $\text{R}_{(f-a)}$  is a fluoropolyoxyalkene chain comprising a number of repeating units from 0 to 10, said recurring units being chosen among the following :  $-\text{CFXO}-$ ,  $-\text{CF}_2\text{CFXO}-$ ,  $-\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$ ,  $-\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$ , with each of X being independently  $-\text{F}$  or  $-\text{CF}_3$  and T being a  $\text{C}_1$ - $\text{C}_3$  perfluoroalkyl alkyl chain.

Claim 3. The copolymer (P) according to Claim 2, wherein chain (R<sub>f</sub>) complies with the following formula:

(R<sub>f</sub>-I)



wherein

- X<sup>1</sup> is independently selected from -F and -CF<sub>3</sub>,
- X<sup>2</sup>, X<sup>3</sup>, equal or different from each other and at each occurrence, are independently -F, -CF<sub>3</sub>, with the proviso that at least one of X is -F;
- g<sub>1</sub>, g<sub>2</sub>, g<sub>3</sub>, and g<sub>4</sub>, equal or different from each other, are independently integers ≥0, such that g<sub>1</sub>+g<sub>2</sub>+g<sub>3</sub>+g<sub>4</sub> is in the range from 2 to 300, preferably from 2 to 100; should at least two of g<sub>1</sub>, g<sub>2</sub>, g<sub>3</sub> and g<sub>4</sub> be different from zero, the different recurring units are generally statistically distributed along the chain.

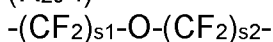
Claim 4. The copolymer according to any one of the preceding Claims, wherein in block (1):

- at least one of L<sup>^</sup> and L, preferably both L<sup>^</sup> and L, is different from 0.; and/or
- R<sub>100</sub>, R<sub>101</sub>, R<sub>102</sub> and R<sub>103</sub>, each independently, is a halogen atom.

Claim 5. The copolymer according to any one of the preceding Claims, wherein in block (2):

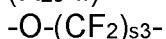
- m is an integer from 1 to 2; and/or
- one of R<sub>5</sub> to R<sub>8</sub> is a group of formula (V) as defined in Claim 1; and/or
- R<sub>20</sub> is a sigma bond or a group selected from those of formula (R<sub>20</sub>-i) to (R<sub>20</sub>-iv) as defined hereinafter:

(R<sub>20</sub>-i)



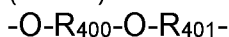
wherein each of s<sub>1</sub> and s<sub>2</sub> is independently an integer from 1 to 6, preferably from 1 to 3;

(R<sub>20</sub>-ii)



wherein s<sub>3</sub> is an integer from 1 to 6, preferably from 1 to 5;

(R<sub>20</sub>-iii)

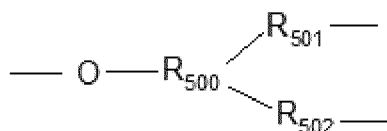


wherein

R<sub>400</sub> is a linear or branched perfluorinated alkyl chain comprising from 1 to 6, preferably from 1 to 3, carbon atoms, and more preferably complying with formula -CF<sub>2</sub>-, -CF<sub>2</sub>CF<sub>2</sub>-, -CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>-, -CF<sub>2</sub>CF(CF<sub>3</sub>)-, and

R<sub>401</sub> is a linear or branched perfluorinated alkyl chain comprising from 1 to 3 carbon atoms, more preferably complying with formula -CF<sub>2</sub>-, -CF<sub>2</sub>CF<sub>2</sub>-, -CF(CF<sub>3</sub>)-,

(R<sub>20</sub>-iv)



wherein

R<sub>500</sub> is a linear perfluorinated alkyl chain comprising from 1 to 6 carbon atoms, preferably from 1 to 3 carbon atoms and optionally interrupted by at least one

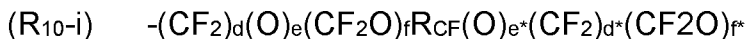
oxygen atom;

R<sub>501</sub> is a chain of formula -OR<sub>503</sub> wherein R<sub>503</sub> is a linear perfluorinated alkyl chain comprising from 1 to 3 carbon atoms;

R<sub>502</sub> is a linear perfluorinated alkyl chain comprising from 1 to 4 carbon atoms and optionally interrupted by at least one oxygen atom;

each of R<sub>501</sub> and R<sub>502</sub> bonding a group X as defined in Claim 1.

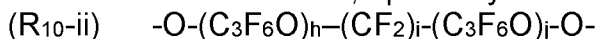
Claim 6. The copolymer according to any one of the preceding Claims, wherein in block (3) and formula (V), R<sub>10</sub> complies with one of the following formulae:



wherein

each of d, d\*, e, e\*, f and f\* is independently zero or 1 and

R<sub>CF</sub> is either a perfluoroalkyl chain comprising from 1 to 12, preferably from 1 to 8 carbon atoms, optionally interrupted by one or more oxygen atoms



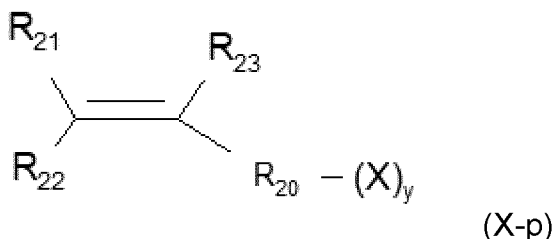
wherein h = j and h + j is from 2 to 6, and i is from 2 to 6.

Claim 7. A process [process (P)] for manufacturing copolymer (P) as defined in any one of Claims 1 to 6, wherein process (P) comprises the steps of:

(a) contacting:

- at least one perfluoropolyether polymer comprising at least one peroxidic group [PFPE peroxy];

- at least one perfluorinated compound of formula (X-p):



wherein

each of R<sub>21</sub> to R<sub>23</sub> is independently -F or perfluorinated linear or branched alkyl chain having from 1 to 6 carbon atoms,

R<sub>20</sub> and y are as defined above for formula (III) and

X is selected from :

(X-a) a group of formula: -OP(=O)(OH)<sub>2</sub>, -OS(=O)<sub>2</sub>OH, -S(=O)<sub>2</sub>OH

(X-b) a group of formula: -S(=O)<sub>2</sub>F;

and at least one of:

- at least one compound [compound (O)] selected in the group comprising, preferably consisting of:

(i) hydrogenated olefin comprising from 2 to 15 carbon atoms, partially or fully halogenated olefin comprising from 2 to 15 carbon atoms;

(ii) CF<sub>2</sub>=CFOR<sub>f</sub>,

wherein

R<sub>f</sub> is a C<sub>1</sub>-C<sub>6</sub> (per)fluoroalkyl group, preferably -CF<sub>3</sub>, -C<sub>2</sub>F<sub>5</sub>, -C<sub>3</sub>F<sub>7</sub>; a group C<sub>1</sub>-C<sub>12</sub> [(per)fluoro]-oxyalkyl comprising catenary oxygen atoms, preferably perfluoro-2-propoxypropyl group;

(iii) CF<sub>2</sub>=CFOCF<sub>2</sub>OR<sub>f2</sub>

wherein

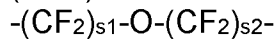


chain comprising from 1 to 6 carbon atoms or  $-C(=O)F$ , said two chain ends being bonded to opposite sides of a perfluoropolyether chain [chain ( $R_f$ )] comprising, preferably consisting of, repeating units ( $R^\circ$ ) being independently selected from the group consisting of formulae (i) to (v) as above defined and having a peroxidic content (PO), defined as grams of active oxygen ( $M_w = 16$ ) in 100 g of PFPE peroxy between 0.1 and 4, preferably between 0.1 and 3.5.

Claim 9. The process (P) according to Claims 7 and 8, wherein in said at least one compound of formula (X-p):

- each of  $R_{21}$ ,  $R_{22}$  and  $R_{23}$  is  $-F$ ; and/or
- $R_{20}$  is a sigma bond or a group selected from those of formula ( $R_{20-i}$ ) to ( $R_{20-iv}$ ) as defined hereinafter:

( $R_{20-i}$ )



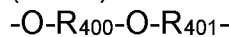
wherein each of  $s_1$  and  $s_2$  is independently an integer from 1 to 6, preferably from 1 to 3;

( $R_{20-ii}$ )



wherein  $s_3$  is an integer from 1 to 6, preferably from 1 to 5;

( $R_{20-iii}$ )

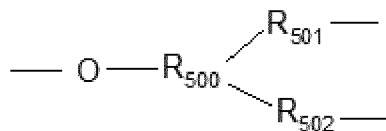


wherein

$R_{400}$  is a linear or branched perfluorinated alkyl chain comprising from 1 to 6, preferably from 1 to 3, carbon atoms, and more preferably complying with formula  $-CF_2-$ ,  $-CF_2CF_2-$ ,  $-CF_2CF_2CF_2-$ ,  $-CF_2CF(CF_3)-$ ; and

$R_{401}$  is a linear or branched perfluorinated alkyl chain comprising from 1 to 3 carbon atoms, more preferably complying with formula  $-CF_2-$ ,  $-CF_2CF_2-$ ,  $-CF(CF_2)-$ ;

( $R_{20-iv}$ )



wherein

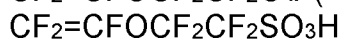
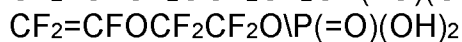
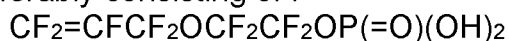
$R_{500}$  is a linear perfluorinated alkyl chain comprising from 1 to 6 carbon atoms, preferably from 1 to 3 carbon atoms and optionally interrupted by at least one oxygen atom;

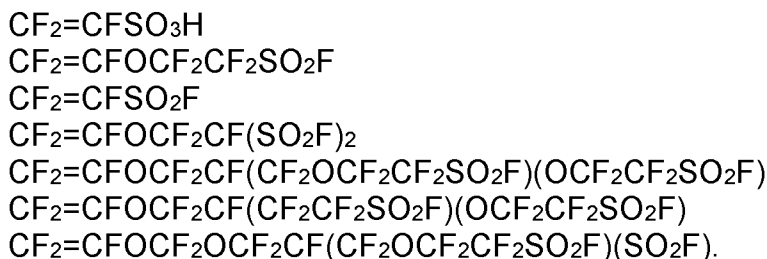
$R_{501}$  is a chain of formula  $-OR_{503}$  wherein  $R_{503}$  is a linear perfluorinated alkyl chain comprising from 1 to 3 carbon atoms;

$R_{502}$  is a linear perfluorinated alkyl chain comprising from 1 to 4 carbon atoms and optionally interrupted by at least one oxygen atom;

each of  $R_{501}$  and  $R_{502}$  bonding a group X as defined in Claim 7.

Claim 10. The process (P) according to Claim 9, wherein said at least one compound of formula (X-p) is selected in the group comprising, more preferably consisting of :





- Claim 11. The process (P) according to any one of Claims 7 to 10, further comprising after step (b) and before step (c1) or (c2), a fluorination step.
- Claim 12. The process (P) according to any one of Claim 7 to 11, wherein:
- step (c1) of salifying is performed with at least one inorganic metal salt, preferably an alkaline metal; or
  - step (c2) of hydrolysis is performed in the presence of an alkaline compound.
- Claim 13. The process (P) according to any one of Claims 7 to 12, wherein the copolymer obtained after step (c2) is reacted with a compound comprising an ammonium group or a phosphonium group thus obtaining copolymer (P) wherein X is an anionic group as defined in Claim 1 salified with an organic salt.
- Claim 14. A method for lubricating at least one element in an electric, electronic or mechanical device, said method comprising a step of applying to such element
- \* at least one copolymer (P) as defined in any one of Claims 1 to 6, and/or
  - \* at least one block copolymer [copolymer (P°)], said copolymer (P°) comprising a first and a second perfluoropolyether chain [PFPE chain] each having two chain ends, wherein the first chain end of each one of said first and second PFPE chain is a chain end of copolymer (P°) and each one comprises a group selected from a perfluorinated linear or branched alkyl chain comprising from 1 to 6 carbon atoms, or  $-\text{C}(=\text{O})\text{O}^- \text{M}^+$  wherein  $\text{M}^+$  is at least one inorganic metal salt or at least one organic group preferably selected from ammonium or phosphonium, and the second chain ends of said first and second PFPE chain are bonded to each other via:
    - at least one first block [block (1)] complying with formula (I):
$$-\text{[CR}_{100}\text{R}_{101}-\text{CR}_{102}\text{R}_{103}]_{\text{L}^\wedge}-(\text{D})_{\text{L}}- \quad (\text{I})$$

wherein

    - $\text{L}^\wedge$  is 0 or an integer from 1 to 250;
    - $\text{R}_{100}$ ,  $\text{R}_{101}$ ,  $\text{R}_{102}$  and  $\text{R}_{103}$  are each independently selected from hydrogen atom, halogen atom, more preferably fluorine or chlorine atom; linear or branched alkyl chain comprising from 1 to 6 carbon atoms;  $-\text{OR}_{200}$  wherein  $\text{R}_{200}$  is a linear or branched perfluorinated chain comprising from 1 to 6 carbon atoms or a group of formula  $-\text{CF}_2\text{OR}_{201}$  in which  $\text{R}_{201}$  is a perfluorinated alkyl chain comprising from 1 to 6 carbon atoms, optionally interrupted by one or more oxygen ether atoms; or
    - one of  $\text{R}_{100}$  and  $\text{R}_{101}$  and one of  $\text{R}_{102}$  and  $\text{R}_{103}$  are a fluorine atom and the other

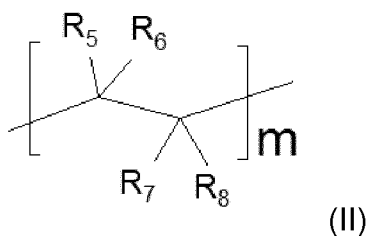
of R<sub>100</sub> and R<sub>101</sub> and the other of R<sub>102</sub> and R<sub>103</sub> together form a perhalogenated cyclic ring having from 4 to 6 members, optionally comprising heteroatoms, such as oxygen atoms;

L is 0 or an integer from 1 to 250, and

D is a group of formula -(CR<sub>100</sub>\*R<sub>101</sub>\*-CR<sub>102</sub>\*R<sub>103</sub>\*)- wherein at least one of R<sub>100</sub>\*, R<sub>101</sub>\*, R<sub>102</sub>\* and R<sub>103</sub>\* is different from R<sub>100</sub>, R<sub>101</sub>, R<sub>102</sub>, and R<sub>103</sub>, such that (D) is different from -[CR<sub>100</sub>R<sub>101</sub>-CR<sub>102</sub>R<sub>103</sub>]<sup>L</sup>-;

with the proviso that, when L<sup>^</sup> and L are both different from 0, the recurring units are statistically distributed;

– at least one second block [block (2)] complying with formula (II):



wherein

m is an integer from 1 to 5;

R<sub>5</sub> to R<sub>8</sub>, each independently, is selected in the group comprising, preferably consisting of, -F, perfluorinated linear or branched alkyl chain having from 1 to 6 carbon atoms, and group of formula (III):

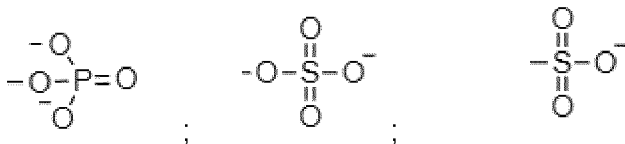
(III) -R<sub>20</sub>-(X)<sub>y</sub>

wherein

R<sub>20</sub> is a sigma bond, or linear or branched perfluoroalkyl chain comprising from 1 to 12 carbon atoms, preferably comprising and/or interrupted by at least one oxygen atom,

X is an anionic functional group selected from:

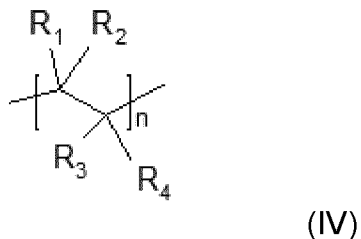
-C(=O)O<sup>-</sup>



each being salified with at least one inorganic metal salt or with at least one organic group preferably selected from ammonium or phosphonium, and y is an integer equal to 1 or 2;

with the proviso that in formula (II), at least one, preferably one, of R<sub>5</sub> to R<sub>8</sub> is group of formula (III);

– at least one third block [block (3)] complying with formula (IV):

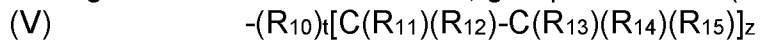


wherein

n is 0 or an integer from 1 to 3;

R<sub>1</sub> to R<sub>4</sub>, each independently, is selected in the group comprising, preferably

consisting of, fluorine atom, perfluorinated linear or branched alkyl group having from 1 to 6 carbon atoms, group of formula (V):



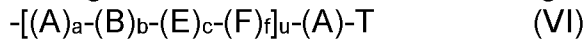
wherein

$R_{10}$  is an oxygen atom, or a bi-/tri-/tetravalent perfluorinated alkyl chain comprising from 1 to 24 carbon atoms and being optionally interrupted by at least one oxygen atom,

$t$  is zero or 1,

$z$  is an integer from 1 to 3,

$R_{11}$  to  $R_{15}$ , each independently, is selected in the group comprising, preferably consisting of: fluorine atom, perfluorinated linear or branched alkyl group having from 1 to 6 carbon atoms and group of formula (VI):



wherein

$u$  is zero or an integer from 1 to 50;

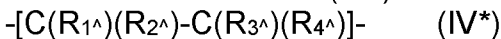
$T$  is a group selected from a perfluorinated linear or branched alkyl chain comprising from 1 to 6 carbon atoms or  $-C(=O)O^- M^+$  wherein  $M^+$  is at least one inorganic metal salt or at least one organic group preferably selected from ammonium or phosphonium

$a$  is zero or 1,

each  $A$  is independently a PFPE chain;

$b$  is zero or an integer from 1 to 3,

$B$  is a block of formula (IV\*)

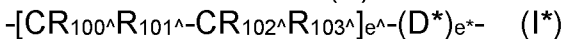


wherein

$R_{1^\wedge}$  to  $R_{4^\wedge}$  each independently has the meaning defined above for each of  $R_1$  to  $R_4$ , respectively;

$c$  is 0 or an integer from 1 to 50,

$E$  is a block of formula (I\*)



wherein

$e^\wedge$  has the same meaning provided above for  $L^\wedge$ ,

each of  $R_{100^\wedge}$ ,  $R_{101^\wedge}$ ,  $R_{102^\wedge}$  and  $R_{103^\wedge}$  has the same meaning provided above for  $R_{100}$ ,  $R_{101}$ ,  $R_{102}$  and  $R_{103}$ , respectively,

$e^*$  has the same meaning provided above for  $L$ , and

$D^*$  has the same meaning provided above for  $D$ ,

with the proviso that, when  $e^\wedge$  and  $e^*$  are both different from 0, the recurring units are statistically distributed;

$f$  is 0 or an integer from 1 to 5, preferably from 1 to 2;

$F$  is a block of formula (II\*)



wherein

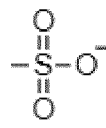
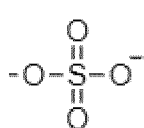
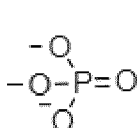
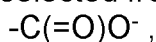
$R_{5^\wedge}$  to  $R_{8^\wedge}$ , each independently, has the meaning provided above for each of  $R_5$  to  $R_8$ , respectively;

with the proviso that :

- in said formula (IV), at least one of  $R_1$  to  $R_4$  is a group of formula (V),
- in said formula (IV\*), at least one of  $R_{1^\wedge}$  to  $R_{4^\wedge}$  is a group of formula (V)
- in said formula (V), one of  $R_{11}$  or  $R_{12}$  and one of  $R_{13}$  to  $R_{15}$ , is a group of formula (VI),

- in said formula (VI), when a, b, c and f are all different from 0, the recurring units (A), (B), (E) and (F) are statistically distributed;
  - and
  - optionally, at least one fourth block [block (4)] comprising a PFPE chain;
- with the proviso that, in copolymer (P):
- the sum of (m+f) is at least 1, preferably from 1 to 100; and
  - when present, said at least one block (1), said at least one block (2), said at least one block (3) and said at least one block (4) are statistically distributed.

Claim 15. The copolymer (P°) according to Claim 14, wherein in block (2), X is selected from:

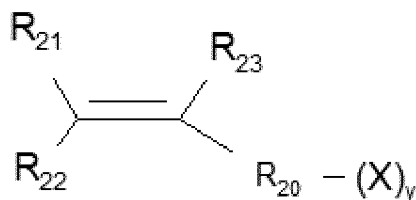


each being salified with at least one inorganic metal salt or with at least one organic group preferably selected from ammonium or phosphonium.

Claim 16. A process [process (P°)] for manufacturing copolymer (P°) as defined in any one of Claims 1 to 6, wherein process (P) comprises the steps of:

(a) contacting:

- at least one perfluoropolyether polymer comprising at least one peroxidic group [PFPE peroxy];
- at least one perfluorinated compound of formula (X-p):



(X-p)

wherein

each of R<sub>21</sub> to R<sub>23</sub> is independently -F or perfluorinated linear or branched alkyl chain having from 1 to 6 carbon atoms,

R<sub>20</sub> and y are as defined above for formula (III) and

X is selected from :

(X-a) a group of formula: -OP(=O)(OH)<sub>2</sub>, -OS(=O)<sub>2</sub>OH, -S(=O)<sub>2</sub>OH

(X-b) a group of formula: -S(=O)<sub>2</sub>F

(X-c) a group of formula: -COF, -C(=O)OH or -CN

and:

- optionally, at least one compound [compound (O)] selected in the group comprising, preferably consisting of:

(i) hydrogenated olefin comprising from 2 to 15 carbon atoms, partially or fully halogenated olefin comprising from 2 to 15 carbon atoms;

(ii) CF<sub>2</sub>=CFOR<sub>f</sub>,

wherein

R<sub>f</sub> is a C<sub>1</sub>-C<sub>6</sub> (per)fluoroalkyl group, preferably -CF<sub>3</sub>, -C<sub>2</sub>F<sub>5</sub>, -C<sub>3</sub>F<sub>7</sub>; a group C<sub>1</sub>-C<sub>12</sub> [(per)fluoro]-oxyalkyl comprising catenary oxygen atoms, preferably

perfluoro-2-propoxypropyl group;

(iii)  $\text{CF}_2=\text{CFOCF}_2\text{OR}_{f2}$

wherein

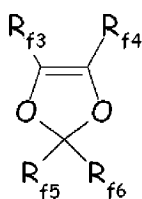
$R_{f2}$  is selected from the group consisting of C<sub>1</sub>-C<sub>6</sub> perfluoro-alkyls; C<sub>5</sub>-C<sub>6</sub> cyclic perfluoro-alkyls, and C<sub>2</sub>-C<sub>6</sub> perfluoro-oxy-alkyls, comprising at least one catenary oxygen atom, preferably  $R_{f2}$  is  $-\text{CF}_2\text{CF}_3$ ,  $-\text{CF}_2\text{CF}_2\text{OCF}_3$ , or  $-\text{CF}_3$ ;

(iv)  $\text{CF}_2=\text{CFCF}_2\text{OR}_{f7}$

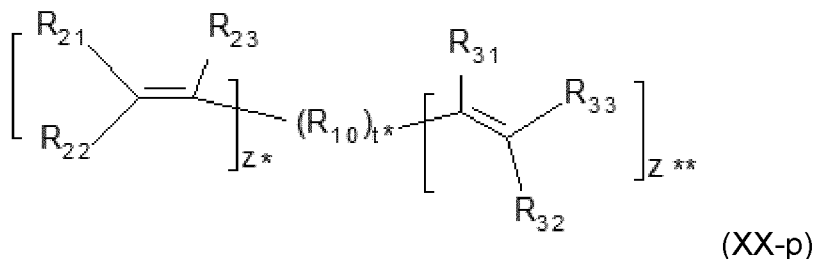
wherein

$R_{f7}$  is selected from the group consisting of C<sub>1</sub>-C<sub>6</sub> perfluoro-alkyls, C<sub>5</sub>-C<sub>6</sub> cyclic perfluoro-alkyls, and C<sub>2</sub>-C<sub>6</sub> perfluoro-oxy-alkyls, comprising at least one catenary oxygen atom;

(v) perfluorodioxoles having formula :



wherein each of  $R_{f3}$ ,  $R_{f4}$ ,  $R_{f5}$ ,  $R_{f6}$ , equal to or different from each other, is independently selected from the group consisting of fluorine atom and C<sub>1</sub>-C<sub>6</sub> perfluoroalkyl groups, optionally comprising one or more than one oxygen atom, such as notably  $-\text{CF}_3$ ,  $-\text{C}_2\text{F}_5$ ,  $-\text{C}_3\text{F}_7$ ,  $-\text{OCF}_3$ ,  $-\text{OCF}_2\text{CF}_2\text{OCF}_3$ ; and/or - optionally, at least one perfluorinated compound of formula (XX-p):



wherein

each of  $R_{21}$  to  $R_{23}$  are as defined above in formula (X-p),

each of  $R_{31}$  to  $R_{33}$  is independently -F or perfluorinated alkyl group having from 1 to 6 carbon atoms,

$R_{10}$  is an oxygen atom, a perfluorinated alkyl chain comprising from 1 to 24 carbon atoms, optionally interrupted by at least one oxygen atom,

$t$  is zero or 1;

each of  $z^*$  and  $z^{**}$  is independently 1 or 2; and

(b) reacting said PFPE peroxy, said at least one compound of formula (X-p), optionally said at least one compound of formula (XX-p) and optionally at least one compound (O), in the presence of UV radiation or under heating; and

\* when in formula (X-p) above, X is (X-a) a group of formula:  $-\text{OP}(=\text{O})(\text{OH})_2$ ,  $-\text{OS}(=\text{O})_2\text{OH}$ ,  $-\text{S}(=\text{O})_2\text{OH}$ , a step (c1) of salifying such group with at least one compound containing an inorganic metal, an ammonium or a phosphonium group;

\* when in formula (X-p) above, X is (X-b) a group  $-\text{S}(=\text{O})_2\text{F}$ , a step (c2) of hydrolysis to provide group  $-\text{S}(=\text{O})_2\text{O}^-$ ;

\* when in formula (X-p) above, X is (X-c) a group of formula:  $-\text{COF}$ ,  $-\text{C}(=\text{O})\text{OH}$

or -CN, at least one of the following steps:  
(c°-3) hydrolysis of group -COF to provide group -COOH, followed by a step of salifying said group -COOH to provide group -COO<sup>-</sup>;  
(c°-4) salifying said group -COOH to provide group -COO<sup>-</sup>; or  
(c°-5) hydrolysis of group -CN to provide group -COO<sup>-</sup>.

# INTERNATIONAL SEARCH REPORT

International application No  
**PCT/EP2024/050486**

**A. CLASSIFICATION OF SUBJECT MATTER**  
**INV. C08G65/00 C08G65/38 C10M157/04**  
**ADD.**

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)  
**C08G C08F C10M C10N**

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 practicable, search terms used)  
**EPO-Internal, CHEM ABS Data**

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
<b>A</b>	<b>US 6 403 539 B1 (MARCHIONNI GIUSEPPE [IT] ET AL) 11 June 2002 (2002-06-11) claims 1,2,7,13 example 1</b> -----	<b>1-16</b>
<b>A</b>	<b>US 6 896 996 B2 (AUSTMONT S P A [IT]) 24 May 2005 (2005-05-24) claims 1,6,17 examples 1A,1B</b> -----	<b>1-16</b>
<b>A</b>	<b>US 2011/230631 A1 (MARCHIONNI GIUSEPPE [IT] ET AL) 22 September 2011 (2011-09-22) cited in the application claim 1; example 1</b> -----	<b>1-16</b>
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Further documents are listed in the continuation of Box C.       See patent family annex.

\* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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</p> <p>"&amp;" document member of the same patent family</p>
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Date of the actual completion of the international search  <b>16 April 2024</b>	Date of mailing of the international search report  <b>06/05/2024</b>
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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  <b>O'Sullivan, Timothy</b>
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## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2024/050486

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO 2019/048394 A1 (SOLVAY SPECIALTY POLYMERS IT [IT]) 14 March 2019 (2019-03-14) claim 1 PREPARATIVE EXAMPLE 1 AND WORKING EXAMPLE 2; paragraph [0073] - paragraph [0083] -----</p>	1-16
A	<p>WO 2017/012909 A1 (SOLVAY SPECIALTY POLYMERS IT [IT]) 26 January 2017 (2017-01-26) paragraph [0086] - paragraph [0092] tables 1,2 -----</p>	1-16
A	<p>WO 2022/078766 A1 (SOLVAY SPECIALTY POLYMERS IT [IT]) 21 April 2022 (2022-04-21) claim 1; example 1 -----</p>	1-16

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Information on patent family members

International application No

**PCT/EP2024/050486**

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