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(71) Applicant: SOLVAY SPECIALTY POLYMERS
ITALY S.P.A. [IT/IT]; Viale Lombardia, 20, 20021 Bollate
(MILANO) (IT).

(72) Inventors: TONELLI, Claudio Adolfo Pietro; 5 Via
G. Verdi, 23877 PADERNO D'ADDA (LECCO) (IT).
WLAŠSICS, Ivan Diego; 86/7 Via Cavour, 12075
GARESSIO (CN) (IT). MARCHIONNI, Giuseppe; 8, Via
Antonio Vallisneri, 20133 MILANO (MI) (IT).

(74) Agent: BENVENUTI, Federica et al.; Rue de Ransbeek,
310, 1120 BRUXELLES (BE).

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(54) Title: FLUORINATED POLYMERS AND USES THEREOF

(57) Abstract: The present invention relates to fluorinated polymers, in particular to (per)fluoropolyethers to be used as lubricants or as additives for (per)fluorinated oils or greases.



Fluorinated polymers and uses thereof

Cross-reference to related patent applications

[0001] This application claims priority to European patent application No. 17161754.1, filed on March 20th, 2017, the whole content of this application being incorporated herein by reference for all purposes.

Technical Field

[0002] The present invention relates to fluorinated polymers, in particular to (per)fluoropolyethers to be used as lubricants or as additives for (per)fluorinated oils or greases.

Background Art

[0003] Lubricating oils and greases based on (per)fluoropolyethers are usually endowed with high thermal stability; however, when they are heated for prolonged times at temperatures higher than 230°C, partial or total degradation of the polymer chain and formation of volatile compounds occurs; this degradation is usually accompanied by the formation of Lewis acids, due to corrosion of the metallic parts in contact with the lubricant and Lewis acids further increase lubricant degradation.

[0004] In order to improve the thermal stability of fluorinated oils, additives may be used, which are typically chosen from fluorinated polymers bearing at one or both ends of the polymer chain non fluorinated aromatic groups that may contain heteroatoms, such as nitrogen and phosphorus. However, the synthesis of these additives is in some instances troublesome. Furthermore, certain non-fluorinated end groups are linked to the polymer chain through moieties like -CH₂OCH₂-, -CH₂(OCH₂CH₂)_mO-, -C(O)O- and -C(O)N(R), which undergo degradation under severe conditions.

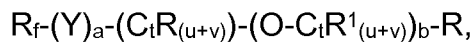
[0005] EP 1354932 A (SOLVAY SOLEXIS S.P.A.) discloses stabilizing additives having a (per)fluoropolyether chain with nitro-containing phenyl end groups, which are linked to the (per)fluoropolyether chain through a moiety

of formula $-\text{CH}_2\text{O}-$ or via an ester group $-\text{C}(=\text{O})\text{O}-$. However, these additives undergo phase separation upon storage at room temperature.

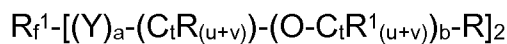
[0006] **US 2007049502** (E.I. DUPONT DE NEMOURS AND COMPANY)

discloses compositions to be used as lubricants or lubricant additives which comprise mono- and/or *bi*-functional aryl perfluoropolyethers.

[0007] The monofunctional aryl perfluoropolyether complies with formula:



while the difunctional aryl perfluoropolyether complies with formula:



wherein:

R_f and R_f^1 are respectively a monovalent or divalent straight or branched (per)fluoropolyether chain having formula weight from about 400 to 15,000:

Y is a divalent radical selected from a group which comprises, *inter alia*, $-\text{CH}_2\text{O}-$ and $-\text{CF}_2-$;

a is 0 or 1;

$(\text{C}_t\text{R}_{(u+v)})_t$ is a divalent aryl group;

$(\text{O}-\text{C}_t\text{R}^1_{(u+v)})_b$ is a divalent aryloxy group;

R is selected from a group comprising hydrogen and nitro groups, but it cannot be solely hydrogen or nitro or combinations thereof;

each R^1 is selected from a group which comprises hydrogen and nitro groups;

t is equal to $6 + u$;

u is any combinations of 0, 2, 4, 6, 8, 10, 12, 14, 16;

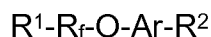
v is independently 2 or 4;

b is 0-5.

[0008] All eighteen examples of this prior art document relate to the synthesis of monofunctional aryl derivatives of branched (per)fluoropolyethers comprising $(\text{OCF}(\text{CF}_3)\text{CF}_2)$ units wherein an aryl group (namely a phenyl group) or an aryloxyaryl (namely a phenoxyphenyl) group is linked to the R_f chain via a $-\text{CF}_2-$ moiety. Examples 7 and 8 relate to phenoxyphenyl derivatives and example 8 in particular discloses the preparation of a

nitrodiphenyl ether derivative by nitration of the diphenylether derivative of example 7, whereby a nitro group is inserted on the phenoxy group.

[0009] **US 5104559** (DOW CHEMICAL CO.) discloses lubricating compounds of formula:



wherein:

R^1 is, *inter alia*, perfluoroalkoxy;

R_f is a perfluoroalkyl chain from 2 to 10 carbon atoms;

Ar is, *inter alia*, a biphenyl radical and R^2 is, *inter alia*, a nitro group.

The lubricants of formula $R^1-R_f-O-Ar-R^2$ can be manufactured according to a procedure comprising the base-catalysed addition of hydroxy-substituted aryl compounds to terminal perfluoroolefins. This document does not contain any hint or suggestion that would have prompted a skilled person to replace the perfluoroalkyl chain R_f with a (per)fluoropolyether chain and to select aromatic moieties comprising two aromatic rings linked together via a ketone or sulfone group.

[0010] **US 4941987** (AUSIMONT S.P.A.) discloses mono- or difunctional (per)fluoropolyether derivatives having an average molecular weight ranging from 1,500 to 10,000 to be used as lubricating greases which comply with formula:



wherein:

R is a perfluoroalkyl radical or $Z-(Y)_n-CFX-$;

Q is a perfluoroalkyl polyether chain or a fluoroalkyl polyether chain;

X is fluorine or trifluoromethyl;

Y is a linking divalent radical which comprises $-CH_2O-$ and $-CF_2-$;

n is 0 or 1;

and Z can be an aromatic radical containing 6 to 10 carbon atoms and optionally substituted with one or more nitro groups. The sole specifically disclosed compound wherein Z bears a nitro group are those of examples 1 and 3, in which Z is p-nitrophenyl.

[0011] **WO 2013/120827** (SOLVAY SPECIALTY POLYMERS ITALY S.P.A.) discloses (per)fluoropolyether compounds comprising a

(per)fluoropolyether chain (R_f) having two chain ends, wherein at least one of said chain ends have a *bi* or *ter*-phenyl group bearing at least one nitro group and, optionally, one or more further substituents, wherein the two or three phenyl groups are linked each other via a sigma bond. This document does not contain any hint or suggestion that would have prompted a skilled person to replace the perfluoroalkyl chain R_f with a (per)fluoropolyether chain and to select aromatic moieties comprising two aromatic rings linked together via a ketone or sulfone group.

Summary of invention

- [0012] The Applicant perceived that despite the efforts made in the art, the need of providing polymers to be used as lubricants or additives for fluorinated oils or greases that are stable at very high temperatures and that can be manufactured in a convenient way, still exists. In particular, the Applicant noted that the compounds disclosed in **WO 2013/120827** (SOLVAY SPECIALTY POLYMERS ITALY S.P.A.) cited above are prepared via a synthesis that proceeds via Suzuki reaction: this synthesis is not convenient on industrial scale as it comprises the use of a boron derivative that is a very expensive reactant.
- [0013] Facing the above problem, the Applicant found that the above problem can be solved by the polymer(s) according to the present invention, i.e. polymer(s) [polymer (P)] comprising at least one (per)fluoropolyether chain [chain (R_{pf})] and at least one group [group (A)] comprising two phenyl rings, wherein at least one of said phenyl rings bears at least one nitro group and wherein said two phenyl rings are linked together via a bridging group [group (T)] selected from $-C(=O)-$ and $-S(=O)_2-$.
- [0014] Advantageously, the Applicant found that polymer (P) according to the present invention can be manufactured via a very convenient and easy synthetic process that comprises a step [step (I)] of contacting
- at least one (per)fluoropolyether polymer [polymer (P_{OH})] comprising at least one chain (R_{pf}) having two chain ends, wherein at least one chain end bears at least one hydroxy group and
 - at least one compound [compound (A)] comprising two phenyl rings,

wherein at least one of said phenyl rings bears at least one leaving group for nucleophilic substitution reaction [group (L_N)] and one nitro group at the ortho position of said group (L_N), and wherein said two phenyl rings are linked together via a bridging group [group (T)] selected from $-C(=O)-$ and $-S(=O)_2-$.

- [0015] The Applicant surprisingly found that the above process can be easily modulated in order to provide polymer (P) having a wide range of weight average molecular weight (Mw), such as from 1,000 to 10,000 g/mol, more preferably from 1,5800 to 8,000 g/mol.
- [0016] More in particular, the Applicant found that with the process of the invention, polymers (P^*) are provided comprising one (per)fluoropolyether chain (R_{pf}) and at least one group (A) as defined above.
- [0017] According to a preferred embodiment, said polymer (P^*) can be used as additives for fluorinated oils and greases, notably as stabilizers against thermooxidation.
- [0018] In addition, the Applicant found that with the process of the invention, polymers (P^{**}) are provided comprising at least two (per)fluoropolyether chains (R_{pf}) and at least three groups (A) as defined above.
- [0019] According to a preferred embodiment, said polymer (P^{**}) can be used as oil, without the need of being added with additives, such as notably thermal-stabilizers, anti-corrosion or anti rust additives, which could give raise to separation after exposure at harsh environment, at high temperatures and in the presence of metals and Lewis acids. However, said polymer (P^{**}) can be also used as additive for fluorinated oils and greases having different chemical formula, notably for perfluoropolyether polymers.
- [0020] Without being bound by any theory, the Applicant is of the opinion that group(s) (A) is(are) responsible for the stabilizing properties, in particular due to the presence of the electro-withdrawing substituent (i.e., the nitro group).

Description of embodiments

[0021] 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 “(per)fluoropolyether” and, when used as substantive, is intended to mean either the singular or the plural form, depending on the context;
- the term “(per)fluoropolyether” is intended to indicate fully or partially fluorinated polymer;
- the expression “ortho position” referred to the group comprising two phenyl rings [group (A)] is intended to indicate the carbon atom of one of the phenyl rings, said carbon atom being adjacent to the carbon atom of the same phenyl ring linked to chain (R_{pf});
- the expression “strong non-nucleophilic base” is intended to indicate a base that does not act as a nucleophile, for example because of its steric hindrance (also referred to as steric bulky);
- the terms “hindrance” and “bulky” are intended as synonyms.

[0022] Preferably, said chain (R_{pf}) is a chain of formula $-(CFX)_aO(R_f)(CFX')_b-$, wherein

a and b, equal or different from each other, are equal to or higher than 1, preferably from 1 to 10, more preferably from 1 to 3;

X and X', equal or different from each other, are -F or -CF₃,

provided that when a and/or b are higher than 1, X and X' are -F;

(R_f) comprises, preferably consists of, repeating units R° , said repeating units being independently selected from the group consisting of:

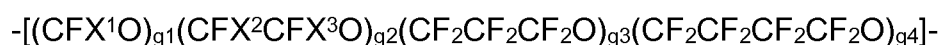
- (i) -CFXO-, wherein X is F or CF₃;
- (ii) -CFXCFXO-, wherein X, equal or different at each occurrence, is F or CF₃, with the proviso that at least one of X is -F;
- (iii) -CF₂CF₂CW₂O-, wherein each of W, equal or different from each other, are F, Cl, H;
- (iv) -CF₂CF₂CF₂CF₂O-;
- (v) -(CF₂)_j-CFZ-O- wherein j is an integer from 0 to 3 and Z is a group of

general formula $-O-R_{(f-a)}-T$, wherein $R_{(f-a)}$ is a fluoropolyoxyalkene chain comprising a number of repeating units from 0 to 10, said recurring units being chosen among the following : $-CFXO-$, $-CF_2CFXO-$, $-CF_2CF_2CF_2O-$, $-CF_2CF_2CF_2CF_2O-$, with each of each of X being independently F or CF_3 and T being a C_1 - C_3 perfluoroalkyl group.

[0023] More preferably, a and b, equal or different from each other, are from 1 to 10, even more preferably from 1 to 3.

[0024] Preferably, chain (R_f) complies with the following formula:

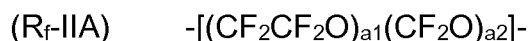
(R_f -I)



wherein

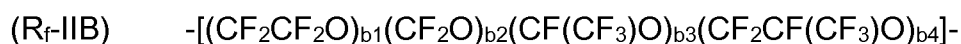
- X^1 is independently selected from $-F$ and $-CF_3$,
- X^2 , X^3 , equal or different from each other and at each occurrence, are independently $-F$, $-CF_3$, with the proviso that at least one of X is $-F$;
- g_1 , g_2 , g_3 , and g_4 , equal or different from each other, are independently integers ≥ 0 , such that $g_1+g_2+g_3+g_4$ is in the range from 2 to 300, preferably from 2 to 100; should at least two of g_1 , g_2 , g_3 and g_4 be different from zero, the different recurring units are generally statistically distributed along the chain.

[0025] More preferably, chain (R_f) is selected from chains of formula:



wherein:

- a_1 and a_2 are independently integers ≥ 0 such that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000 (as determined by NMR).; both a_1 and a_2 are preferably different from zero, with the ratio a_1/a_2 being preferably comprised between 0.1 and 10;



wherein:

- b_1 , b_2 , b_3 , b_4 , are independently integers ≥ 0 such that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000 (as determined by NMR); preferably b_1 is 0, b_2 , b_3 , b_4 are > 0 , with the ratio $b_4/(b_2+b_3)$ being ≥ 1 ;



wherein:

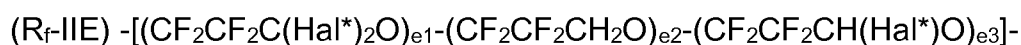
$cw = 1$ or 2 ;

$c1$, $c2$, and $c3$ are independently integers ≥ 0 chosen so that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000 (as determined by NMR); preferably $c1$, $c2$ and $c3$ are all > 0 , with the ratio $c3/(c1+c2)$ being generally lower than 0.2;



wherein:

d is an integer > 0 such that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000 (as determined by NMR);

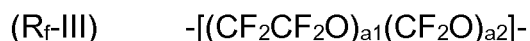


wherein:

- Hal^* , equal or different at each occurrence, is a halogen selected from fluorine and chlorine atoms, preferably a fluorine atom;

- $e1$, $e2$, and $e3$, equal to or different from each other, are independently integers ≥ 0 such that the $(e1+e2+e3)$ sum is comprised between 2 and 300.

[0026] 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 10,000, preferably between 400 and 5,000 (as determined by NMR), with the ratio $a1/a2$ being generally comprised between 0.1 and 10, more preferably between 0.2 and 5.

[0027] According to a preferred embodiment, said chain (R_{pf}) is linked to said at least one group (A) via a linking group [group (L)].

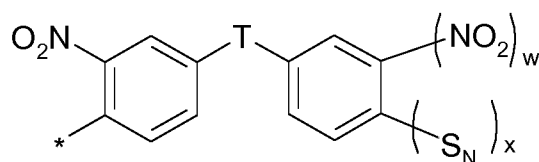
[0028] Preferably, said group (L) is a divalent alkyl chain comprising from 1 to 20, more preferably from 1 to 10, carbon atoms and at least one oxygen atom.

[0029] More preferably, said group (L) is a chain of formula $-CH_2O-$ or $-CH(CF_3)O-$.

[0030] Said at least one group (A) can be a monovalent group or a divalent group. Without being bounded by any theory, monovalent group (A) is typically a group located at the end of the polymeric chain, while divalent group (A) typically links two chains (R_{pf}).

Preferably, said monovalent group (A) complies with the following formula (A-I):

(A-I)



wherein

T is $-C(=O)-$ or $-S(=O)_2-$;

S_N is selected from halogen atom, triflate, nonaflate and group $-OR_1$, wherein R_1 is an optionally halogenated, more preferably optionally fluorinated, alkyl chain comprising from 1 to 6 carbon atoms;

w and x are, each independently, zero or 1; and

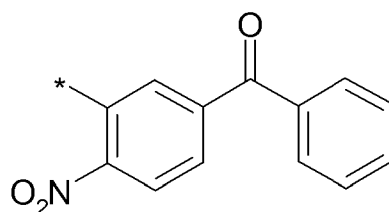
the symbol * indicates the bond with group (L) as defined above.

[0031] More preferably, L_N is halogen atom selected from fluorine or chlorine, even more preferably fluorine, or $-OR_1$, wherein R_1 is a partially fluorinated alkyl chain comprising from 1 to 3 carbon atoms.

[0032] It will be apparent to those skilled in the art that when w and/or x is/are zero, the corresponding carbon atom(s) bear(s) a hydrogen atom.

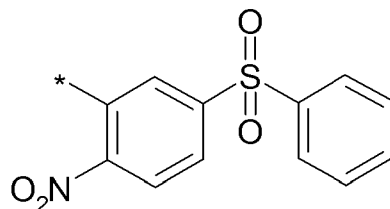
[0033] More preferably, said monovalent group (A) complies with the following formulae (A-I-i) to (A-I-vi):

(A-I-i)

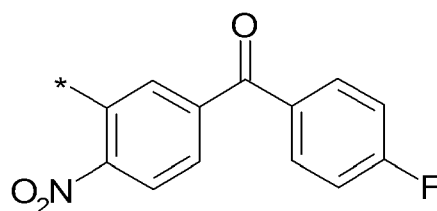


(A-I-ii)

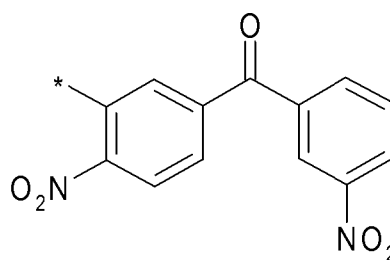
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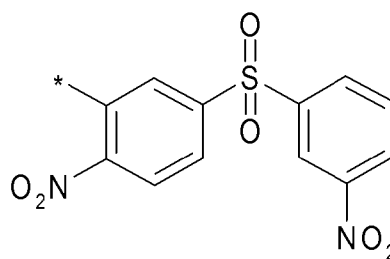
(A-I-iii)



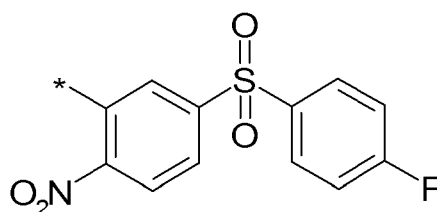
(A-I-iv)



(A-I-v)

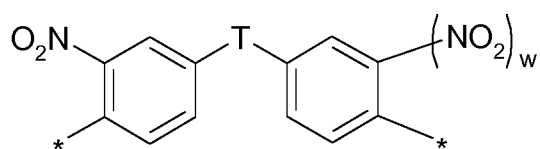


(A-I-vi)



[0034] Preferably, said divalent group (A) complies with the following formula (A-II):

(A-II)

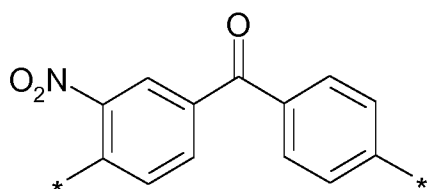


wherein

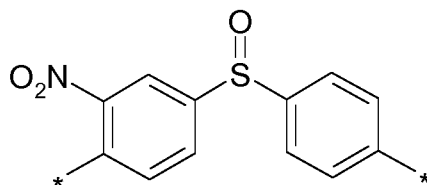
T and w have the same meanings as in formula (A-I) and each symbol * indicates the bond with one group (L) as defined above.

[0035] More preferably, said divalent group (A) complies with the following formulae (A-II-i) to (A-II-iv):

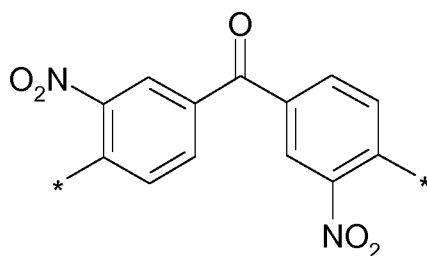
(A-II-i)



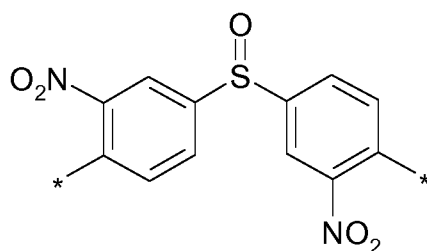
(A-II-ii)



(A-II-iii)



(A-II-iv)



[0036] According to a preferred embodiment, polymer (P*) is mono-functional, i.e. it comprises one chain (R_{pf}) having two chain ends, wherein one chain end comprises said monovalent group (A-I) as defined above, and the other

chain end comprises a (per)fluorinated alkyl group comprising from 1 to 3 carbon atoms.

[0037] According to a more preferred embodiment, polymer (P*) is bi-functional, i.e. it comprises one chain one chain (R_{pf}) having two chain ends, wherein both chain ends comprise said monovalent group (A-I) as defined above.

[0038] According to another preferred embodiment, said polymer (P**) comprises at least two chains (R_{pf}) each having two chain ends, wherein said chains (R_{pf}) are linked together at one chain ends by one divalent group (A) as defined above and said chains (R_{pf}) bear on the other chain end one monovalent group (A) as defined above.

[0039] According to a more preferred embodiment, said polymer (P**) complies with the following general formula:



wherein

each (A^*) is a group of formula (A-I) as defined above,

(A^{**}) is a group of formula (A-II) as defined above,

each L corresponds to group (L) as defined above,

(R_{pf}) corresponds to chain (R_{pf}) as defined above, and

z is an integer from 1 to 10.

[0040] Preferably, polymer (P_{OH}) is a (per)fluoropolyether polymer comprising one chain (R_{pf}) as defined above for polymer (P) having two chain ends, wherein at least one chain end bears one hydroxy group.

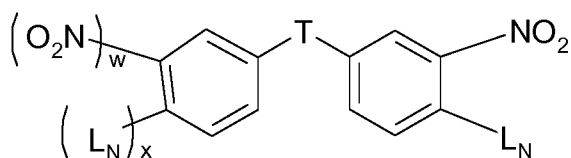
[0041] Preferably, said polymer (P_{OH}) comprises one chain (R_{pf}) as described above for polymer (P).

[0042] More preferably, said polymer (P_{OH}) comprises one chain (R_{pf}) having two chain ends, wherein at least one chain end bears one hydroxy group.

According to a preferred embodiment, both chain ends of said chain (R_{pf}) bear one hydroxy group.

[0043] Good results have been obtained within the present invention starting from (per)fluoropolyether polymers commercially available from Solvay Specialty Polymers Italy S.p.A. under the tradename Fomblin®.

- [0044] Preferably, said at least one group (L_N) is selected from halogen atom, triflate and nonaflate. More preferably, said group (L_N) is a halogen atom selected from fluorine or chlorine. Fluorine is particularly preferred.
- [0045] More preferably, said compound (A) bears two groups (L_N), as defined above.
- [0046] According to preferred embodiment, said compound (A) complies with the following chemical formula ($A^{\wedge}$):
- ($A^{\wedge}$)



wherein

T is $-C(=O)-$ or $-S(=O)_2-$,

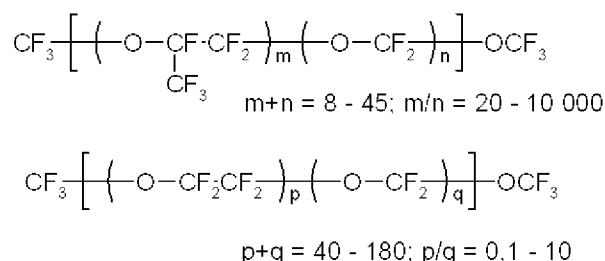
L_N has the same meanings defined above for group (L_N);

w and x are, each independently, zero or 1.

- [0047] Said compound (A) can be contacted with said polymer (P_{OH}) as such, or it can be first dissolved in an optionally fluorinated inorganic aprotic solvent [solvent (S)] and then contacted with said polymer (P_{OH}).
- [0048] Said solvent (S) is preferably selected in the group comprising halogenated solvents, such as fluorinated solvents.
- [0049] Suitable examples of fluorinated solvents are halogenated hydrocarbons, hexafluoroxylene, chlorotrifluorotoluene, trifluorotoluene, hexafluorobenzene and mixtures thereof.
- [0050] According to a preferred embodiment, said step (I) is performed in the presence of a strong non-nucleophilic base, which is preferably selected from elements belonging to Group Ia of the periodic table, such as sodium and potassium metals; bulky alcoholates, such as potassium tert-butanolate and potassium neopentanolate; and bulky amines, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).
- [0051] Good results have been obtained using potassium tert-butanolate.
- [0052] Preferably, said step (I) is performed in the presence of a molar excess of said base compared to the molar amount of the polymer (P_{OH}).

- [0053] Preferably, said step (I) is performed under heating. More preferably, heating is performed at a temperature of from 40°C up to the reflux temperature of the base used in the reaction.
- [0054] Polymers (P) of the present invention are endowed with lubricant properties and are stable at very high temperatures; therefore, they can be conveniently used as base oils or as thermal stabilizers for the preparation of lubricant compositions in the form of oils or greases.
- [0055] Thus, a further object of the present invention is represented by lubricant compositions in the form of greases or oils comprising at least one polymer (P) according to the present invention.
- [0056] It is generally understood that oils are compounds having kinematic viscosity (ASTM D445) at 40°C of from 30 to 30 000 cSt; greases are derived from such oils by addition of suitable thickeners, such as notably polytetrafluoroethylene (PTFE) or inorganic compounds, e.g. talc.
- [0057] Generally, the lubricant compositions according to the present invention will have a kinematic viscosity in the above mentioned conditions of 30 to 3,000 cSt, preferably from 50 to 500 cSt, when determined at 20°C according to ASTM D445.
- [0058] According to a first preferred embodiment, lubricant compositions in the form of oils [compositions (C1)] containing at least one polymer (P), even more preferably at least one polymer (P*) as defined above, as thermal stabilizers, comprise (preferably consist of):
- (i) at least one polymer (P) as defined above, preferably in an amount ranging from 0.01 % to 20% wt., based on the total weight of said composition (C1) and
 - (ii) one or more base oils, preferably in an amount ranging from 80% to 99.99% wt. based on the total weight of said composition (C1).
- [0059] Said composition (C1) can optionally contain further ingredients.
- [0060] Suitable further ingredients are selected from thickening agents, preferably in an amount ranging from 1% to 30% wt. based on the total weight of said composition (C1) and further additives, each additive being used in an amount ranging from 1% to 5% wt based on the total weight of said composition (C1).

[0061] Base oils may be fluorinated or non-fluorinated (hydrogenated) oils or mixtures thereof. Preferably, fluorinated oils are (per)fluoropolyether oils; examples of (per)fluoropolyether oils (iii) suitable for the preparation of the compositions (C1) are those identified as formulae (1a) – (8a) in **EP 2089443 A** (SOVLAY SOELXIS S.P.A.) or as formulae (1) – (8) in **WO 2009/141284** (SOLVAY SOLEXIS S.P.A.) or as formulae (1) to (9) in **WO 2011/042374** (SOLVAY SOLEXIS S.P.A.) . More preferably, the (per)fluoropolyether oils are those commercially available under the trade name FOMBLIN® (type Y, M, W, or Z) from Solvay Specialty Polymers Italy S.p.A.; such oils generally comprise at least one oil (i.e. only one or mixture of more than one oil) complying with either of formulae herein after:



[0062] One or more polymer (P**) according to the present invention different from the one using as ingredient (i) can also be used as fluorinated base oil (ii) in compositions (C1); for example, if one polymer (P*) is used as ingredient (i), one or more polymer (P**) can be used as ingredient (ii).

[0063] Suitable non fluorinated oils to be used as base oils in compositions (C1) are preferably selected from mineral, paraffinic, aromatic oils, polyalphaolefins, alkyl esters, silicone esters, naphthalene derivatives, polyalkylated cycloalkanes, polyphenylethers.

[0064] According to a second preferred embodiment, lubricant compositions in the form of greases [compositions (C2)] containing at least one polymer (P) according to the invention comprise (preferably consists of):
(i*) at least one polymer (P**) as defined above, preferably in an amount ranging from 50% to 90% wt.;

(iii*) one or more thickening agent, preferably in an amount ranging from 10 % to 50% wt. and;

(iv*) optionally, one or more additives.

[0065] Examples of suitable thickening agents are PTFE, talc, silica, boron nitride, polyurea, alkali or alkali-earth metals terephthalate, calcium and lithium soaps and complexes thereof; among them, PTFE is preferred.

[0066] Examples of suitable additives are antirust agents, antioxidants, thermal stabilizers, pour point depressants, anti-wear agents, including those for high pressures, dispersants, tracers, dyestuffs, talc and inorganic fillers. Examples of dispersants are, for example, surfactants, preferably non-ionic surfactants, more preferably (per)fluoropolyether surfactants and (per)fluoroalkyl surfactants. Examples anti-wear additives are phosphazene derivatives of (per)fluoropolyethers, like those disclosed in EP 1336614 A (SOLVAY SOLEXIS S.P.A.) .

[0067] In a further embodiment, the present invention relates to a method for thermo-stabilizing fluorinated oils and greases, said method comprising contacting said fluorinated oil and grease with at least one polymer (P) as defined in the present invention.

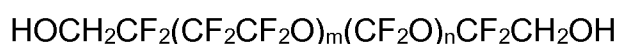
[0068] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

[0069] The invention will be disclosed in greater detail by means of the following experimental section.

Experimental section

[0070] Materials and Methods

[0071] The PFPE polymer precursors having the formula and properties as reported herein below were obtained by Solvay Specialty Polymers Italy S.p.A.:



(PFPE-I) $m/n = 1$; M_n (average numerical weight of chain R_f determined by ^{19}F -NMR analysis) = 1500; M_w = 1582 g/mol; EW = 863 g/eq.

(PFPE-II) $m/n = 1$; $M_n = 2000$; $M_w = 2150$ g/mol; $EW = 1131$ g/eq.

(PFPE-III) $m/n = 1$; $M_n = 3000$; $M_w = 3050$ g/mol; $EW = 1605$ g/eq.

(PFPE-IV) $m/n = 1$; $M_n = 4000$; $M_w = 4250$ g/mol; $EW = 2237$ g/eq.

[0072] The reagents and solvents were commercially available and were used without further purification.

[0073] The average number molecular weight (M_n) was determined by NMR (^{19}F -NMR and ^1H -NMR).

[0074] Examples 1 to 4 - Synthesis of polymers (P^*) having formula :



[0075] **Example 1 – Synthesis of polymer (P^*)**

wherein $R_f = (\text{CF}_2\text{CF}_2\text{O})_m(\text{CF}_2\text{O})_n$; $m/n = 1$; $M_n = 1500$

[0076] A round-bottomed glass reactor, equipped with a mechanical stirrer, a reflux condenser (the refrigerant liquid was Galden®HT-110 – obtained from Solvay Specialty Polymers Italy S.p.A.) with an inert gas (N_2) compensator on top, a dripping funnel and an internal thermometer, was charged with anhydrous PFPE-I (584 g; 369 mmols; 677 meq). The mechanical stirrer was turned on to about 300 rpm, the (PFPE-I) was heated to 45°C and a 9,56 w/v solution of tBuOK/tBuOH (795 ml; 677 mmol tBuOK) was dripped at a rate of 300 mmol/h. The temperature was raised to about 57°C and kept with stirring for 2 hours. The solution thus obtained was stripped with 90% v/v of tBuOH to obtain a clear to yellowish oil.

[0077] Then, 3-nitro-4-fluorobenzophenone (92% w/w NO_2 -Aromatic; 403 g; 147mols) was dissolved in hexafluoroxylene (HFX - 2000 mL) in about 1 hour at 50°C with mild stirring. A yellow homogeneous solution was obtained.

[0078] Then, the oil comprising the (PFPE-I) was dripped in the solution of 3-nitro-4-fluorobenzophenone at 75°C and at a rate of about 100 mmol/h with 300 rpm mechanical stirring. During the addition of (PFPE-I) the

internal reaction temperature was raised to about 110°C (the reflux temperature of residual t-BuOH in HFX) with 300 rpm mechanical stirring, for a total reaction time of 5 hours. A first aliquot of t-BuOK (203 mmol) was added with a solid dispenser in the crude reaction mixture at a rate of 400 mmol/h. A second aliquot t-BuOK (101 mmol) was added after 20 hrs of reaction time and a third aliquot (50 mmol) was added after 27 hrs of total reaction time. At this point, the termination of the end-capping reaction was aided by adding 10 mol% of the starting molar amount of 3-nitro-4-fluorobenzophenone (13 grams; 44.3 mmol; solid dispenser). The conversion of the pre-terminals was followed by ^{19}F -NMR.

[0079] The crude reaction mixture was first cooled to room temperature and then centrifuged (10000 rpm; 25°C; 60 min) in order to separate the residual solid particulates, comprising mainly unreacted t-BuOK and starting 3-nitro-4-fluorobenzophenone.

[0080] The centrifuged supernatant was transferred to a separatory funnel and was washed 2 times with aqueous 10% $\text{H}_3\text{O}^+\text{Cl}^-$ (1:0.5 v/v organic:water). The washing was considered completed when the final pH of the H_2O layer was below 3.

[0081] The washed crude mixture was then dried over MgSO_4 , filtered with 5 μm PTFE membrane, and the solvent evaporated first at 70°C and 0.1 mm Hg residual P (employing a Rotavapor) and then at 100°C and 0,07 P_{RES} with a mechanical pump in order to sublime most of the residual, unreacted 4-fluorobenzophenone as well as unreacted 3-nitro-4-fluorobenzophenone.

[0082] Isolated yield = 88 mol% of a dark viscous liquid

Average MW = 2026 g/mole.

EW = 1107 g/eq.

PFPE segment average MW = 1516 g/mole

[0083] **Example 2 – Synthesis of polymer (P^*)**

wherein $\text{R}_f = (\text{CF}_2\text{CF}_2\text{O})_m(\text{CF}_2\text{O})_n$; $m/n = 1$; $\text{M}_n = 2000$

[0084] The synthesis was performed as described in Example 1 starting from (PFPE-II).

[0085] Isolated yield = 85 mol% of a dark viscous liquid

Average MW = 2625 g/mol

EW = 1381 g/eq.

PFPE segment average MW = 2116 g/mol

[0086] **Example 3 – Synthesis of polymer (P*)**

wherein $R_f = (CF_2CF_2O)_m(CF_2O)_n$; $m/n = 1$; $M_n = 3000$

[0087] The synthesis was performed as described in Example 1 starting from (PFPE-III).

[0088] Isolated yield = 90 mol% of a dark viscous liquid

Average MW = 3523 g/mol

EW= 1854 g/eq.

PFPE segment average MW = 3016 g/mol

[0089] **Example 4 – Synthesis of polymer (P*)**

wherein $R_f = (CF_2CF_2O)_m(CF_2O)_n$; $m/n = 1$; $M_n = 4000$

[0090] The synthesis was performed as described in Example 1 starting from (PFPE-IV).

[0091] Isolated yield = 90 mol% of a dark viscous liquid

Average MW = 4658 g/mol

EW= 2451 g/eq.

PFPE segment average MW = 4150 g/mol

[0092] **Examples 5 to 8 - Synthesis of polymers (P*) having formula :**



[0093] **Example 5 – Synthesis of polymer (P*)**

wherein $R_f = (CF_2CF_2O)_m(CF_2O)_n$; $m/n = 1$; $M_n = 1500$

[0094] The synthesis was performed as described in Example 1 starting from (PFPE-I) and employing 3-Nitro-4-fluorobenzenesulfone.

[0095] Isolated yield = 87 mol% of a dark viscous liquid

Average MW = 2096 g/mol

EW= 1145 g/eq.

PFPE segment average MW = 1145 g/mol

[0096] Example 6 – Synthesis of polymer (P*)

wherein $R_f = (CF_2CF_2O)_m(CF_2O)_n$; $m/n = 1$; $M_n = 2000$

[0097] The synthesis was performed as described in Example 1 starting from (PFPE-II) and employing 3-Nitro-4-fluorobenzosulfone.

[0098] Isolated yield = 85 mol% of a dark viscous liquid

Average MW = 2696 g/mol

EW= 1418 g/eq.

PFPE segment average MW = 2116 g/mol

[0099] Example 7 – Synthesis of polymer (P*)

wherein $R_f = (CF_2CF_2O)_m(CF_2O)_n$; $m/n = 1$; $M_n = 3000$

[00100] The synthesis was performed as described in Example 1 starting from (PFPE-III) and employing 3-Nitro-4-fluorobenzosulfone.

[00101] Isolated yield = 90 mol% of a dark viscous liquid

Average MW = 3596 g/mol

EW= 1892 g/eq.

PFPE segment average MW = 3016 g/mol

[00102] Example 8 – Synthesis of polymer (P*)

wherein $R_f = (CF_2CF_2O)_m(CF_2O)_n$; $m/n = 1$; $M_n = 4000$

[00103] The synthesis was performed as described in Example 1 starting from (PFPE-IV) and employing 3-Nitro-4-fluorobenzosulfone.

[00104] Isolated yield = 90 mol% of a dark viscous liquid

Average MW = 4730 g/mol

EW= 2489 g/eq.

PFPE segment average MW = 4150 g/mol.

[00105] Examples 9 and 10 - Synthesis of polymers (P*) having formula :**[00106] Example 9 – Synthesis of polymer (P*)**

wherein $R_f = (CF_2CF_2O)_m(CF_2O)_n$; $m/n = 1$; $M_n = 3000$

[00107] The synthesis was performed as described in Example 1 starting from (PFPE-III) and employing 3-nitro-4,4'-difluorobenzophenone.

[00108] Isolated yield = 86 mol% of a dark viscous liquid

Average MW = 3664 g/mol

EW= 1928 g/eq.

[00109] PFPE segment average MW = 3116 g/mol.

[00110] **Example 10 – Synthesis of polymer (P*)**

wherein $R_f = (CF_2CF_2O)_m(CF_2O)_n$; $m/n = 1$; $M_n = 2000$

[00111] The synthesis was performed as described in Example 1 starting from (PFPE-II) and employing 3-nitro-4,4'-difluorobenzophenone.

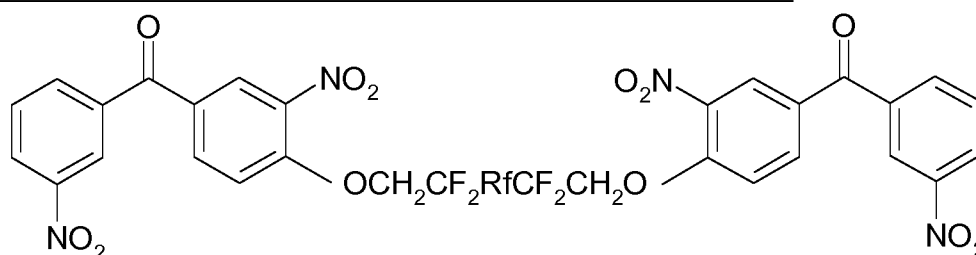
[00112] Isolated yield = 87 mol% of a dark viscous liquid

Average MW = 2736 g/mol

EW= 1440 g/eq.

[00113] PFPE segment average MW = 2116 g/mol.

[00114] **Example 11 - Synthesis of polymer (P*) having formula :**



wherein $R_f = (CF_2CF_2O)_m(CF_2O)_n$; $m/n = 1$; $M_n = 4000$

[00115] A round-bottomed glass reactor, equipped with a mechanical stirrer, a reflux condenser (Galden® HT-110 as the refrigerant liquid), an internal thermometer, a trap composed of 2 drexels placed in series (one charged with NaOH in pellets and one empty) and dripping funnel, was charged with 4-fluorobenzophenone (734 mmols, 146 g) and was melted at 120°C under a static inert atmosphere (under N_2 gas) and vigorous stirring (500 rpm). A homogeneous solution composed of 734 mmols of H_2SO_4 (96%; 75 g) and 734 mmols of HNO_3 (65%; 71 g) was placed in the dripping funnel and added to the liquid 4-fluorobenzophenone at a rate of approximately 100 mmol/h. The reaction mixture was heated to 140°C. The reaction mixture appeared dis-homogeneous with the aromatic layer

on top. As the acid mixture was added, orange fumes developed inside the reactor.

[00116] The conversion to 3-nitro-4-fluoro-benzophenone was followed by quantitative ^{19}F -NMR. The reaction was continued for about 9 hours, until conversion of starting 4-fluorobenzophenone reached about 87 mol%.

[00117] The crude mixture was then cooled to 95°C. As the phases were separated, the lower acid mixture was poured in a separatory funnel and let cool to room temperature. The crude solid thus obtained was diluted in an equivolume of CH_2Cl_2 and washed 2 times with 1 equi-volume/washing of 10% $\text{NaOH}_{(\text{aq})}$. The lower organic layer was then separated and the solvent first stripped with a Rotavapor at 60°C and 0,3 mbar P_{RES} and then heated to 100°C and 0,14 mbar of residual pressure, to eliminate more than 90 mol% of the starting unreacted 4-fluorobenzophenone by sublimation.

[00118] The product, identified as 3-nitro-4-fluorobenzophenone, was obtained as a yellow crystalline solid in 90 mol% isolated yield.

[00119] This intermediate was re-nitrated employing 734 mmols of fresh H_2SO_4 (96%; 75 g) and 734 mmols of fresh HNO_3 (65%; 71 g). The reaction was carried out in exactly the same manner as described above.

[00120] The crystalline solid thus obtained was identified as a 80/20 molar mixture of 3,3'-dinitro-4-fluorobenzophenone/3-nitro-4-fluorobenzophenone,. The mixture was dissolved in the minimal amount of hot (90°C) hexafluoroxilene and the solution was then let to cool to room temperature overnight.

[00121] The yellow crystalline solid obtained were composed of more than 95 mol% of 3,3'-dinitro-4-fluorobenzophenone. The 3-nitro-4-fluorobenzophenone remains enriched in the mother liquor.

[00122] The following values were obtained for the final isolated product:

yield = 93 mol%

selectivity = 96/4 in moles of Bis/Mono nitrated aromatic.

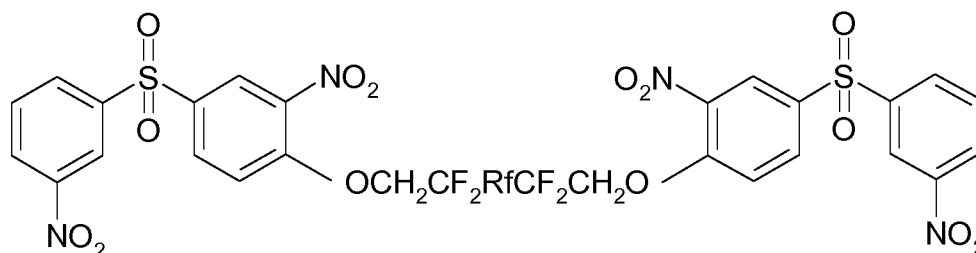
residual 4-fluoroarylbenzophenone < 1 mol%

Mw (average) = 288 g/mole

conversion: 85 mol%

[00123] The crystalline 3,3'-dinitro-4-fluorobenzophenone was then reacted with (PFPE-IV) following the same procedure described in Example 1 above.

[00124] Example 12 - Synthesis of polymer (P*) having formula :



wherein $R_f = (CF_2CF_2O)_m(CF_2O)_n$; $m/n = 1$; $M_n = 2000$

[00125] The reaction was performed as described in Example 11 starting from (PFPE-II) and employing 4-fluorobenzosulphone (734 mmols, 173 g).

[00126] The mono-nitrated intermediate (3-nitro-4-fluorobenzosulphone) was isolated as a yellow-orange crystalline solid and obtained in 85 mol% isolated yield.

[00127] The crystalline solid obtained after the second nitration reaction was a 75/25 molar mixture of 3,3'-dinitro-4-fluorobenzosulphone/3-nitro-4-fluorobenzosulphone. The mixture was dissolved in the minimal amount of hot (95°C) hexafluoroxilene. The hot solution was let slowly cool to room temperature overnight.

[00128] The crystals obtained were >90 mol% 3,3'-dinitro-4-fluorobenzosulphone. The 3-nitro-4-fluorobenzosulphone remains enriched in the mother liquor.

[00129] The following values were obtained for the final isolated product:

yield = 90 mol%

selectivity = 91/9 in moles of Bis/Mono nitrated aromatic.

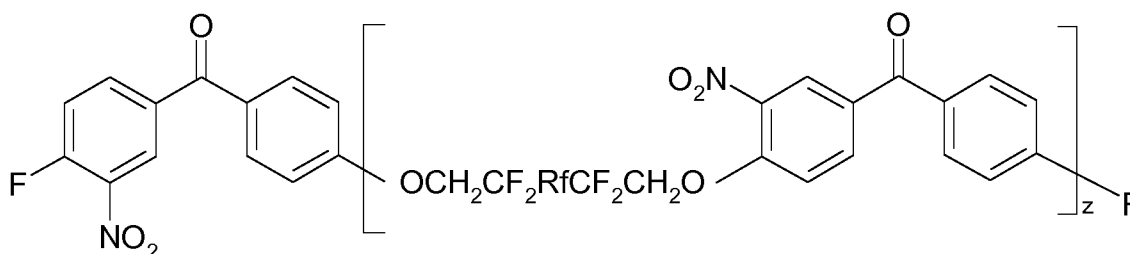
residual 4-fluoroarylbenzosulphone < 1 mol%

Mw (average) = 286 g/mole

conversion: 85 mol%

[00130] The crystalline 3,3'-dinitro-4-fluorobenzosulphone was then reacted with (PFPE-II) following the same procedure described in Example 1 above.

[00131] Examples 13 to 16 - Synthesis of polymers (P**) having formula :



[00132] Before beginning each of the following synthesis, the necessary amount of (PFPE) was dried by placing it in a round-bottomed flask and heated with magnetic stirring (900 – 1000 rpm) at 80°C under vacuum (0,1 mbar P_{RES}).

[00133] **Example 13 – Synthesis of polymer (P^{**})**

wherein $\text{R}_f = (\text{CF}_2\text{CF}_2\text{O})_m(\text{CF}_2\text{O})_n$; $m/n = 1$; $M_n = 1500$; $z = 2$

[00134] A round-bottomed glass reactor, equipped with a mechanical stirrer, a reflux condenser (the refrigerant liquid was Galden®HT-110 – obtained from Solvay Specialty Polymers Italy S.p.A.) with an inert gas (N_2) compensator on top, a dripping funnel and an internal thermometer, was charged with anhydrous PFPE-I (584 g; 369 mmols; 677 meq). The mechanical stirrer was turned on to about 300 rpm, the (PFPE-I) was heated to 45°C and a 9,56 w/v solution of tBuOK/tBuOH (795 ml; 677 mmol tBuOK) was dripped at a rate of 300 mmol/h. The temperature was raised to about 57°C and kept with stirring for 2 hours. The solution thus obtained was stripped with 90% v/v of tBuOH to obtain a clear to yellowish oil.

[00135] While tBuOH evaporation was proceeding, the 3-nitro-4,4'-difluoro-benzophenone (92% w/w NO_2 -Aromatic; 130 g; 443 mmols) was dissolved in HFX (1000 mL) for about 1 h at 50°C with mild stirring. A yellow homogeneous solution was obtained.

[00136] The solution thus obtained was then dripped into the yellowish oil at 75°C at a rate of about 200 mmol/h under stirring (300 rpm). When the addition was completed, the crude mixture was heated to an internal temperature of 116°C (the reflux temperature of residual t-BuOH in HFX) with 300 rpm mechanical stirring, for a total reaction time of 5 hours. A first aliquot of t-BuOK (203 mmol) was added with a solid dispenser in the crude reaction mixture at a rate of 400 mmol/h. A second aliquot t-BuOK (101 mmol) was

added after 20 hrs of reaction time and a third aliquot (50 mmol) was added after 27 hrs of total reaction time. After 27 hours of total reactiontime, the termination of the oligomerization was aided by adding 10 mol% of the starting molar amount of 3-nitro-4-fluorobenzophenone (13 grams; 44.3 mmol; solid dispenser). The conversion of the pre-terminals was followed by ^{19}F -NMR of the crude reaction mixture.

[00137] The crude reaction mixture was first cooled to room temperature and then centrifuged (10000 rpm; 25°C; 60 min) in order to separate the residual solid particulates, comprising mainly unreacted t-BuOK and slightly excess of starting 3-nitro-4,4'-difluorobenzophenone.

[00138] The centrifuged supernatant was transferred to a separatory funnel and was washed 2 times with aqueous 10% $\text{H}_3\text{O}^+\text{Cl}^-$ (1:0.5 v/v organic:water). The washing was considered completed when the final pH of the H_2O layer was below 3.

[00139] The washed crude mixture was then dried over MgSO_4 , filtered with 5 μm PTFE membrane, and the solvent evaporated first at 70°C and 0.1 mm Hg residual P (employing a Rotavapor) and then at 100°C and 0,07 P_{RES} with a mechanical pump in order to sublime most of the residual, unreacted 4,4'-difluorobenzophenone as well as unreacted 3-nitro-4,4'-difluorobenzophenone.

[00140] The following values were obtained:

isolated yield = 88 mol% of a dark viscous liquid

average MW = 4952 g/mole.

EW = 2706 g/eq.

PFPE segment average Mw = 1516 g/mole

[00141] **Example 14 – Synthesis of polymer (P^{**})**

wherein $\text{R}_f = (\text{CF}_2\text{CF}_2\text{O})_m(\text{CF}_2\text{O})_n$; $m/n = 1$; $\text{M}_n = 2000$; $z = 2$

[00142] The synthesis was performed as described in Example 13 starting from (PFPE-II).

[00143] Isolated yield = 85 mol% of a dark viscous liquid

Average MW = 6297 g/mol

EW = 3314 g/eq.

PFPE segment average MW = 2130 g/mol

[00144] Example 15 – Synthesis of polymer (P^{})**

wherein $R_f = (CF_2CF_2O)_m(CF_2O)_n$; $m/n = 1$; $M_n = 3000$; $z = 2$

[00145] The synthesis was performed as described in Example 13 starting from (PFPE-III).

[00146] Isolated yield = 85 mol% of a dark viscous liquid

Average MW = 9002 g/mol

EW = 4737 g/eq.

PFPE segment average MW = 3020 g/mol

[00147] Example 16 – Synthesis of polymer (P^{})**

wherein $R_f = (CF_2CF_2O)_m(CF_2O)_n$; $m/n = 1$; $M_n = 4000$; $z = 2$

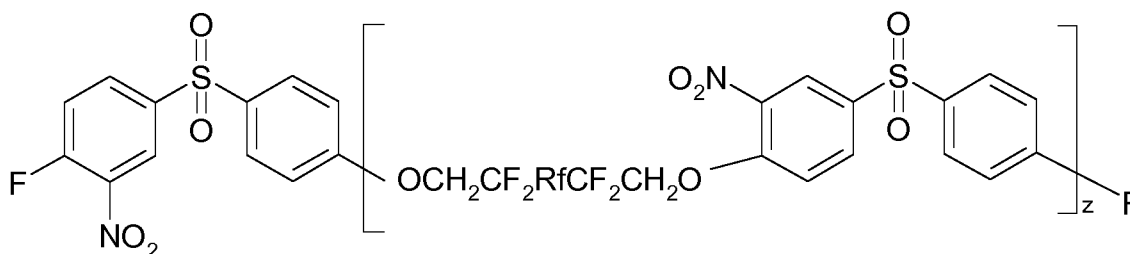
[00148] The synthesis was performed as described in Example 13 starting from (PFPE-IV).

[00149] Isolated yield = 85 mol% of a dark viscous liquid

Average MW = 11886 g/mol

EW = 6256 g/eq.

PFPE segment average MW = 4200 g/mol

[00150] Examples 17 to 20 - Synthesis of polymers (P^{}) having formula :****[00151] Example 17 – Synthesis of polymer (P^{**})**

wherein $R_f = (CF_2CF_2O)_m(CF_2O)_n$; $m/n = 1$; $M_n = 1500$; $z = 2$

[00152] The synthesis was performed as described in Example 13 starting from (PFPE-I) and using 3-nitro-4,4'-difluorobenzosulphone.

[00153] Isolated yield = 88 mol% of a dark viscous liquid

Average MW = 4711 g/mol

EW = 2574 g/eq.

PFPE segment average MW = 1516 g/mol

[00154] Example 18 – Synthesis of polymer (P^{})**

wherein $R_f = (CF_2CF_2O)_m(CF_2O)_n$; $m/n = 1$; $M_n = 2000$; $z = 2$

[00155] The synthesis was performed as described in Example 13 starting from (PFPE-II) and using 3-nitro-4,4'-difluorobenzosulphone.

[00156] Isolated yield = 88 mol% of a dark viscous liquid

Average MW = 6795 g/mol

EW = 3576 g/eq.

PFPE segment average MW = 2130 g/mol

[00157] **Example 19 – Synthesis of polymer (P^{**})**

wherein $R_f = (CF_2CF_2O)_m(CF_2O)_n$; $m/n = 1$; $M_n = 3000$; $z = 2$

[00158] The synthesis was performed as described in Example 13 starting from (PFPE-III) and using 3-nitro-4,4'-difluorobenzosulphone.

[00159] Isolated yield = 88 mol% of a dark viscous liquid

Average MW = 9376 g/mol

EW = 4935 g/eq.

PFPE segment average MW = 3020 g/mol

[00160] **Example 20 – Synthesis of polymer (P^{**})**

wherein $R_f = (CF_2CF_2O)_m(CF_2O)_n$; $m/n = 1$; $M_n = 4000$; $z = 2$

[00161] The synthesis was performed as described in Example 13 starting from (PFPE-IV) and using 3-nitro-4,4'-difluorobenzosulphone.

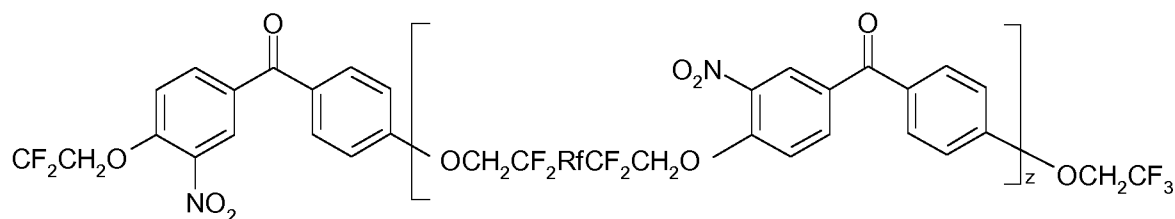
[00162] Isolated yield = 88 mol% of a dark viscous liquid

Average MW = 12368 g/mol

EW = 6510 g/eq.

PFPE segment average MW = 4200 g/mol

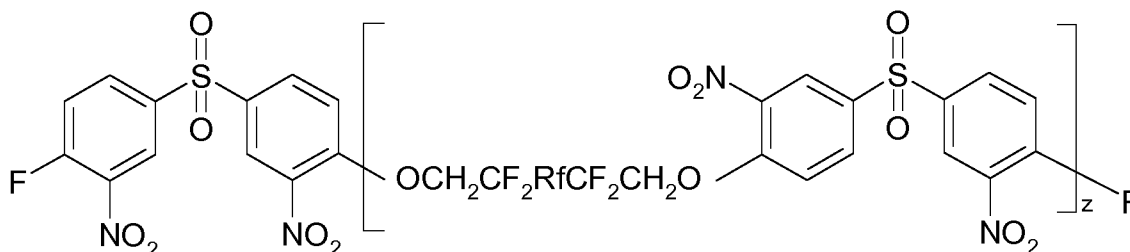
[00163] **Example 21 - Synthesis of polymer (P^{**}) having formula :**



wherein $R_f = (CF_2CF_2O)_m(CF_2O)_n$; $m/n = 1$; $M_n = 2000$; $z = 2$

[00164] Polymer (P^{**}) 21 was obtained by treating polymer (P^{**}) 14 with an excess of trifluoroethanol, in the presence of ter-BuOK as the organic base, until complete conversion of the fluorine atom to groups -OCH₂CF₃.

[00165] Example 22 - Synthesis of polymer (P**) having formula :



wherein $R_f = (CF_2CF_2O)_m(CF_2O)_n$; $m/n = 1$; $M_n = 4000$; $z = 2$

[00166] The reaction was performed following the procedure of Example 12, using 4,4'-difluorobenzosulphone (734 mmol, 186 g).

[00167] Yield = 90 mol%

selectivity = 91/9 in moles of Bis/Mono nitrated aromatic.

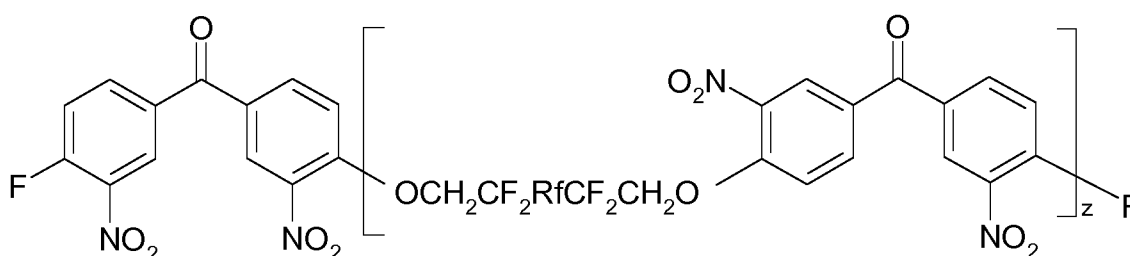
residual 4-fluoroarylbenzosulphone < 1 mol%

Mw (average) = 339 g/mol

conversion: 85 mol%

[00168] The thus obtained crystalline 3,3'-dinitro-4,4'-difluorobenzosulphone was reacted with (PFPE-II) as described in Example 1 above.

[00169] Example 23 - Synthesis of polymer (P**) having formula :



wherein $R_f = (CF_2CF_2O)_m(CF_2O)_n$; $m/n = 1$; $M_n = 4000$; $z = 2$

[00170] The reaction was performed following the procedure of Example 22, using difluoro-diphenylketone and (PFPE-IV).

[00171] Thermooxidation test

[00172] The thermooxidation test was carried out using the equipment described in: **SNYDER, Carl E., et al.** Development of Polyperfluoroalkylethers as High Temperature Lubricants and Hydraulic Fluids. *ASLE Transactions*. 1975, vol.3, no.13, p.171-180. The operating conditions were as follows:

- Test temperature: 270 °C for oils and 250°C for greases;
- Air flow: 1 L/h;
- Metals dipped in the fluid: stainless steel (AISI 304) and Ti alloy (Al 6%, V 4%).

[00173] A sample of the fluid to be tested, containing the compounds of the Examples as additives in the amount specifically indicated below, was introduced in the glass test tube of the equipment (see for example Fig. 1 of the above-cited reference), the glass tube was weighted and heated at the test temperature. When the required time had elapsed, the glass test tube was cooled to room temperature and weighted again. The difference of the weight before and after heating, referred to the weight of the sample before the test, gave the percent weight loss of the tested fluid. At the end of the test the appearance of the metals dipped into the fluid was visually evaluated.

[00174] The results of the tests are summarized in Table 1 below, in which Reference 1 is a Fomblin® M30 PFPE oil without additive.

Table 1

Product	24 h Δw (%)	48 h Δw (%)	72 h Δw (%)	96 h Δw (%)	192 h Δw (%)	240 h Δw (%)
Example 4	0.20	0.42	0.50	0.56	1.3	1.52
Example 8	0.25	0.50	0.58	0.65	1.39	1.62
Example11	0.10	0.21	0.30	0.36	0.71	0.95
Example 22	0.5	0.9	1.3	1.6	2.0	2.2
Reference 1(*)	45	80	95	100	-	-

[00175] (*) comparison

[00176] The above results confirmed the stability to thermos-oxidation of the compounds according to the present invention.

[00177] Samples of greases were also prepared using 30% by weight of PTFE and 70% by weight of base oil Fomblin® PFPE M30.

[00178] A sample (sample 1) containing only PTFE and Fomblin® PFPE M30 was used as reference.

[00179] Another sample (sample 2) was added with 2 wt.% of the compound Example 2.

[00180] A third sample (sample 3) was added with 2wt.% of the compound (Ia) of example 7 prepared as disclosed in WO 2013/120827 (SOLVAY SPECIALTY POLYMERS ITALY S.P.A.) cited in the background section.

[00181] 10 wt.% of fine powdered iron was added to each sample. The penetration value of the greases, measured by ASTM D217 method, was 292 mm/10'.

[00182] 50 g of these samples were then poured into a glass cup with an internal diameter of 96 mm and placed in a ventilated oven at 250°C for 100 h. The weight loss of each cup was checked during the test to evaluate the stability of the greases. The greases behaviour in terms of weight loss % as a function of time is summarized in the following Table 2.

Table 2

Time (hours)	Sample 1 (*) weight loss (%)	Sample 2 weight loss (%)	Sample 3(*) weight loss (%)
24	11.38	0.88	0.75
48	38.00	1.44	1.70
72	51.21	1.58	1.92
100	56.56	2.49	3.04

[00183] (*) comparison

[00184] The results reported in the above table confirm the very high efficiency of the compounds of the invention as thermal stabilizers for (per)fluorinated greases in air and in presence of metals, especially for a time of 48 hours and more.

[00185] Thermostability test

[00186] The thermal stability test is carried out on neat sample placed in a close NMR tube and monitoring, as a function of time and temperature, the extent of degradation. In particular, the diagnostic pre-terminal signal of the PFPE chain (i.e. $\text{Rf}-\text{CF}_2-\text{CH}_2\text{O}-$) gave a direct measure of the degradation. Plotting the degradation as a function of time, a first order kinetics was observed for all samples, and consequently a $t_{1/2}$ for all samples was obtained. In brief, the data represent, for each explored temperature, the time necessary (in hour) to degrade half of the product.

[00187] The results expressed as $t_{1/2}$ hours are summarized in the following Table 3.

[00188] As comparison, DA410 having the following chemical formula (wherein p and q are integers such that the weigh number molecular weight is 2000) was used:

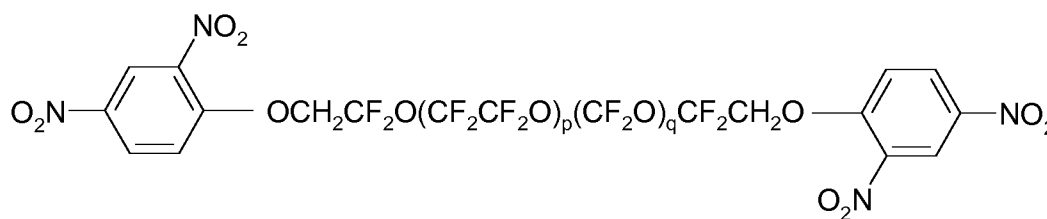


Table 3

°C	Example 9 $t_{1/2}$	Example 10 $t_{1/2}$	Example 18 $t_{1/2}$	DA410(*) $t_{1/2}$
270	1968	2891	2570	550
290	950	1720	1650	101
310	450	915	875	21
330	260	520	430	5
350	140	307	290	1

[00189] (*) comparison

[00190] The results reported in the above table confirm that the compounds according to the present invention shows superior thermal stability compared to DA410.

[00191] Tribology Test

[00192] The test was performed following the method of ASTM D6425-11, in the following conditions:

- preload: 50N for 30 seconds
- load: 300N for 2 hours
- stroke: 1.0 mm
- frequency: 50 Hz
- temperature: 50°C
- geometry: sphere (10 mm diameter) onto disk (24 mm diameter, 7.8 mm thickness) made of AISI 52100 alloy steel.

[00193] The tribometer allows the user to record the evolution of the coefficient of friction (CoF) during the steady-state tests. In particular, the results are expressed in terms of:

- final friction coefficient (CoF end), which is the numerical value registered at the end of the test. This value of CoF corresponds to the value reached in the steady state (steady state);
- wear (mm) on the sphere: the value is calculated as the average of the two perpendicular diameters (d1 and d2), the sign of wear on the ball being measured through an optical microscope (Motic).

[00194] Compound of Example 14 was subjected to the tribological test. The results are reported in the following Table 4.

Table 4

Measure	CoF end	Average CoF	St.Dev. CoF	Wear 1 (mm)	Wear 2 (mm)	Average wear (mm)	St.Dev. wear (mm)
m03020	0.120	0.118	0.004	0.73	0.72	0.75	0.03
m03021	0.115			0.76	0.78		

[00195] The above data showed that the compound according to the invention provides good lubrication properties as its coefficient of friction (CoF) is low for low wear values.

Claims

Claim 1. A polymer [polymer (P)] comprising at least one (per)fluoropolyether chain [chain (R_{pf})] and at least one group [group (A)] comprising two phenyl rings, wherein at least one of said phenyl rings bears at least one nitro group and wherein said two phenyl rings are linked together via a bridging group [group (T)] selected from $-C(=O)-$ and $-S(=O)_2-$.

Claim 2. The polymer (P) according to claim 1, wherein said chain (R_{pf}) is a chain of formula $-(CFX)_aO(R_f)(CFX')_b-$, wherein
 a and b, equal or different from each other, are equal to or higher than 1, preferably from 1 to 10, more preferably from 1 to 3;
 X and X', equal or different from each other, are $-F$ or $-CF_3$,
 provided that when a and/or b are higher than 1, X and X' are $-F$;
 (R_f) comprises, preferably consists of, repeating units R° , said repeating units being independently selected from the group consisting of:
 (i) $-CFXO-$, wherein X is F or CF_3 ;
 (ii) $-CFXCFXO-$, wherein X, equal or different at each occurrence, is F or CF_3 , with the proviso that at least one of X is $-F$;
 (iii) $-CF_2CF_2CW_2O-$, wherein each of W, equal or different from each other, are F, Cl, H;
 (iv) $-CF_2CF_2CF_2CF_2O-$;
 (v) $-(CF_2)_j-CFZ-O-$ wherein j is an integer from 0 to 3 and Z is a group of general formula $-O-R_{(f-a)}-T$, wherein $R_{(f-a)}$ is a fluoropolyoxyalkene chain comprising a number of repeating units from 0 to 10, said recurring units being chosen among the following : $-CFXO-$, $-CF_2CFXO-$, $-CF_2CF_2CF_2O-$, $-CF_2CF_2CF_2CF_2O-$, with each of each of X being independently F or CF_3 and T being a C_1 - C_3 perfluoroalkyl group.

Claim 3. The polymer (P) according to claim 2, wherein said chain (R_f) complies with the following formula:

(R_f -I)



wherein

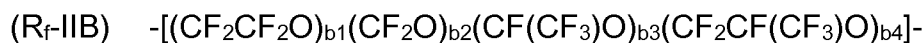
- X^1 is independently selected from -F and $-CF_3$,
- X^2 , X^3 , equal or different from each other and at each occurrence, are independently -F, $-CF_3$, with the proviso that at least one of X is -F;
- g_1 , g_2 , g_3 , and g_4 , equal or different from each other, are independently integers ≥ 0 , such that $g_1+g_2+g_3+g_4$ is in the range from 2 to 300, preferably from 2 to 100; should at least two of g_1 , g_2 , g_3 and g_4 be different from zero, the different recurring units are generally statistically distributed along the chain.

Claim 4. The polymer (P) according to claim 3, wherein said chain (R_f) is selected from those of formula (R_f -IIA) to (R_f -IIE) :



wherein:

- a_1 and a_2 are independently integers ≥ 0 such that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000 as determined by NMR; both a_1 and a_2 are preferably different from zero, with the ratio a_1/a_2 being preferably comprised between 0.1 and 10;



wherein:

- b_1 , b_2 , b_3 , b_4 , are independently integers ≥ 0 such that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000 as determined by NMR; preferably b_1 is 0, b_2 , b_3 , b_4 are > 0 , with the ratio $b_4/(b_2+b_3)$ being ≥ 1 ;



wherein:

$cw = 1$ or 2 ;

- c_1 , c_2 , and c_3 are independently integers ≥ 0 chosen so that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000 as determined by NMR; preferably c_1 , c_2 and c_3 are all > 0 , with the ratio $c_3/(c_1+c_2)$ being generally lower than 0.2;



wherein:

d is an integer > 0 such that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000 as determined by NMR;

(R_f-IIE) -[(CF₂CF₂C(Hal*)₂O)_{e1}-(CF₂CF₂CH₂O)_{e2}-(CF₂CF₂CH(Hal*)O)_{e3}]-

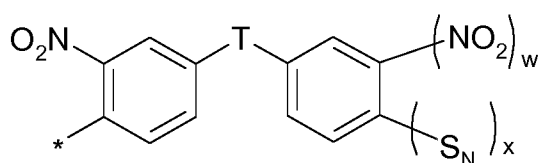
wherein:

- Hal*, equal or different at each occurrence, is a halogen selected from fluorine and chlorine atoms, preferably a fluorine atom;

- e1, e2, and e3, equal to or different from each other, are independently integers ≥ 0 such that the (e1+e2+e3) sum is comprised between 2 and 300.

Claim 5. The polymer (P) according to claim 1, wherein said chain (R_{pf}) is linked to said at least one group (A) via a linking group [group (L)], said group (L) being a divalent alkyl chain comprising from 1 to 20 carbon atoms and at least one oxygen atom.

Claim 6. The polymer (P) according to claim 1, wherein said at least one group (A) is a monovalent group complying with the following formula (A-I):
(A-I)



wherein

T is -C(=O)- or -S(=O)₂- ;

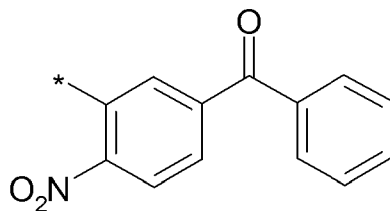
S_N is selected from halogen atom, triflate, nonaflate and group -OR₁, wherein R₁ is an optionally halogenated, more preferably optionally fluorinated, alkyl chain comprising from 1 to 6 carbon atoms;

w and x are, each independently, zero or 1; and

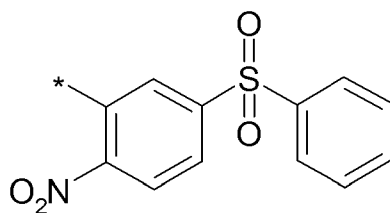
the symbol * indicates the bond with group (L) as defined in claim 5.

Claim 7. The polymer (P) according to claim 8, wherein said monovalent group (A) complies with the following formulae (A-I-i) to (A-I-vi):
(A-I-i)

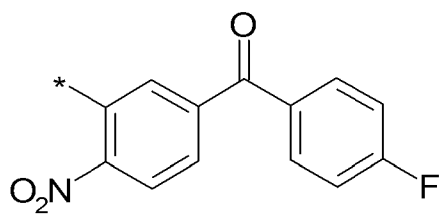
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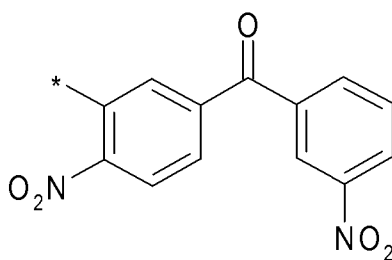
(A-I-ii)



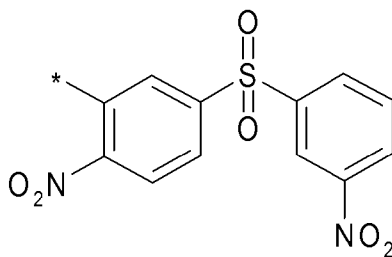
(A-I-iii)



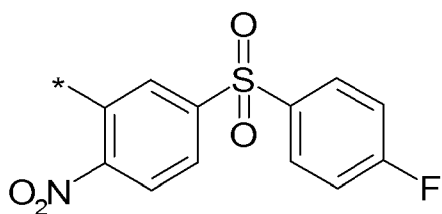
(A-I-iv)



(A-I-v)

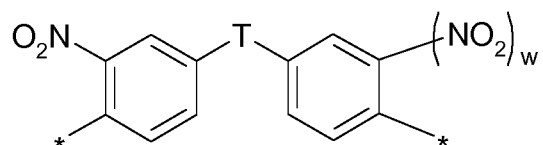


(A-I-vi)



Claim 8. The polymer (P) according wherein said at least one group (A) is a divalent group complying with the following formula (A-II):

(A-II)



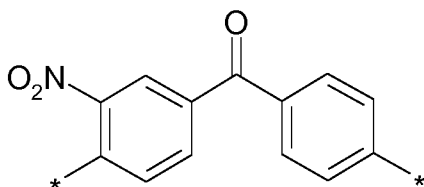
wherein

T and w have the same meanings as in formula (A-I) and

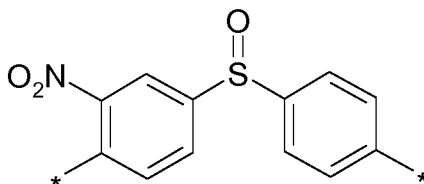
each symbol * indicates the bond with one group (L) as defined in claim 5.

Claim 9. The polymer (P) according to claim 1, wherein said divalent group (A) complies with the following formulae (A-II-i) to (A-II-iv):

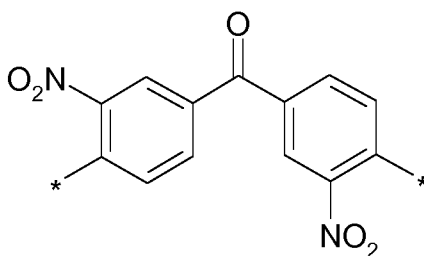
(A-II-i)



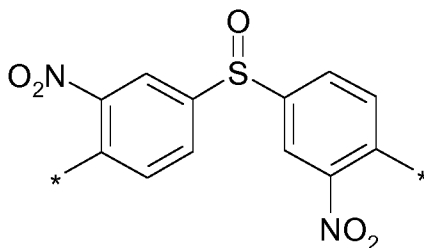
(A-II-ii)



(A-II-iii)



(A-II-iv)



Claim 10. The polymer (P) according to any one of claims 1 to 9, which comprises one chain (R_{pf}) having two chain ends, wherein at least one, more preferably both, of said chain ends comprises one monovalent group (A) as defined in claims 6 and 7.

Claim 11. The polymer (P) according to any one of claims 1 to 9, which comprises at least two (per)fluoropolyether chains (R_{pf}) each having two chain ends, wherein said chains (R_{pf}) are linked together at one chain ends by one divalent group (A) as defined in claims 8 and 9 and said chain (R_{pf}) bear on the other chain end a monovalent group (A) as defined in claims 6 and 7.

Claim 12. The polymer (P) according to any one of the preceding claims, which complies with the following formula:



wherein

each (A^*) is a group of formula (A-I) as defined in claims 6 and 7,

(A^{**}) is a group of formula (A-II) as defined in claims 8 and 9,

each L corresponds to group (L) as defined in claim 5,

(R_{pf}) corresponds to chain (R_{pf}) as defined in claim 2, and

z is an integer from 1 to 10.

Claim 13. A process for the synthesis of polymer (P) as defined in any one of claims 1 to 11, said process comprising one step [step (I)] of contacting

- at least one (per)fluoropolyether polymer [polymer (P_{OH})] comprising at least one chain (R_{pf}) having two chain ends, wherein at least one chain end bears at least one hydroxy group and
- at least one compound [compound (A)] comprising two phenyl rings, wherein at least one of said phenyl rings bears at least one leaving group for nucleophilic substitution reaction [group (L_N)] and one nitro group at the ortho position of said group (L_N), and wherein said two phenyl rings are linked together via a bridging group [group (T)] selected from $-C(=O)-$ and $-S(=O)_2-$.

Claim 14. A method for thermo-stabilizing fluorinated oils and greases, said method comprising contacting said fluorinated oil and grease with at least one polymer (P) as defined in any one of claims 1 to 12.

Claim 15. A lubricant composition selected from:

- an oil [compositions (C1)] comprising:

- (i) at least one polymer (P) as defined in claim 10, preferably in an amount ranging from 0.01 % to 20% wt., based on the total weight of said composition (C1) and

- (ii) one or more base oils, preferably in an amount ranging from 80% to 99.99% wt. based on the total weight of said composition (C1); or

- a grease [compositions (C2)] comprising:

- (i*) at least one polymer (P) as defined in claims 11 or 12, preferably in an amount ranging from 50% to 90% wt. based on the total weight of said composition (C2);

- (ii*) at least one thickening agent, preferably in an amount ranging from 10 % to 50% wt. based on the total weight of said composition (C2).

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/056493

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G65/00 C08G65/333 C08G65/334
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

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2013/120827 A2 (SOLVAY SPECIALTY POLYMERS IT [IT]) 22 August 2013 (2013-08-22) cited in the application page 5, paragraph [0016] examples 1-13 claims 1-16	1-15
A	EP 1 354 932 A1 (SOLVAY SOLEXIS SPA [IT]) 22 October 2003 (2003-10-22) cited in the application examples 1,2 claims 1-11	1-15
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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

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

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Date of the actual completion of the international search

3 May 2018

Date of mailing of the international search report

14/05/2018

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

Popescu, Teodora

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2018/056493

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2007/049502 A1 (HOWELL JON L [US] ET AL) 1 March 2007 (2007-03-01) cited in the application examples 1-18 claims 1-29 -----	1-15
A	WO 2008/027512 A2 (DU PONT [US]; HOWELL JON LEE [US]; MINOR BARBARA HAVILAND [US]; NAPPA) 6 March 2008 (2008-03-06) claim 2 -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2018/056493

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