

Description

Novel (per)fluoropolyether polymers

Cross reference to related applications

[0001] This application claims priority from European application No. 15175979.2 filed on 9th July 2015, the whole content of this application being incorporated herein by reference for all purposes.

Technical Field

[0002] The present invention relates to novel (per)fluoropolyether polymers and their use as lubricant, in particular for Magnetic Recording Media (MRM).

Background Art

[0003] Thin film Magnetic Recording Media (MRM), such as hard disks, are used to store large amounts of data and are typically composed of multiple layers, including a non-magnetic substrate having sequentially deposited on each side thereof an underlayer and at least one magnetic layer. A carbon overcoat is typically deposited over the magnetic recording layer to protect the recording layer from wear and environmental corrosion.

[0004] A thin layer of lubricant is applied over the protective carbon overcoat to improve the tribological performance of the hard disk drive, so as to improve the durability and reliability of a magnetic recording medium. To this aim, the liquid lubricant must adhere to the carbon overcoat such that the rotational velocity of the disk does not cause a significant amount of the lubricant to be lost from the disk surface.

[0005] (Per)fluoropolyethers (PFPEs) and derivatives thereof are currently used in the lubrication of MRM.

[0006] **KASAI PH, Raman V.** Perfluoropolyethers with dialkylamine end groups: ultrastable lubricant for magnetic disk application. *Tribology Letters*. Feb. 2002, vol.12, no.2, p.117-122. disclose that perfluoropolyether molecular chains are prone to undergo the intramolecular disproportionation reaction, which is catalysed by Lewis acid and, in the head-disk environment, it occurs when the successive ether oxygen flanking a methylene unit (-CF₂-) come into contact with Lewis acid sites that may exist on the metal oxide surface.

However, it was shown that addition of X1P, partially fluorinated

hexaphenoxy cyclotriphosphazene, markedly increases the durability of the magnetic disk system. The efficacy of X1P was attributed to the strong nucleophilic (Lewis base) nature of the triphosphazene ring.

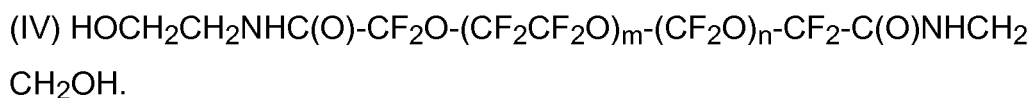
Accordingly, the above authors synthesized perfluoropolyethers with dialkylamine end groups of formula:



wherein $-NR_2$ was a group deriving from di-n-propylamine and morpholine. However, this article does not disclose perfluoropolyethers terminated with dialkylamine end groups wherein the alkyl chain is substituted with at least one hydroxyl group.

[0007] Hydroxy-terminated polymeric materials comprising a (per)fluoropolyether backbone have been disclosed for example in **US 3810874** (MINNESOTA MINING AND MANUFACTURING COMPANY) 14.05.1974, which relates to polyfunctional poly(perfluoroalkylen-oxides) and their preparation.

Among the others, Example 1 provides a pre-polymer of formula (IV), wherein the alkyl chain bearing the hydroxy group is linked to the PFPE backbone through an amide moiety:



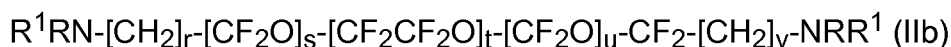
[0008] **US 6468947** (SEAGATE TECHNOLOGY LLC) discloses a lubricant composition comprising a first fluoropolyether and a decomposition inhibiting amount of a second fluoropolyether having at least one nitrogen containing group, in particular an amine or amide moiety. In particular, examples of the decomposition-inhibiting lubricants comprise a fluoropolyether chain substituted with one or two groups comprising an amide moiety and having the following formula:



[0009] **US 7510999** (HITACHI GLOBAL STORAGE TECHNOLOGIES) discloses a lubricant composition comprising a first liquid lubricant and a second liquid lubricant, wherein the first liquid lubricant contains a cyclotriphosphazene ring attached to at least one perfluoropolyether having a single terminal hydroxyl group and the second liquid lubricant contains a perfluoropolyether having two end groups selected from

hydroxyl, tertiary amine and combinations thereof.

The second liquid lubricant can have the following structure (IIb):

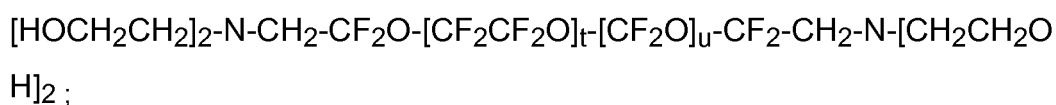


wherein R and R¹ are independently selected from

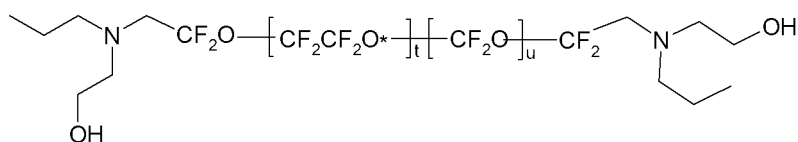
-[OCH₂CH₂]_yOH, -OCH₂CH(OH)CH₂OH, -CH₂CH₂OH and -CH₂CH₂CH₃ and wherein y is an integer from 1 to 6.

In particular, suitable second liquid lubricants have the following chemical structures ZDEA and ZEEA:

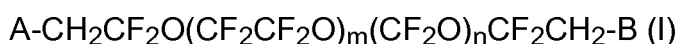
ZDEA:



ZEEA:



[0010] **US 2006052262** (MATSUMURA OIL RESEARCH CORP.) discloses a compound of formula (I), a lubricant and a magnetic disk using the compound of formula (I):



wherein A is amino group having hydroxyl group, B is hydroxyl group or amino group having or not having hydroxyl group, wherein m is a real number of 5 to 36 and n is a real number from 4 to 30.

[0011] **US 2009/0318664** (SEAGATE TECHNOLOGY LLC.) discloses a compound comprising a backbone with a perfluoropolyether chain, one or more cyclophosphazene rings attached to or incorporated into the backbone.

[0012] **WO 2014/195299** (SOLVAY SPECIALTY POLYMERS ITALY S.P.A.) discloses a method for manufacturing cyclophosphazenes PFPE derivatives to be used in lubrication of magnetic recording media (MRM), comprising the following steps:

1) 1) providing a mixture (M) containing:

a) a (per)fluoropolyether (PFPE) polyol [PFPE (P_{pol})] comprising a

fluoropolyoxyalkylene chain (R_f) having two chain ends, each chain end comprising at least one hydroxy group, and b) the corresponding alkoxide of perfluoropolyether (P_{pol}) [$PFPE (P_{alk})$], wherein the equivalent concentration of $PFPE (P_{alk})$ in $PFPE (P_{pol})$ is lower than 30%, preferably ranging from 5% to 15%;

2) contacting mixture (M) with a perhalocyclophosphazene (CP_{halo}) to provide a mixture (M1) containing an equivalent ratio of $PFPE (P_{alk})/(CP_{halo})$ of at least 1;

3) allowing mixture (M1) to react until complete disappearance of P-Cl groups to provide a mixture (M2);

4) submitting mixture (M2) to hydrolysis to provide a mixture (M3);

5) optionally removing (P_{pol}) from mixture (M3) to provide a mixture (M4).

[0013] **WO 03/067285** (CORNING INCORPORATED) discloses compounds having an aromatic or heteroaromatic moiety, at least two fluorinated alkylene, arylene or polyether moieties, each fluorinated alkylene, arylene or polyether moiety being linked to the aromatic or heteroaromatic moiety through an -O- or -S- linkage; at least one ethylenically unsaturated moiety, each ethylenically unsaturated moiety being linked to one of the fluorinated alkylene, arylene or polyether moieties.

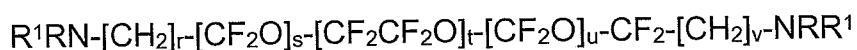
[0014] **US 2005/0277558** (HITACHI GLOBAL STORAGE TECHNOLOGIES NETHERLANDS B.V) discloses a lubricant composition for use as a lubricant for magnetic recording media, comprising a first liquid lubricant and a second liquid lubricant, wherein the first liquid lubricant contains a cyclotriphosphazene ring attached to at least one perfluoropolyether having a single terminal hydroxyl group, and the second liquid lubricant contains a perfluoropolyether having two end groups selected from hydroxyl, tertiary amine, and combinations thereof.

Summary

[0015] The Applicant has perceived that the industry of the magnetic recording media (MRM) is always looking for new polymers that can be used as lubricants, in particular in Magnetic Recording Media (MRM).

[0016] Thus, in one embodiment, the present disclosure relates to a polymer [polymer (P)] comprising:

- at least one (per)fluoropolyether chain [chain (R_{pf})] and
- at least one chain [chain (C)] comprising at least one hydroxy group and at least one group [group (H)] comprising a heteroatom selected from the elements belonging to group 15 of the periodic table, provided that polymer (P) does not comprise amide group(s) and is different from a polymer of formula



wherein

r, s, t, u and v are independently zero or an integer, with the proviso that s, t and u are not all zero, and

R and R^1 are independently selected from $-[OCH_2CH_2]_yOH$, $-OCH_2CH(OH)CH_2OH$, $-CH_2CH_2OH$ and $-CH_2CH_2CH_3$.

- [0017] More preferably, said heteroatom selected from the elements belonging to group 15 of the periodic table is nitrogen or phosphorous.
- [0018] When the heteroatom is phosphorous, it is preferably phosphorous(III) and said at least one group (H) is a phosphino group and the polymer (P) will be hereinafter referred to as polymer (P_P).
- [0019] When the heteroatom is nitrogen, it is preferably nitrogen(III) and said at least one group (H) is an amino group, more preferably a secondary or tertiary amino group, and the polymer (P) will be hereinafter referred to as polymer (P_N).
- [0020] The Applicant has found that advantageously, when chain (C) comprises at least one heteroatom belonging to group 15 of the periodic table, said heteroatom retains its base properties and behaves as Lewis base, such that polymer (P) is less subject to the degradation process catalysed by the Lewis acids that may be present in the head-disk environment.
- [0021] In addition, the presence of at least one hydroxy group in polymer (P) allows to increase the adhesion of the polymer itself to the magnetic layer or to the carbon overcoat of the MRM.
- [0022] In one aspect, there is provided a polymer [polymer (P)], which is polymer (P_N^*) comprising:

at least two chains (R_{pf}), each chain (R_{pf}) having two chain ends, wherein:

- said at least two chains (R_{pf}) are linked together at one chain end through a divalent chain [chain ($*C^*$)] comprising at least one hydroxy group and at least two amino groups,

- at least one of the said at least two chains (R_{pf}) bears on its opposite chain end a monovalent chain [chain (C^*)] comprising at least one hydroxy group and at least one amino group, 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 -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-, -CF₂CFXO-, -CF₂CF₂CF₂O-, -CF₂CF₂CF₂CF₂O-, with each of X being independently F or CF₃ and T being a C₁-C₃ perfluoroalkyl group.

[0022a] In a second aspect, the present disclosure relates to the use of polymer (P) as defined above as lubricant for magnetic recording media (MRM).

- [0022b] In another embodiment, the present disclosure relates to a process [process P_N] for the manufacture of polymer (P_N) described herein, said process comprising the following steps: (a) providing at least one PFPE alcohol, (b) reacting said PFPE alcohol with a compound bearing at least one sulfonic group to obtain a sulfonic PFPE ester, (c) reacting the sulfonic PFPE ester obtained in step (b) with at least one organic amine to obtain polymer (P_N).
- [0022c] In another aspect, the present disclosure relates to a process [process P_N^*] for the manufacture of polymer (P_N^*) described herein, said process comprising the following steps:
- (a*) providing at least one PFPE alcohol,
 - (b*) reacting said PFPE alcohol with a compound bearing at least one sulfonic group to obtain a sulfonic PFPE ester,
 - (c*) reacting the sulfonic PFPE ester obtained in step (b) with at least one polyamine to obtain a PFPE-oligomer comprising at least two chains (R_{pf}),
 - (d*) optionally purifying the PFPE-oligomer obtained in step (c),
 - (e*) reacting said PFPE-oligomer with at least one monoamine to obtain polymer (P_N^*).
- [0023] In a further embodiment, the present disclosure relates to a method for lubricating a magnetic recording media (MRM), said method comprising providing a

magnetic recording media (MRM) comprising at least one magnetic layer, optionally covered by at least one carbon overcoat, and applying at least one polymer (P) as defined above on said magnetic layer or on said carbon overcoat.

[0024] The Applicant has found that polymer (P) can be advantageously used as such as lubricant for MRM, i.e. without the need of adding any additive to polymer (P) to improve its durability performance. This results in at least two advantages: on the one hand, it avoids phase separation due to immiscibility between the different components of the composition to occur, as was the case when e.g. X1P was used as additive, and on the other hand it prevents undesired alterations of the lubricant composition over time.

Description of embodiments

[0025] 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 expressions “5- to 10-membered aromatic moiety” and “5- or 6-membered aromatic moiety” indicate any cyclic ring derived from an aromatic compound and comprising from 5 to 10 members or 5 or 6 members in the cyclic ring, respectively;
- the expression “aromatic moiety” indicates any cyclic ring derived from an aromatic compound;
- the expression “aromatic compound” indicates any cyclic compound having a number of π electrons equal to $4n+2$, wherein n is 0 or any positive integer, such as for example benzene, naphthalene, pyridine, quinoline, isoquinoline, pyrazine, pyrimidine, furan, benzofuran, pyrrole,

indole, thiophene, benzothiophene, imidazole, benzimidazole, pyrazole, benzoxazole, isoxazole, benzisoxazole, thiazole, benzothiazole;

- the term “alkylene” is intended to indicate a divalent alkyl chain and hence the expression “divalent alkyl chain” and the term “alkylene” are used as synonymous.

[0026] 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-, -CF₂CFXO-, -CF₂CF₂CF₂O-, -CF₂CF₂CF₂CF₂O-, with each of each of X being independently F or CF₃ and T being a C₁-C₃ perfluoroalkyl group.

[0027] More preferably, a and b, equal or different from each other, are from 1 to 10, even more preferably from 1 to 3.

[0028] Preferably, chain (R_f) complies with the following formula:

(R_f -I)

-[(CFX¹O)_{g1}(CFX²CFX³O)_{g2}(CF₂CF₂CF₂O)_{g3}(CF₂CF₂CF₂CF₂O)_{g4}]-

wherein

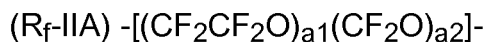
- X¹ is independently selected from -F and -CF₃,

- X², X³, equal or different from each other and at each occurrence, are

independently -F, -CF₃, with the proviso that at least one of X is -F;

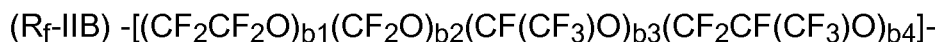
- g₁, g₂, g₃, and g₄, equal or different from each other, are independently integers ≥ 0 , such that g₁+g₂+g₃+g₄ is in the range from 2 to 300, preferably from 2 to 100; should at least two of g₁, g₂, g₃ and g₄ be different from zero, the different recurring units are generally statistically distributed along the chain.

[0029] More preferably, chain (R_f) is selected from chains of formula:



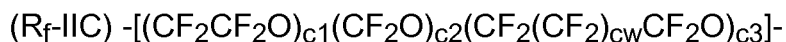
wherein:

- a₁ and a₂ are independently integers ≥ 0 such that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000; both a₁ and a₂ are preferably different from zero, with the ratio a₁/a₂ being preferably comprised between 0.1 and 10;



wherein:

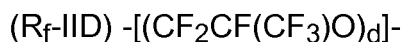
b₁, b₂, b₃, b₄, are independently integers ≥ 0 such that the number average molecular weight is between 400 and 10,000, preferably between 400 and 5,000; preferably b₁ is 0, b₂, b₃, b₄ are > 0 , with the ratio b₄/(b₂+b₃) being ≥ 1 ;



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; 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;



wherein:

- Hal*, equal or different at each occurrence, is a halogen selected from

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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.

[0030] Still more preferably, chain (R_f) complies with formula (R_f-III) here below:

(R_f-III) -[(CF₂CF₂O)_{a1}(CF₂O)_{a2}]-

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, with the ratio a1/a2 being generally comprised between 0.1 and 10, more preferably between 0.2 and 5.

[0031] Preferably, said chain (C) is a linear or branched alkyl chain comprising from 1 to 20, more preferably from 1 to 10 carbon atoms, optionally interrupted by a heteroatom selected from N, O, S and/or by a 5- to 10-membered, more preferably a 5- or 6-membered, aromatic moiety optionally comprising at least one heteroatom selected from N, O and S.

[0032] Preferably, said 5- to 10-membered aromatic moiety optionally comprising at least one heteroatom selected from N, O and S is an aromatic moiety deriving from benzene, naphthalene, pyridine, quinoline, isoquinoline, pyrazine, pyrimidine, furan, benzofuran, pyrrole, indole, thiophene, benzothiophene, imidazole, benzimidazole, pyrazole benzoxazole, isoxazole, benzisoxazole, thiazole, benzothiazole.

[0033] More preferably, said chain (C) is a linear or branched alkyl chain comprising from 1 to 6 carbon atoms.

[0034] In a preferred embodiment, said chain (R_{pf}) and the at least one heteroatom of said group (H) are linked together via a bridging group [group (B)].

[0035] Preferably, group (B) is a divalent alkyl chain comprising from 1 to 20, more preferably from 1 to 10 carbon atoms, said alkyl chain being optionally interrupted by at least one oxygen atom and/or optionally substituted with at least one hydroxy group and/or with a perfluoroalkyl group comprising from 1 to 3 carbon atoms.

[0036] More preferably, group (B) is a chain of formula -CH(CF₃)- or -CH₂(OCH₂

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$\text{CH}_2)_n$ wherein n is 0 or an integer from 1 to 10, more preferably from 1 to 5.

[0037] In a preferred embodiment, polymer (P_N) comprises:

- one (per)fluoropolyether chain [chain (R_{pf})] and
- at least one chain [chain (C)] comprising at least one hydroxy group and at least one amino group,

wherein

said chain (R_{pf}) is a chain of formula $-(\text{CFX})_a\text{O}(\text{R}_f)(\text{CFX}')_b-$,

wherein X , X' , a and b are as defined above and

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

(i-a) $-\text{CF}(\text{CF}_3)\text{O}-$;

(ii-a) $-\text{CFXCFXO}-$, wherein X , equal or different at each occurrence, is F or CF_3 , with the proviso that at least one of X is $-\text{CF}_3$;

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

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

(v-a) $-(\text{CF}_2)_j-\text{CFZ}-\text{O}-$ 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 each of X being independently F or CF_3 and T being a C_1 - C_3 perfluoroalkyl group.

[0038] Preferably, in polymer (P_N), said chain (R_{pf}) and the nitrogen atom of said at least one amino group are linked together via a bridging group [group (B)], as defined above.

[0039] Preferably, polymer (P_N) comprises two chains (C) as defined above, each of said chains (C) being bonded to the opposite side of said chain (R_{pf}) via a bridging group (B) as defined above.

[0040] More preferably, polymer (P_N) complies with the following formula:

$\text{T}-(\text{R}_{pf})-(\text{B})-(\text{C})$

wherein C , B and R_{pf} are as defined above and

T is selected from the group comprising $-\text{H}$, $-\text{F}$, $-\text{Cl}$, a straight or branched perfluoroalkyl group comprising from 1 to 3 carbon atoms, or a chain

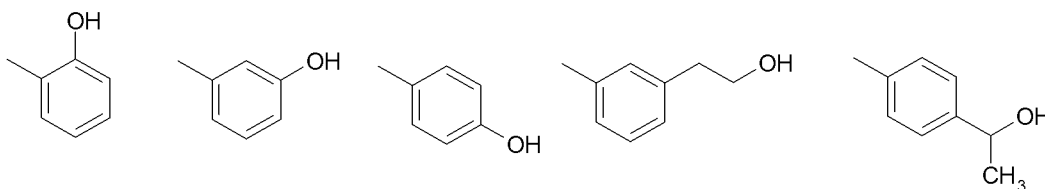
-(B)-(C) wherein (B) and (C) are as defined above.

- [0041] In a more preferred embodiment according to the present invention, polymer (P_N^*) comprises at least two chains (R_{pf}) as defined above, each chain (R_{pf}) having two chain ends, wherein:
- said at least two chains (R_{pf}) are linked together at one chain end through a divalent chain [chain (C^*)] comprising at least one hydroxy group and at least two amino groups,
 - at least one of said at least two chains (R_{pf}) bears on its opposite chain end a monovalent chain [chain (C^*)] comprising at least one hydroxy group and at least one amino group.
- [0042] Preferably, in polymer (P_N^*), said chains (R_{pf}) are bonded to the nitrogen atom of the amino groups of chain (C^*) and of chain (C^*) via a group (B) as defined above.
- [0043] Preferably, said chain (C^*) is a linear or branched alkyl chain comprising from 1 to 20 carbon atoms, said alkyl chain being optionally interrupted by one or more heteroatoms and being optionally substituted with a 5- to 10-membered aromatic moiety; or a 5- to 10-membered aromatic moiety optionally substituted with a linear or branched alkyl chain comprising from 1 to 6 carbon atoms.
- [0044] More preferably, said chain (C^*) complies with formula (C^*-I):
- $$-N(R_1)(R_2) (C^*-I)$$
- wherein
- R_1 and R_2 , identical or different from each other, are hydrogen; a linear or branched alkyl chain comprising from 1 to 10, more preferably from 1 to 6, carbon atoms, said alkyl chain being optionally substituted with a 5- to 10-membered aromatic moiety, said alkyl chain and/or said aromatic moiety being substituted with at least one hydroxy group; a 5- to 10-membered aromatic moiety optionally substituted with a linear or branched alkyl chain comprising from 1 to 6 carbon atoms, said aromatic moiety and/or said alkyl chain being substituted with at least one hydroxy group;
- provided that at least one of R_1 and R_2 is different from hydrogen.
- [0045] More preferably, R_1 and R_2 , identical or different from each other, are

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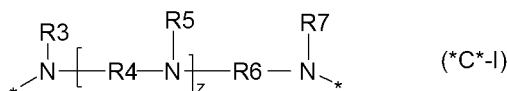
hydrogen; a linear or branched alkyl chain comprising from 1 to 6 and more preferably from 1 to 3 carbon atoms and at least one hydroxy group; a 5- or 6-membered aromatic moiety optionally substituted with a linear or branched alkyl chain comprising from 1 to 3 carbon atoms, wherein at least one of said aromatic moiety and of said alkyl chain comprises at least one hydroxy group.

[0046] Preferably, R₁ and R₂, identical or different from each other, are selected from hydrogen, -CH₂OH, -CH₂CH₂OH, -CH₂CH₂CH₂OH, -CH₂-CH(CH₃)(OH), -CH(CH₂OH)₂, -CH₂-CH(OH)-CH₂OH, -C(CH₂OH)₃, -C(CH₃)(CH₂OH)₂, -C(CH₃)₂(CH₂OH),



[0047] Preferably, said chain (*C*) is a linear or branched alkyl chain comprising from 1 to 10, more preferably from 1 to 6 carbon atoms, and being optionally interrupted by at least one heteroatom selected from N, O and S and/or by a 5- to 10-membered, more preferably a 5- or 6-membered aromatic moiety optionally comprising one or more heteroatoms and optionally substituted with a linear or branched alkyl chain comprising from 1 to 6 carbon atoms, said aromatic moiety and/or said alkyl chain being optionally substituted with at least one hydroxy group.

[0048] More preferably, said chain (*C*) complies with the following formula (*C*-I):



wherein

- R₃, R₅ and R₇, equal to or different from each other, are independently selected from hydrogen; linear or branched alkyl chain comprising from 1 to 10, preferably from 1 to 6 carbon atoms; and a 5- to 10-membered aromatic moiety optionally comprising at least one heteroatom selected

from N, O and S and optionally substituted with a linear or branched alkyl chain comprising from 1 to 6 carbon atoms, said alkyl chain and/or said aromatic moiety optionally comprising at least one hydroxy group;

- R_4 and R_6 , equal to or different from each other, are independently a linear or branched alkylene chain comprising from 1 to 10, preferably from 1 to 6 carbon atoms, said alkylene chain being optionally substituted with at least one hydroxy group and/or optionally interrupted by one or more heteroatoms selected from N, O and S and/or by a 5- to 10-membered aromatic moiety optionally comprising at least one heteroatom selected from N, O and S; and

- z is 0 or an integer equal to or higher than 1, more preferably 0 or an integer from 1 to 20;

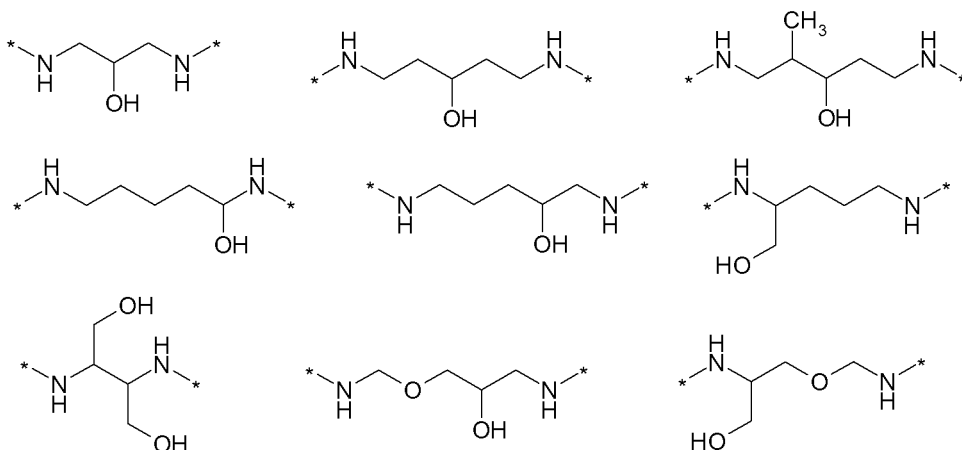
provided that at least one of R_3 , R_4 , R_5 , R_6 or R_7 comprises at least one hydroxy group.

[0049] Even more preferably, z is 0.

[0050] Even more preferably, R_3 and R_7 equal to or different from each other, are independently selected from hydrogen, linear or branched alkyl chain comprising from 1 to 6 carbon atoms.

[0051] Even more preferably, R_6 is a linear or branched alkylene chain comprising from 1 to 6 carbon atoms, said alkyl chain being optionally substituted with at least one hydroxy group and/or by a 5- or 6-membered aromatic moiety;
provided that at least one of R_3 , R_6 or R_7 comprises at least one hydroxy group.

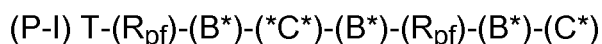
[0052] Examples of said chain ($*C*$) are the following:



wherein the symbol (*) indicates the bond to chain (R_{pf}).

[0053] More preferably, polymer (P_N^*) comprises two chains (R_{pf}) as defined above and chain ($*C^*$) comprises two amino groups.

[0054] In a more preferred embodiment, polymer (P_N^*) complies with the following formula (P-I):



wherein

(R_{pf}), (B^*), ($*C^*$) and (C^*) are as defined above and

T is selected from the group comprising -H, -F, -Cl, a straight or branched perfluoroalkyl group comprising from 1 to 3 carbon atoms, or chain $-(B^*)-(C^*)$ wherein (B^*) and (C^*) are as defined above.

[0055] More preferably, T is chain $-(B^*)-(C^*)$.

[0056] Polymer (P) according to the present invention can be conveniently prepared using processes known to the skilled persons.

[0057] Good results have been obtained starting from PFPE alcohols, i.e. polymers comprising a fully or partially fluorinated polyether chain (R_f) having at least two chain ends, preferably two chain ends, wherein at least one chain end bears at least one hydroxy group.

[0058] Thus, a further aspect of the present invention relates to a process [process P_N] for the manufacture of polymer (P_N), said process comprising the following steps:

(a) providing at least one PFPE alcohol,

(b) reacting said PFPE alcohol with a compound bearing at least one sulfonic group to obtain a sulfonic PFPE ester,

(c) reacting the sulfonic PFPE ester obtained in step (b) with at least one organic amine to obtain polymer (P_N).

[0059] Suitable PFPE alcohols can be obtained according to methods known in the art and are commercially available, for example from Solvay Specialty Polymers Italy S.p.A. under the trade name Fomblin®.

[0060] Preferably, step (b) is performed according to methods known in the art, for example as disclosed by **TONELLI, Claudio, et al.** Perfluoropolyether functional oligomers: unusual reactivity in organic chemistry. *Journal of*

Fluorine Chemistry. 2002, vol.118, p.107-121. , in particular as reported on page 119 paragraph 3.5.4.1.

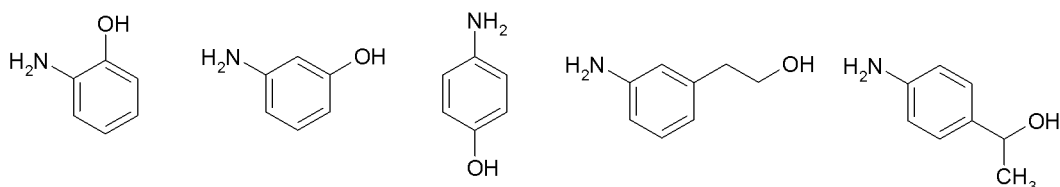
- [0061] Preferably, said step (b) is performed at a temperature below 0°C, more preferably from -5°C to -50°C, even more preferably from -10°C to -25°C.
- [0062] Preferred compounds bearing at least one sulfonic group are selected in the group comprising alkane-sulfonyl halides, such as methanesulfonyl chloride; aromatic sulfonyl halides, such as p-toluenesulfonyl chloride; perfluoroalkane-sulfonyl halides such as trifluoromethanesulfonyl chloride and perfluoro-1-butan sulfonyl fluoride. Perfluoro-1-butan sulfonyl fluoride is particularly preferred.
- [0063] Preferably, step (c) is performed in the presence of an excess of sulfonic PFPE ester.
- [0064] Preferably, step (c) is performed in the presence of a suitable solvent, typically selected from perfluorocarbons (PFCs), hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs) and 1,3-bis(trifluoromethyl)benzene. The preferred solvent being 1,3-bis(trifluoromethyl)benzene.
- [0065] Preferably, the organic amine used in step (c) is an organic aliphatic or aromatic compound comprising at least one primary or secondary amine group.
- [0066] Said organic amine is a monoamine, i.e. an amine comprising one primary or one secondary amine group, or a polyamine, i.e. an amine comprising at least two primary or secondary amine groups or a combination thereof.
- [0067] More preferably, said aliphatic organic amine comprises a linear or branched alkyl chain having from 1 to 10, more preferably from 1 to 6 carbon atoms, said alkyl chain comprising at least one hydroxy group.
- [0068] More preferably, said aromatic organic amine comprises a 5- to 10-membered, more preferably a 6- to 10-membered, aromatic moiety, optionally comprising one or more heteroatoms selected from N, O and S, said aromatic moiety being optionally substituted with an alkyl chain comprising from 1 to 6 carbon atoms, said aromatic moiety and/or said alkyl chain being substituted with one hydroxy group.
- [0069] A preferred monoamine to be used in process (P_N) can be represented with formula (A-m):

HN(R₁)(R₂) (A-m)

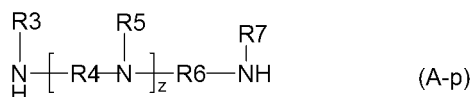
wherein R₁ and R₂ are as defined above.

[0070] Examples of suitable aliphatic and aromatic monoamines that can be used in process (P_N) include – without being limited thereto – those represented in the following group (M-I):

(M-I) NH₂CH₂OH, NH(CH₂OH)₂, NH₂CH₂CH₂OH, NH(CH₂CH₂OH)₂, NH₂CH₂CH₂CH₂OH, NH(CH₂CH₂CH₂OH)₂, NH₂CH₂-CH(CH₃)(OH), NH₂CH(CH₂OH)₂, NH₂CH₂-CH(OH)-CH₂OH, NH₂C(CH₂OH)₃, NH₂C(CH₃)(CH₂OH)₂, NH₂C(CH₃)₂(CH₂OH), NH[CH₂-CH(CH₃)(OH)]₂, NH[CH(CH₂OH)]₂, NH[CH₂-CH(OH)-CH₂OH]₂, NH[C(CH₂OH)₃]₂, NH[C(CH₃)(CH₂OH)]₂, NH[C(CH₃)₂(CH₂OH)]₂, HOCH₂CH₂-NH-C(CH₂OH)₃,



[0071] A preferred polyamine to be used in process (P_N) complies with the following formula (A-p):



wherein:

z, R₃, R₄, R₅, R₆ and R₇ are as defined above.

[0072] Even more preferably, z is 0.

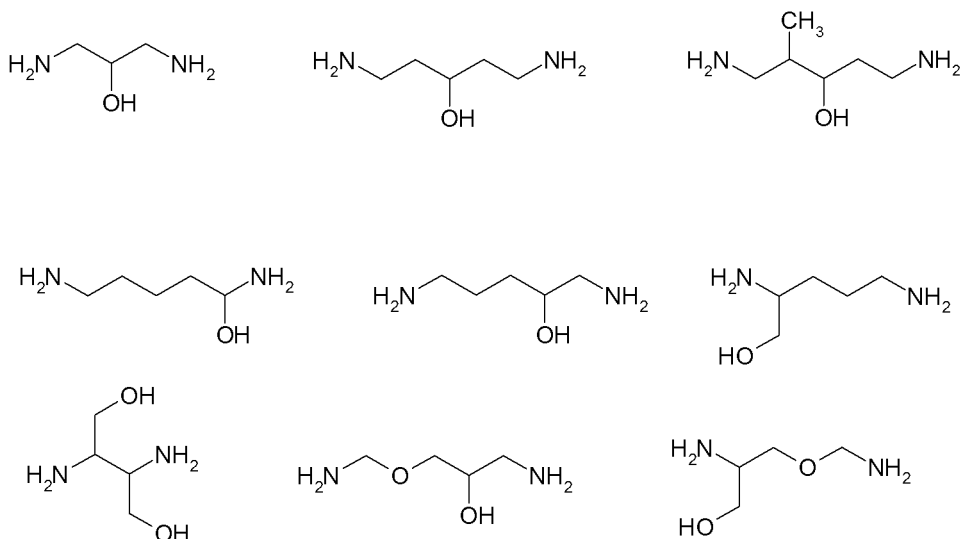
[0073] Even more preferably, R₃ and R₇ equal to or different from each other, are independently selected from hydrogen, linear or branched alkyl chain comprising from 1 to 6 carbon atoms.

[0074] Even more preferably, R₆ is a linear or branched alkylene chain comprising from 1 to 6 carbon atoms, said alkyl chain being optionally substituted with at least one hydroxy group and/or by a 5- or 6-membered aromatic moiety;
provided that at least one of R₃, R₆ or R₇ comprises at least one hydroxy group.

[0075] In a preferred embodiment, said polyamine is a diamine.

[0076] Examples of suitable aliphatic diamines are represented in the following group (D-I):

(D-I)



[0077] As an alternative process, polymer (P_N) can be prepared by reacting a PFPE ester, i.e. a polymer comprising a fully or partially fluorinated polyether chain (R_f) having at least two chain ends, preferably two chain ends, wherein at least one chain end bears at least one ester group, with a suitable organic amine as disclosed above to obtain the corresponding PFPE-amide, and then reducing said PFPE-amide by using a suitable reducing agent to the corresponding polymer (P_N).

[0078] In a further aspect, the present invention relates to a process [process P_N*] for the manufacture of polymer (P_N*) as defined above comprising the following steps:

- (a*) providing at least one PFPE alcohol,
- (b*) reacting said PFPE alcohol with a compound bearing at least one sulfonic group to obtain a sulfonic PFPE ester,
- (c*) reacting the sulfonic PFPE ester obtained in step (b) with at least one polyamine to obtain a PFPE-oligomer comprising at least two chains (R_{pf}),
- (d*) optionally purifying the PFPE-oligomer obtained in step (c),
- (e*) reacting said PFPE-oligomer with at least one monoamine to obtain polymer (P_N*).

- [0079] Advantageously, the PFPE alcohol is as defined above with respect to process (P_N).
- [0080] Preferably, step (b^*) is performed under the same conditions and using the same reagents disclosed above for step (b).
- [0081] Preferably, the polyamine in step (c^*) complies with formula (A-p) above. More preferably, the polyamine is a diamine, such as for example one of those represented above in group (D-I).
- [0082] Preferably, step (c^*) is performed in the presence of a suitable solvent, typically selected from those listed above with respect to step (c).
- [0083] In a preferred embodiment, the PFPE-oligomer obtained in step (c^*) comprises two chains (R_{pf}) and hence it is referred to as "PFPE-dimer".
- [0084] To this aim, step (c^*) is performed in the presence of an excess of sulfonic PFPE ester.
- [0085] Preferably, said step (d^*) is performed for example by chromatography, including for example column chromatography, flash column chromatography, and supercritical chromatography, solubility fractionation and fractional distillation.
- [0086] Preferably, said step (d^*) is performed by column chromatography or by supercritical chromatography.
- [0087] Preferably, when step (d^*) is performed by column chromatography, suitable solvents can be selected for example in the group comprising fluorinated or partially fluorinated solvents, such as hexafluoroxylene; hydrofluoroethers, including methoxy nonafluorobutane (NovecTM HFE-7100 commercially available from 3M, U.S.A.), ethoxy nonafluorobutane; and mixtures thereof. These solvents can be optionally used in admixture with a solvent selected from the group comprising polar aprotic solvents, such as acetonitrile, dimethylformamide, dimethylacetamide, dimethylsulfoxide, acetone, dichloromethane and tetrahydrofuran.
- [0088] Preferably, when step (d^*) is performed by supercritical chromatography, a solvent such as CO_2 is preferably used, optionally in admixture with a polar solvent such as methanol or ethanol.
- [0089] Preferably, the organic amine in step (e^*) is a monoamine complying with

formula (A-m) above, and more preferably it is selected among those listed in group (M-I) above.

- [0090] Preferably, said step (e*) is performed in the presence of a suitable solvent, typically selected from those listed above with respect to step (c).
- [0091] Magnetic Recording Media (MRM) typically comprise multiple layers, including a non-magnetic substrate having sequentially deposited on each side thereof an underlayer, at least one magnetic layer and a protective overcoat, preferably a carbon overcoat.
- [0092] In a preferred embodiment, polymer (P_N), and even more preferably polymer (P_N*), as defined above is used as lubricant for MRM.
- [0093] The step of applying a polymer according to the present invention to the MRM can be performed by any conventional method known in the art.
- [0094] For example, polymer (P) can be directly applied on the magnetic layer, or on the protective overcoat if present, of the disk of the MRM.
- [0095] Alternatively, polymer (P) can be first dissolved in a suitable solvent, such as hydrofluoroethers (HFEs) for example Novec™ HFEs (commercially available from 3M™), hydrofluorocarbons (HFCs) for example Vertrel® HFCs (commercially available from DuPont™), perfluorinated hydrocarbons, chlorofluorocarbons, hydrochlorofluorocarbons and combinations thereof, thus obtaining a solution [solution (S)], then the disk is submerged in said solution (S) and slowly withdrawn therefrom.
- [0096] A conventional lifter-type dipper may be used to submerge the disk of the recording medium in said solution (S).
- [0097] Optionally, the coated disk thus obtained is subjected to further treatments, such as for example exposure to UV radiation.
- [0098] The skilled person can optimize the duration of submergence and the speed of withdrawal to achieve a desired coating thickness.
- [0099] Preferably, the coating comprising any one of polymer (P) according to the present invention has a thickness from about 2 to about 30 angstroms (Å), more preferably from 2 to 15 Å.
- [0100] 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.

[0101] The invention will be herein after 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

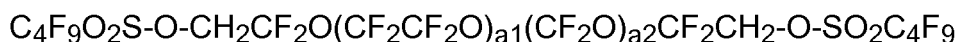
[0102] Example 1

[0103] Step 1 – Synthesis of ZDOL nonaflate

[0104] 154 g of perfluoro-1-butanesulfonyl fluoride ($\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$ – 96%, 489 mmol) and 54 g of triethylamine (TEA – 534 mmol) were placed in a 1000-ml round-bottom flask equipped with mechanical stirrer, dropping funnel, thermometer and condenser. After the temperature was cooled down, 175 g of Fomblin[®] ZDOL PFPE (EW = 431, 406 meq) were added through the dropping funnel during about 2 hours while keeping the reaction mixture under stirring and the temperature at -15/-20°C. After the addition was completed the cooling bath was removed and the reaction mixture was allowed to warm to room temperature. ¹⁹F-NMR showed a quantitative conversion of Fomblin[®] ZDOL PFPE into the corresponding nonaflate derivative.

The mixture was then added with 100 g of Galden[®] D100 (mixture 1:1 by weight of perfluoropropyltetrahydropyran and perfluorobutyltetrahydrofuran), 76 g of methyl alcohol and vigorously shaken.

After phase separation, the lower organic layer was collected and washed two times with 70 g of methyl alcohol. Every time the resulting two phases were vigorously stirred at room temperature for a few minutes and, after separation, the lower organic layer was collected. The solvents were then removed by distillation at 80°C under reduced pressure to afford 278 g ZDOL nonaflate of formula:



wherein the ratio $a1/a2$ was about 1.

[0105] Step 2 – Reaction between ZDOL nonaflate and 1,3-diamino-2-propanol

[0106] 275 g of ZDOL nonaflate (EW = 716, 384 meq) obtained as described in

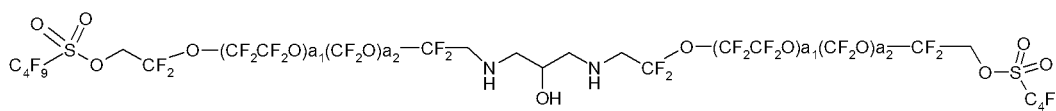
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Step 1 above, 150 g of 1,3-bis(trifluoromethyl)benzene (HFX) and 20 g of potassium carbonate (145 mmol) were placed in a 500-ml round-bottom flask equipped with mechanical stirrer, dropping funnel, thermometer and condenser. After heating at reflux, a solution of 1,3-diamino-2-propanol (2 g, 22 mmol) in *tert*-butanol (18 g) was added drop-wise under vigorous stirring during 3 hours.

After further 4 hours of reaction under stirring a complete conversion was achieved, as confirmed by ^1H -NMR and ^{19}F -NMR.

After cooling down to room temperature, the mass was filtered through a 0.45 μm PTFE membrane, the filtrate (472 g) collected and stripped of solvents under vacuum at 80°C.

265 g of crude product were obtained, containing unreacted ZDOL nonaflate used in excess and the desired compound having the following formula:



[0107] Step 3 – Isolation of the target compound by silica column chromatography

[0108] The crude product obtained in step 2 above (265 g) was chromatographed over a 56 mm diameter column filled with silica (280 g, particle size between 200 and 500 μm).

The excess of ZDOL nonaflate was eluted first by 1953 g of NovecTM HFE-7100 and recovered (220 g) after solvent removal.

The target product was then recovered by eluting with increasing concentrations of acetonitrile in NovecTM HFE-7100 (2 to 5% w/w).

[0109] Step 4 – Reaction with diethanolamine

[0110] 23 g of the target product (EW = 1167, 19.7 meq) obtained as disclosed in Step 3 above, 20 g of HFX and 8.8 g of diethanolamine (99.5%, 83.3 mmol) were placed in a 50-ml round-bottom flask equipped with mechanical stirrer, thermometer and condenser. The reaction mixture was vigorously stirred at reflux until complete conversion (monitored by ^{19}F

NMR).

After cooling down to room temperature and phase separation, the lower organic layer was washed with 20 g distilled water and 6 g isobutyl alcohol for two times.

After phase separation, the lower organic layer was collected and the solvents were removed by distillation at 80°C under reduced pressure, thus obtaining 15 g of the product having the following structure: $(\text{HOCH}_2\text{CH}_2)_2\text{N}-\text{CH}_2-\text{CF}_2\text{O}(\text{R}_f)\text{CF}_2-\text{CH}_2-\text{NHCH}_2\text{CH}(\text{OH})\text{CH}_2\text{NH}-\text{CH}_2-\text{CF}_2\text{O}(\text{R}_f)\text{CF}_2-\text{CH}_2-\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$

wherein

(R_f) is $-(\text{CF}_2\text{CF}_2\text{O})_{a1}(\text{CF}_2\text{O})_{a2}-$ and the ratio $a1/a2$ is about 1.

Claims

1. A polymer [polymer (P)], which is polymer (P_N^*) comprising:

at least two chains (R_{pf}), each chain (R_{pf}) having two chain ends, wherein:

- said at least two chains (R_{pf}) are linked together at one chain end through a divalent chain [chain ($*C^*$)] comprising at least one hydroxy group and at least two amino groups,

- at least one of the said at least two chains (R_{pf}) bears on its opposite chain end a monovalent chain [chain (C^*)] comprising at least one hydroxy group and at least one amino group,

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 -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;

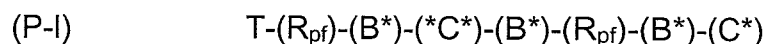
(iii) $-\text{CF}_2\text{CF}_2\text{CW}_2\text{O}-$, wherein each of W, equal or different from each other, are F, Cl, H;

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

(v) $-(\text{CF}_2)_j\text{-CFZ-O-}$ wherein j is an integer from 0 to 3 and Z is a group of general formula $-\text{O-R}_{(\text{f-a})}\text{-T}$, wherein $\text{R}_{(\text{f-a})}$ 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 F or CF_3 and T being a $\text{C}_1\text{-C}_3$ perfluoroalkyl group.

2. The polymer (P) according to claim 1, wherein in said polymer (P_N^*), said chains (R_{pf}) are bonded to the nitrogen atom of the amino groups of chain ($^*\text{C}^*$) and of chain (C^*) via a group (B),
said group (B) being a divalent alkyl chain comprising from 1 to 20 carbon atoms, said alkyl chain being optionally interrupted by at least one oxygen atom and/or optionally substituted with at least one hydroxy group and/or with a perfluoroalkyl group comprising from 1 to 3 carbon atoms .

3. The polymer (P) according to claim 1 or 2, wherein said polymer (P_{N^*}) comprises two chains (R_{pf}) as defined in claim 1 and chain ($*C^*$) comprises two amino groups.
4. The polymer (P) according to any one of claims 1 to 3, said polymer (P_{N^*}) complying with the following formula (P-I):



wherein

(R_{pf}) is as defined in claim 1;

(B^*) is a divalent alkyl chain comprising from 1 to 20 carbon atoms, said alkyl chain being optionally interrupted by at least one oxygen atom and/or optionally substituted with at least one hydroxy group and/or with a perfluoroalkyl group comprising from 1 to 3 carbon atoms;

($*C^*$) is a linear or branched alkyl chain comprising from 1 to 10 carbon atoms, and being optionally interrupted by at least one heteroatom selected from N, O and S and/or by a 5- to 10-membered aromatic moiety optionally comprising one or more heteroatoms and optionally substituted with a linear or branched alkyl chain comprising from 1 to 6 carbon atoms, said aromatic moiety and/or said alkyl chain being optionally substituted with at least one hydroxy group;

(C^*) is a linear or branched alkyl chain comprising from 1 to 20 carbon atoms, said alkyl chain being optionally interrupted by one or more heteroatoms and

being optionally substituted with a 5- to 10-membered aromatic moiety, or a 5- to 10-membered aromatic moiety optionally substituted with a linear or branched alkyl chain comprising from 1 to 6 carbon atoms, wherein said alkyl chain or said a 5- to 10-membered aromatic moiety further comprising at least one hydroxy group and at least one amino group; and

T is selected from the group comprising -H, -F, -Cl, a straight or branched perfluoroalkyl group comprising from 1 to 3 carbon atoms, or chain $-(B^*)-(C^*)$.

5. A process [process P_N^*] for the manufacture of polymer (P_N^*) according to any one of claims 1 to 4, said process comprising the following steps:
 - (a*) providing at least one PFPE alcohol,
 - (b*) reacting said PFPE alcohol with a compound bearing at least one sulfonic group to obtain a sulfonic PFPE ester,
 - (c*) reacting the sulfonic PFPE ester obtained in step (b) with at least one polyamine to obtain a PFPE-oligomer comprising at least two chains (R_{pf}),
 - (d*) optionally purifying the PFPE-oligomer obtained in step (c),
 - (e*) reacting said PFPE-oligomer with at least one monoamine to obtain polymer (P_N^*).

6. The process of claim 5, wherein step (c*) is performed in the presence of an excess of sulfonic PFPE ester.
7. Use of polymer (P) according to any one of claims 1 to 4, as lubricant for magnetic recording media (MRM).